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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

93724 7590 02/27/2024

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

EXAMINER	
CHU, YONG LIANG	

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
02/27/2024	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00001

APPLICATION NO.	ISSUE DATE	PATENT NO.
16/839,862	27-Feb-2024	11911743

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
PHILADELPHIA, PA 19103-7348

EGRANT NOTIFICATION

Your electronic patent grant (eGrant) is now available, which can be accessed via Patent Center at https://patentcenter.uspto.gov

The electronic patent grant is the official patent grant under 35 U.S.C. 153. For more information, please visit https://www.uspto.gov/electronicgrants

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
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APPLICATION NO.	ISSUE DATE	PATENT NO.	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	02/27/2024	11911743	123450-013001	5111

93724 7590 02/07/2024

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

ISSUE NOTIFICATION

The projected patent number and issue date are specified above. The patent will issue electronically. The electronically issued patent is the official patent grant pursuant to 35 U.S.C. § 153. The patent may be accessed on or after the issue date through Patent Center at https://patentcenter.uspto.gov/. The patent will be available in both the public and the private sides of Patent Center. Further assistance in electronically accessing the patent, or about Patent Center, is available by calling the Patent Electronic Business Center at 1-888-217-9197.

The USPTO is implementing electronic patent issuance with a transition period, during which period the USPTO will mail a ceremonial paper copy of the electronic patent grant to the correspondence address of record. Additional copies of the patent (i.e., certified and presentation copies) may be ordered for a fee from the USPTO's Certified Copy Center at https://certifiedcopycenter.uspto.gov/index.html. The Certified Copy Center may be reached at (800)972-6382.

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(application filed on or after May 29, 2000)

The Patent Term Adjustment is 205 day(s). Any patent to issue from the above-identified application will include an indication of the adjustment on the front page.

If a Continued Prosecution Application (CPA) was filed in the above-identified application, the filing date that determines Patent Term Adjustment is the filing date of the most recent CPA.

Applicant will be able to obtain more detailed information by accessing the Patent Center (https://patentcenter.uspto.gov).

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Application Assistance Unit (AAU) of the Office of Patents Stakeholder Experience (OPSE), Stakeholder Support Division (SSD) at (571)-272-4200.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00003

INVENTOR(s) (Please see PATENT CENTER site https://patentcenter.uspto.gov for additional inventors):

Rebecca L. DISTEFANO, Oakdale, PA;
Richard A. MIMNA, Oakdale, PA;

APPLICANT(s) (Please see PATENT CENTER site https://patentcenter.uspto.gov for additional applicants):

CALGON CARBON CORPORATION, Moon Township, PA;

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The USA offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to encourage and facilitate business investment. To learn more about why the USA is the best country in the world to develop technology, manufacture products, and grow your business, visit SelectUSA.gov.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00004

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ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	01/18/2024 03:31:42 PM Z ET	123450-013001

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	64000812	AUTHORIZED BY	Douglas Kayuha
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	E20241HF34026338	Paula Watson

PRE-AUTHORIZED ACCOUNT

604406

PRE-AUTHORIZED CATEGORY

37 CFR 1.16 (National application filing, search, and examination fees); 37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.20 (Post Issuance fees); 37 CFR 1.21 (Miscellaneous fees and charges)

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1501	UTILITY ISSUE FEE	1200.00	1	1200.00
			TOTAL AMOUNT:	$1,200.00

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement

Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications. **Because electronic patent issuance may occur shortly after issue fee payment, any desired continuing application should preferably be filed prior to payment of this issue fee in order not to jeopardize copendency.**

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

93724 7590 10/18/2023
DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

TITLE OF INVENTION: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	01/18/2024

EXAMINER	ART UNIT	CLASS-SUBCLASS
CHU, YONG LIANG	1731	502-418000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

☐ Change of correspondence address (or Change of Correspondence Address form PTO/AIA/122 or PTO/SB/122) attached.

☐ "Fee Address" indication (or "Fee Address" Indication form PTO/AIA/47 or PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1 DLA Piper LLP (US)
2
3

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE: CALGON CARBON CORPORATION
(B) RESIDENCE: (CITY and STATE OR COUNTRY): MOON TOWNSHIP, PENNSYLVANIA

Please check the appropriate assignee category or categories (will not be printed on the patent) : ☐ Individual ☒ Corporation or other private group entity ☐ Government

4a. Fees submitted: ☒ Issue Fee ☐ Publication Fee (if required)

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

☒ Electronic Payment via Patent Center or EFS-Web ☐ Enclosed check ☐ Non-electronic payment by credit card (Attach form PTO-2038)

☒ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. 60-4406

5. **Change in Entity Status** (from status indicated above)

☐ Applicant certifying micro entity status. See 37 CFR 1.29
NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

☐ Applicant asserting small entity status. See 37 CFR 1.27
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

☐ Applicant changing to regular undiscounted fee status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature /Douglas Kayuha/ Date January 18, 2024

Typed or printed name Douglas Kayuha Registration No. 79855

PTOL-85 Part B (08-18) Approved for use through 01/31/2020 OMB 0651-0033 U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00007

UNITED STATES
PATENT AND TRADEMARK OFFICE

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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**01/18/2024 03:31:42 PM Z ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	64000812	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Douglas Kayuha

Documents

TOTAL DOCUMENTS: 1

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
123450-013001 Issue Fee Transmittal.pdf	1	Issue Fee Payment (PTO-85B)	126 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450-013001 Issue Fee Transmittal.pdf	E5B9D991C96479D502DE737B9DCBFAAAE4F38FDAB75C32A9C05A576C92A0091B1FB3A07188270E0DC4F1DE10DD4726C78C00B3EB944A7D13EE112A5BC7A81244

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized

by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

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National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

93724 7590 12/08/2023

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

EXAMINER	
CHU, YONG LIANG	

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
12/08/2023	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Notice of Allowability	Application No. 16/839,862	Applicant(s) DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the submission by 11/10/2023.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1 and 3-14 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some* c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☑ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YONG L CHU/
Primary Examiner, Art Unit 1731

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00011

DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

The previous Notice of Allowance (NOA) mailed on 10/25/2023 has been vacated. This NOA replaces the previous one.

Claim 2 is cancelled. Claims 1, and 3-14 are pending in the instant application.

Response to Amendment

The Amendments by Applicants' representative Nicholas C. Kokkinos filed on 10/02/2023 has been entered.

Information Disclosure Statements

Applicant's Information Disclosure Statements, filed on 09/22/2023 and 11/10/2023, have been considered. Please refer to Applicant's copies of the PTO-1449 submitted herewith.

Response to Amendment/Argument

Object to Amendment

Applicant's amendment overcomes the objection. The objection is hereby **withdrawn**.

Reasons for Allowance

The present invention is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to

perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, and reactivated carbon according to claim 1. Applicant's specification [0050-0051] describes EXAMPLE 1 of producing the first sorbent material by reactivating exhausted or used absorbing filter for treating groundwater with elevated calcium level under elevated temperatures with steam in a rotating kiln to restore its surface activity and break down any organic compounds.

The closest prior art is Wang *et al.*, *Chemosphere*, (**2015)**, v.131, p.178-183. Wang *et al.* discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM comprising a step of mixing 1g of sludge B1 (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration, see "2.3 *Aqueous solution composition*" at page 180. However, Wang *et al.* does not teach about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof., nor the sorbent material used in the claimed method includes one or more of carbonaceous char, activated carbon, and reactivated carbon. In addition, Wang teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS because Wang describes a decrease in the Kd value of the sludge that was burned at 300 °C for 1 hour compared to sludge that was not burned. Therefore, Wang discourages using a sorbent material including one or more of carbonaceous char, activated carbon, and reactivated carbon in the process. Therefore, Wang *et al.* neither anticipate nor render instant claims obvious because there is no motivation disclosed by Wang for further modification in the reference. Therefore, claims 1, and 3-14 are allowed.

Conclusions

- Claims 1, and 3-14 are allowed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Telephone Inquiry

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Yong Chu, whose telephone number is (571)272-5759. The examiner can normally be reached on M-F 8:30am-5:00pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Bryan D. Ripa can be reached on 571-270-7875. The fax phone number for the organization where this application or proceeding is assigned is (571) 273-8300.

/YONG L CHU/
Primary Examiner, Art Unit 1731

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

CPC						
Symbol					**Type**	**Version**
B01J	/	20	/	20	F	2013-01-01
B01J	/	20	/	041	I	2013-01-01
C02F	/	1	/	283	I	2013-01-01
B01D	/	53	/	02	I	2013-01-01
B01J	/	20	/	3028	I	2013-01-01
C02F	/	2101	/	36	A	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/YONG L CHU/ Primary Examiner, Art Unit 1731	05 December 2023	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	None

U.S. Patent and Trademark Office — Part of Paper No.: 20231205

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00015

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

INTERNATIONAL CLASSIFICATION				
CLAIMED				
B01J	/	20	/	20
B01J	/	20	/	04
B01J	/	20	/	30
B01D	/	53	/	02
C02F	/	1	/	28

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**
502	418

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE (Assistant Examiner) (Date)	**Total Claims Allowed:** 13	
/YONG L CHU/ Primary Examiner, Art Unit 1731 (Primary Examiner) 05 December 2023 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure None

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00016

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE		**Total Claims Allowed:**	
(Assistant Examiner)	(Date)	13	
/YONG L CHU/ Primary Examiner, Art Unit 1731	05 December 2023	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	None

U.S. Patent and Trademark Office Part of Paper No.: 20231205

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00017

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J20/20; 041; 3028	02/25/2022	YC
B01D53/02	02/25/2022	YC
C02F1/283	02/25/2022	YC

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00018

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

Search Notes		
Search Notes	**Date**	**Examiner**
EAST	02/25/2022	YC
STN	02/25/2022	YC
Patent global Dossier of 16/839,862	02/25/2022	YC
Google scholar search--PFAS removal from wastewater Ca2+ Mg2+--02252022	02/25/2022	YC
The PCT search report "Y" references are not good prior art. Much better prior art references are found and cited by this examiner. A lot of search time spent	02/25/2022	YC
ODP search (PALM inventor name and assignee, EAST and STN search)	02/25/2022	YC
PE2E-search	10/24/2022	YC
ODP search (inventor name and assignee PE2E-search)	07/21/2023	YC
ODP search (inventor name and assignee PE2E-search)	10/06/2023	YC
PE2E-search	10/06/2023	YC
PE2E-search	12/05/2023	YC

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
See search report	See search report	10/06/2023	YC

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00019

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/25/2022	10/24/2022	07/21/2023	10/06/2023	10/20/2023	12/05/2023			
1	1	✓	✓	=	=	=	=			
	2	✓	✓	-	-	-	-			
2	3	✓	✓	=	=	=	=			
3	4	✓	✓	=	=	=	=			
4	5	✓	✓	=	=	=	=			
5	6	✓	✓	=	=	=	=			
6	7	✓	✓	=	=	=	=			
7	8	✓	✓	=	=	=	=			
8	9	✓	✓	=	=	=	=			
9	10	✓	✓	=	=	=	=			
10	11	✓	✓	=	=	=	=			
11	12	✓	✓	=	=	=	=			
12	13	✓	✓	=	=	=	=			
13	14				=	=	=			

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00020

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

U.S.PATENTS						Remove
Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					
If you wish to add additional U.S. Patent citation information please click the Add button.						Add

U.S.PATENT APPLICATION PUBLICATIONS						Remove
Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
/Y.L.C/	1	20160167982	A1	2016-06-16	Stouffer et al.	
If you wish to add additional U.S. Published Application citation information please click the Add button.						Add

FOREIGN PATENT DOCUMENTS								Remove
Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐
If you wish to add additional Foreign Patent Document citation information please click the Add button								Add

NON-PATENT LITERATURE DOCUMENTS			Remove
Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

/Y.L.C/	1	Pietrzak et al. “Preparation of Nitrogen-Enriched Activated Carbons from Brown Coal” 2006, Energy & Fuels 20:1275-1280	☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature	/YONG L CHU/	Date Considered	12/05/2023

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L1	1	"20140112856".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:57 PM
L2	1	"20140336568".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:58 PM
L3	1	"20200179902".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L4	1	"20080283446".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L5	1	"20190270081".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L6	118	((("CALGON") near3 ("CARBON") near3 ("CORPORATION"))).AS,AANM.	(USPAT)	OR	ON	ON	2023/07/21 10:32 AM
L7	53	((("DISTEFANO") near3 ("Rebecca")) OR (("MIMNA") near3 ("Richard"))).INV.	(US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT)	OR	ON	ON	2023/07/21 10:32 AM
L8	17	L7 AND L6	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:32 AM
L9	50	(B01J20/20.cpc. OR B01J20/041.cpc. OR B01J20/3028.cpc.) AND B01D53/02.cpc. AND C02F1/283.cpc.	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:39 AM
L10	1	L9 AND (perfluoroalkyl OR polyfluoroalkyl OR PFAS)	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:41 AM
L11	17	"839862".ap.	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:41 PM
L12	18	l8	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L13	0	L12 NOT L8	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L14	51	L9	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L15	0	L14 NOT L9	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L16	1	"20160167982".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2023/12/05 04:32 PM

PE2E SEARCH - Search History (Interference)

There are no Interference searches to show.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00023

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**11/10/2023 03:07:52 PM Z ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	63219932	AUTHORIZED BY	Emma Holland
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	**E2023A0F09036172**	**Paula Watson**

PRE-AUTHORIZED ACCOUNT	PRE-AUTHORIZED CATEGORY
604406	**37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.20 (Post Issuance fees); 37 CFR 1.21 (Miscellaneous fees and charges)**

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1806	SUBMISSION OF AN INFORMATION DISCLOSURE STATEMENT	260.00	1	260.00
			TOTAL AMOUNT:	**$260.00**

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d)

and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: PTA.IDS
Document Description: Patent Term Adjustment Stmt Under 37 CFR 1.704(d)

PTO/SB/133 (10-21)

PATENT TERM ADJUSTMENT STATEMENT UNDER 37 CFR 1.704(d)		
	Application Number	16/839,862
	Filing Date	April 3, 2020
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Practitioner Docket No.	123450-013001

APPLICANT HEREBY STATES THE FOLLOWING (please review 37 CFR 1.704(d) before filing this form):

☑ Each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

AND/OR

☐ Each item of information contained in the information disclosure statement is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

INSTRUCTIONS:

- **This form will not satisfy the requirement of 37 CFR 1.97(e).** The present statement is filed under 37 CFR 1.704(d) and will not substitute for compliance with any of the requirements of 37 CFR 1.97 and 1.98. For an information disclosure statement to comply with 37 CFR 1.97(c) or (d), the information disclosure statement must be accompanied by a statement under 37 CFR 1.97(e) notwithstanding any statement filed under 37 CFR 1.704(d).
- The present form (PTO/SB/133) should be filed concurrently with the information disclosure statement to derive benefit under 37 CFR 1.704(d).

Signature	/Emma K. Holland/	Date	2023-11-10
Typed or Printed Name	Emma K. Holland	Practitioner Registration Number	79,947

***Note**: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature. If necessary, submit multiple forms for more than one signature, see below*.*

☑ *Total of 1 forms are submitted.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(**Not for submission under 37 CFR 1.99)**

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. DISTEFANO
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20160167982	A1	2016-06-16	Stouffer et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							☐

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

	1	Pietrzak et al. “Preparation of Nitrogen-Enriched Activated Carbons from Brown Coal” 2006, Energy & Fuels 20:1275-1280	☐

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☐ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached certification statement.

☒ The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

☐ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Emma K. Holland/	Date (YYYY-MM-DD)	2023-11-10
Name/Print	Emma K. Holland	Registration Number	79947

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00031

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**11/10/2023 03:07:52 PM Z ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	63219932	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Emma Holland

Documents

TOTAL DOCUMENTS: 4

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
123450-013001 SIDS Transmittal 10-Nov-23.pdf	2	Letter specifying the conditions for filing under 37 CFR 1.97	109 KB
123450-013001 Safe Harbor 10-Nov-23.pdf	2	Patent Term Adjustment Statement under 37 CFR 1.704(d) filed with an IDS	656 KB
123450-013001 SB08_10-NOV-2023.pdf	4	Information Disclosure Statement (IDS) Form (SB08)	1244 KB
Pietrzak1275.pdf	6	Non Patent Literature	866 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450-013001 SIDS Transmittal 10-Nov-23.pdf	6A4A0DC11475179B83EFB16325A82F7EBFDD383DFAB8FF07788E2A811185C6BD6A36FB7643A38818FFF847157F68B4C8D484E353A5C4204781052511E8745631
123450-013001 Safe Harbor 10-Nov-23.pdf	C50CB7C4D053CE2CBDC33F7F5CFA0F809F46DC90E3D004D6103C625F01A8784D5D47868BB60A2A330979DE6B9B12026FBBC286F959B8C78DD83C3E44EEE75D1B
123450-013001 SB08_10-NOV-2023.pdf	5E2B3F0E749E21824CC0EA11FD9948FDD52A25BF2DA7E02FBE3AAE9C6A43BCA96063B2AA96E20B6836E4A329EB0733799C6DD700D446C9C3950ED09C501B97D6
Pietrzak1275.pdf	878A6E0FD741AAF42067316DC53D9F50C31A8370A07001E32F521B0B5BDABA0FDB7403A6029966740483699591BD2466D2CB4570EEAEF867CE1B66DFE0F5EB89

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(d) and C.F.R. §1.97(e)(2) / Fee Authorization

This Information Disclosure Statement is being filed under 37 C.F.R. §1.97(d) after the mailing date of a Final Office Action or Notice of Allowance, but before the payment of the issue fee. The undersigned asserts in accordance with 37 CFR 1.97(e)(2), that no item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the Information Disclosure Statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the Information Disclosure Statement under 37 C.F.R. §1.97(e)(2). Accordingly, the Information Disclosure Statement Fee of $260.00 is submitted herewith under 37 C.F.R. § 1.17(p). However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

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Statement under 37 C.F.R. §1.704(d)(i) / Patent Term Adjustment

Applicant states that each item of information contained in the Information Disclosure Statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in § 1.56 (c) more than thirty days prior to the filing of the Information Disclosure Statement. Thus, Applicant holds that the submission of this Statement does not affect any Patent Term Adjustment.

Respectfully submitted,

DLA PIPER LLP (US)

/ Emma K. Holland /

Emma K. Holland
Reg. No. 79,947

DLA PIPER LLP (US)
1650 Market Street, Suite 5000
Philadelphia, PA 19103-7348
Telephone: (215) 656-3300
Date: November 10, 2023

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

93724 7590 10/25/2023

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

EXAMINER
CHU, YONG LIANG

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
10/25/2023	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Corrected ***Notice of Allowability***	**Application No.** 16/839,862	**Applicant(s)** DISTEFANO et al.	
	Examiner YONG L CHU	**Art Unit** 1731	**AIA (FITF) Status** Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to Applicant's submission on 10/02/2023.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1 and 3-14 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some* c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☐ Notice of References Cited (PTO-892)
2. ☐ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☑ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YONG L CHU/
Primary Examiner, Art Unit 1731

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DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

The Notice of Allowance (NOA) mailed on 10/18/2023 has been vacated. This corrected NOA replaces the previous one.

Claim 2 is cancelled. Claims 1, and 3-14 are pending in the instant application.

Response to Amendment

The Amendments by Applicants' representative Nicholas C. Kokkinos filed on 10/02/2023 has been entered.

Information Disclosure Statements

Applicant's Information Disclosure Statement, filed on 09/22/2023, has been considered. Please refer to Applicant's copy of the PTO-1449 submitted herewith.

Response to Amendment/Argument

Object to Amendment

Applicant's amendment overcomes the objection. The objection is hereby **withdrawn**.

Examiner's Amendment

An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

The application has been amended as following:

Claim 3, line 1, **after** "The method of", **DELETE** "claim 2", and **INSERT** --claim 1--.

Claim 4, line 1, **after** "The method of", **DELETE** "claim 2", and **INSERT** --claim 1--.

Claim 5, line 1, **after** "The method of", **DELETE** "claim 2", and **INSERT** --claim 1--.

Reasons for Allowance

The present invention is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, and reactivated carbon according to claim 1. Applicant's specification [0050-0051] describes EXAMPLE 1 of producing the first sorbent material by reactivating exhausted or used absorbing filter for treating groundwater with elevated calcium level under elevated temperatures with steam in a rotating kiln to restore its surface activity and break down any organic compounds.

The closest prior art is Wang *et al.*, *Chemosphere*, (**2015)**, v.131, p.178-183. Wang *et al.* discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM comprising a step of mixing 1g of sludge B1 (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration, see "2.3 *Aqueous solution composition*" at page 180. However, Wang *et al.* does not teach about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof.,

nor the sorbent material used in the claimed method includes one or more of carbonaceous char, activated carbon, and reactivated carbon. In addition, Wang teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS because Wang describes a decrease in the Kd value of the sludge that was burned at 300 °C for 1 hour compared to sludge that was not burned. Therefore, Wang discourages using a sorbent material including one or more of carbonaceous char, activated carbon, and reactivated carbon in the process. Therefore, Wang *et al.* neither anticipate nor render instant claims obvious because there is no motivation disclosed by Wang for further modification in the reference. Therefore, claims 1, and 3-14 are allowed.

Conclusions

- Claims 1, and 3-14 are allowed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Telephone Inquiry

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Yong Chu, whose telephone number is (571)272-5759. The examiner can normally be reached on M-F 8:30am-5:00pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Bryan D. Ripa can be reached on 571-270-7875. The fax phone number for the organization where this application or proceeding is assigned is (571) 273-8300.

/YONG L CHU/
Primary Examiner, Art Unit 1731

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/25/2022	10/24/2022	07/21/2023	10/06/2023	10/20/2023				
1	1	✓	✓	=	=	=				
	2	✓	✓	-	-	-				
2	3	✓	✓	=	=	=				
3	4	✓	✓	=	=	=				
4	5	✓	✓	=	=	=				
5	6	✓	✓	=	=	=				
6	7	✓	✓	=	=	=				
7	8	✓	✓	=	=	=				
8	9	✓	✓	=	=	=				
9	10	✓	✓	=	=	=				
10	11	✓	✓	=	=	=				
11	12	✓	✓	=	=	=				
12	13	✓	✓	=	=	=				
13	14				=	=				

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00042

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

CPC						
Symbol					**Type**	**Version**
B01J	/	20	/	20	F	2013-01-01
B01J	/	20	/	041	I	2013-01-01
C02F	/	1	/	283	I	2013-01-01
B01D	/	53	/	02	I	2013-01-01
B01J	/	20	/	3028	I	2013-01-01
C02F	/	2101	/	36	A	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE		Total Claims Allowed:	
(Assistant Examiner)	(Date)	13	
/YONG L CHU/ Primary Examiner, Art Unit 1731	20 October 2023	O.G. Print Claim(s)	O.G. Print Figure
(Primary Examiner)	(Date)	1	None

U.S. Patent and Trademark Office — Part of Paper No.: 20231020

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00043

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

INTERNATIONAL CLASSIFICATION				
CLAIMED				
B01J	/	20	/	20
B01J	/	20	/	04
B01J	/	20	/	30
B01D	/	53	/	02
C02F	/	1	/	28

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**
502	418

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE (Assistant Examiner) (Date)	**Total Claims Allowed:** 13	
/YONG L CHU/ Primary Examiner, Art Unit 1731 (Primary Examiner) 20 October 2023 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure None

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00044

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 13	
/YONG L CHU/ Primary Examiner, Art Unit 1731 (Primary Examiner)	20 October 2023 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure None

U.S. Patent and Trademark Office Part of Paper No.: 20231020

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00045

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

NOTICE OF ALLOWANCE AND FEE(S) DUE

93724 7590 10/18/2023

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

EXAMINER	
CHU, YONG LIANG	
ART UNIT	PAPER NUMBER
1731	

DATE MAILED: 10/18/2023

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

TITLE OF INVENTION: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	01/18/2024

THE APPLICATION IDENTIFIED ABOVE HAS BEEN EXAMINED AND IS ALLOWED FOR ISSUANCE AS A PATENT. PROSECUTION ON THE MERITS IS CLOSED. THIS NOTICE OF ALLOWANCE IS NOT A GRANT OF PATENT RIGHTS. THIS APPLICATION IS SUBJECT TO WITHDRAWAL FROM ISSUE AT THE INITIATIVE OF THE OFFICE OR UPON PETITION BY THE APPLICANT. SEE 37 CFR 1.313 AND MPEP 1308.

THE ISSUE FEE AND PUBLICATION FEE (IF REQUIRED) MUST BE PAID WITHIN THREE MONTHS FROM THE MAILING DATE OF THIS NOTICE OR THIS APPLICATION SHALL BE REGARDED AS ABANDONED. THIS STATUTORY PERIOD CANNOT BE EXTENDED. SEE 35 U.S.C. 151. THE ISSUE FEE DUE INDICATED ABOVE DOES NOT REFLECT A CREDIT FOR ANY PREVIOUSLY PAID ISSUE FEE IN THIS APPLICATION. IF AN ISSUE FEE HAS PREVIOUSLY BEEN PAID IN THIS APPLICATION (AS SHOWN ABOVE), THE RETURN OF PART B OF THIS FORM WILL BE CONSIDERED A REQUEST TO REAPPLY THE PREVIOUSLY PAID ISSUE FEE TOWARD THE ISSUE FEE NOW DUE.

HOW TO REPLY TO THIS NOTICE:

I. Review the ENTITY STATUS shown above. If the ENTITY STATUS is shown as SMALL or MICRO, verify whether entitlement to that entity status still applies.

If the ENTITY STATUS is the same as shown above, pay the TOTAL FEE(S) DUE shown above.

If the ENTITY STATUS is changed from that shown above, on PART B - FEE(S) TRANSMITTAL, complete section number 5 titled "Change in Entity Status (from status indicated above)".

For purposes of this notice, small entity fees are 40% the amount of undiscounted fees, and micro entity fees are 20% the amount of undiscounted fees.

II. PART B - FEE(S) TRANSMITTAL, or its equivalent, must be completed and returned to the United States Patent and Trademark Office (USPTO) with your ISSUE FEE and PUBLICATION FEE (if required). If you are charging the fee(s) to your deposit account, section "4b" of Part B - Fee(s) Transmittal should be completed. If an equivalent of Part B is filed, a request to reapply a previously paid issue fee must be clearly made, and delays in processing may occur due to the difficulty in recognizing the paper as an equivalent of Part B.

III. All communications regarding this application must give the application number. Please direct all communications prior to issuance to Mail Stop ISSUE FEE unless advised to the contrary.

IMPORTANT REMINDER: Maintenance fees are due in utility patents issuing on applications filed on or after Dec. 12, 1980. It is patentee's responsibility to ensure timely payment of maintenance fees when due. More information is available at www.uspto.gov/PatentMaintenanceFees.

PTOL-85 (Rev. 02/11)

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00046

PART B - FEE(S) TRANSMITTAL

Complete and send this form, together with applicable fee(s), by mail or fax, or via EFS-Web.

By mail, send to: Mail Stop ISSUE FEE
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

By fax, send to: (571)-273-2885

INSTRUCTIONS: This form should be used for transmitting the ISSUE FEE and PUBLICATION FEE (if required). Blocks 1 through 5 should be completed where appropriate. All further correspondence will be mailed to the current correspondence address as indicated unless corrected below or directed otherwise in Block 1, by (a) specifying a new correspondence address; and/or (b) indicating a separate "FEE ADDRESS" for maintenance fee notifications. **Because electronic patent issuance may occur shortly after issue fee payment, any desired continuing application should preferably be filed prior to payment of this issue fee in order not to jeopardize copendency.**

CURRENT CORRESPONDENCE ADDRESS (Note: Use Block 1 for any change of address)

93724 7590 10/18/2023
DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

Note: A certificate of mailing can only be used for domestic mailings of the Fee(s) Transmittal. This certificate cannot be used for any other accompanying papers. Each additional paper, such as an assignment or formal drawing, must have its own certificate of mailing or transmission.

Certificate of Mailing or Transmission

I hereby certify that this Fee(s) Transmittal is being deposited with the United States Postal Service with sufficient postage for first class mail in an envelope addressed to the Mail Stop ISSUE FEE address above, or being transmitted to the USPTO via EFS-Web or by facsimile to (571) 273-2885, on the date below.

(Typed or printed name)
(Signature)
(Date)

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

TITLE OF INVENTION: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

APPLN. TYPE	ENTITY STATUS	ISSUE FEE DUE	PUBLICATION FEE DUE	PREV. PAID ISSUE FEE	TOTAL FEE(S) DUE	DATE DUE
nonprovisional	UNDISCOUNTED	$1200	$0.00	$0.00	$1200	01/18/2024

EXAMINER	ART UNIT	CLASS-SUBCLASS
CHU, YONG LIANG	1731	502-418000

1. Change of correspondence address or indication of "Fee Address" (37 CFR 1.363).

❑ Change of correspondence address (or Change of Correspondence Address form PTO/AIA/122 or PTO/SB/122) attached.

❑ "Fee Address" indication (or "Fee Address" Indication form PTO/AIA/47 or PTO/SB/47; Rev 03-02 or more recent) attached. **Use of a Customer Number is required.**

2. For printing on the patent front page, list
(1) The names of up to 3 registered patent attorneys or agents OR, alternatively,
(2) The name of a single firm (having as a member a registered attorney or agent) and the names of up to 2 registered patent attorneys or agents. If no name is listed, no name will be printed.

1_____
2_____
3_____

3. ASSIGNEE NAME AND RESIDENCE DATA TO BE PRINTED ON THE PATENT (print or type)

PLEASE NOTE: Unless an assignee is identified below, no assignee data will appear on the patent. If an assignee is identified below, the document must have been previously recorded, or filed for recordation, as set forth in 37 CFR 3.11 and 37 CFR 3.81(a). Completion of this form is NOT a substitute for filing an assignment.

(A) NAME OF ASSIGNEE (B) RESIDENCE: (CITY and STATE OR COUNTRY)

Please check the appropriate assignee category or categories (will not be printed on the patent) : ❑ Individual ❑ Corporation or other private group entity ❑ Government

4a. Fees submitted: ❑Issue Fee ❑Publication Fee (if required)

4b. Method of Payment: *(Please first reapply any previously paid fee shown above)*

❑ Electronic Payment via Patent Center or EFS-Web ❑ Enclosed check ❑ Non-electronic payment by credit card (Attach form PTO-2038)

❑ The Director is hereby authorized to charge the required fee(s), any deficiency, or credit any overpayment to Deposit Account No. _____

5. **Change in Entity Status** (from status indicated above)

❑ Applicant certifying micro entity status. See 37 CFR 1.29
NOTE: Absent a valid certification of Micro Entity Status (see forms PTO/SB/15A and 15B), issue fee payment in the micro entity amount will not be accepted at the risk of application abandonment.

❑ Applicant asserting small entity status. See 37 CFR 1.27
NOTE: If the application was previously under micro entity status, checking this box will be taken to be a notification of loss of entitlement to micro entity status.

❑ Applicant changing to regular undiscounted fee status.
NOTE: Checking this box will be taken to be a notification of loss of entitlement to small or micro entity status, as applicable.

NOTE: This form must be signed in accordance with 37 CFR 1.31 and 1.33. See 37 CFR 1.4 for signature requirements and certifications.

Authorized Signature _____ Date _____

Typed or printed name _____ Registration No. _____

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00047

UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

93724 7590 10/18/2023

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EXAMINER	
CHU, YONG LIANG	
ART UNIT	**PAPER NUMBER**
1731	

DATE MAILED: 10/18/2023

Determination of Patent Term Adjustment under 35 U.S.C. 154 (b)
(Applications filed on or after May 29, 2000)

The Office has discontinued providing a Patent Term Adjustment (PTA) calculation with the Notice of Allowance.

Section 1(h)(2) of the AIA Technical Corrections Act amended 35 U.S.C. 154(b)(3)(B)(i) to eliminate the requirement that the Office provide a patent term adjustment determination with the notice of allowance. See Revisions to Patent Term Adjustment, 78 Fed. Reg. 19416, 19417 (Apr. 1, 2013). Therefore, the Office is no longer providing an initial patent term adjustment determination with the notice of allowance. The Office will continue to provide a patent term adjustment determination with the Issue Notification Letter that is mailed to applicant approximately three weeks prior to the issue date of the patent, and will include the patent term adjustment on the patent. Any request for reconsideration of the patent term adjustment determination (or reinstatement of patent term adjustment) should follow the process outlined in 37 CFR 1.705.

Any questions regarding the Patent Term Extension or Adjustment determination should be directed to the Office of Patent Legal Administration at (571)-272-7702. Questions relating to issue and publication fee payments should be directed to the Customer Service Center of the Office of Patent Publication at 1-(888)-786-0101 or (571)-272-4200.

Exhibit 1042
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OMB Clearance and PRA Burden Statement for PTOL-85 Part B

The Paperwork Reduction Act (PRA) of 1995 requires Federal agencies to obtain Office of Management and Budget approval before requesting most types of information from the public. When OMB approves an agency request to collect information from the public, OMB (i) provides a valid OMB Control Number and expiration date for the agency to display on the instrument that will be used to collect the information and (ii) requires the agency to inform the public about the OMB Control Number's legal significance in accordance with 5 CFR 1320.5(b).

The information collected by PTOL-85 Part B is required by 37 CFR 1.311. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 30 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, Virginia 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-1450. Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Notice of Allowability	Application No. 16/839,862	Applicant(s) DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☑ This communication is responsive to the submission filed 10/02/2023.
   ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2. ☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

3. ☑ The allowed claim(s) is/are 1 and 3-14 . As a result of the allowed claim(s), you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information , please see **http://www.uspto.gov/patents/init_events/pph/index.jsp** or send an inquiry to **PPHfeedback@uspto.gov.**

4. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

   Certified copies:

   a) ☐ All b) ☐ Some* c) ☐ None of the:

   1. ☐ Certified copies of the priority documents have been received.
   2. ☐ Certified copies of the priority documents have been received in Application No. _____ .
   3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

   * Certified copies not received: _____ .

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.
THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
   ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date _____ .

   Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).

6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☑ Notice of References Cited (PTO-892)
2. ☑ Information Disclosure Statements (PTO/SB/08), Paper No./Mail Date _____.
3. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material _____.
4. ☐ Interview Summary (PTO-413), Paper No./Mail Date. _____.
5. ☑ Examiner's Amendment/Comment
6. ☑ Examiner's Statement of Reasons for Allowance
7. ☐ Other _____.

/YONG L CHU/
Primary Examiner, Art Unit 1731

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DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Claim 2 is cancelled. Claims 1, and 3-14 are pending in the instant application.

Response to Amendment

The Amendments by Applicants' representative Nicholas C. Kokkinos filed on 10/02/2023 has been entered.

Information Disclosure Statements

Applicant's Information Disclosure Statement, filed on 09/22/2023, has been considered. Please refer to Applicant's copy of the PTO-1449 submitted herewith.

Response to Amendment/Argument

Object to Amendment

Applicant's amendment overcomes the objection. The objection is hereby **withdrawn**.

Reasons for Allowance

The present invention is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material includes one or more of carbonaceous

char, activated carbon, and reactivated carbon according to claim 1. Applicant's specification [0050-0051] describes EXAMPLE 1 of producing the first sorbent material by reactivating exhausted or used absorbing filter for treating groundwater with elevated calcium level under elevated temperatures with steam in a rotating kiln to restore its surface activity and break down any organic compounds.

The closest prior art is Wang *et al.*, *Chemosphere*, (**2015)**, v.131, p.178-183. Wang *et al.* discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM comprising a step of mixing 1g of sludge B1 (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration, see "2.3 *Aqueous solution composition*" at page 180. However, Wang *et al.* does not teach about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof., nor the sorbent material used in the claimed method includes one or more of carbonaceous char, activated carbon, and reactivated carbon. In addition, Wang teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS because Wang describes a decrease in the Kd value of the sludge that was burned at 300 °C for 1 hour compared to sludge that was not burned. Therefore, Wang discourages using a sorbent material including one or more of carbonaceous char, activated carbon, and reactivated carbon in the process. Therefore, Wang *et al.* neither anticipate nor render instant claims obvious because there is no motivation disclosed by Wang for further modification in the reference. Therefore, claims 1, and 3-14 are allowed.

Conclusions

- Claims 1, and 3-14 are allowed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Telephone Inquiry

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Yong Chu, whose telephone number is (571)272-5759. The examiner can normally be reached on M-F 8:30am-5:00pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Bryan D. Ripa can be reached on 571-270-7875. The fax phone number for the organization where this application or proceeding is assigned is (571) 273-8300.

/YONG L CHU/
Primary Examiner, Art Unit 1731

Notice of References Cited	Application/Control No. 16/839,862	Applicant(s)/Patent Under Reexamination DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
	A					
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
*	U	Wang et al., Chemosphere, (2015), v.131, p.178-183.
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

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Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/25/2022	10/24/2022	07/21/2023	10/06/2023					
1	1	✓	✓	=	=					
	2	✓	✓	-	-					
2	3	✓	✓	=	=					
3	4	✓	✓	=	=					
4	5	✓	✓	=	=					
5	6	✓	✓	=	=					
6	7	✓	✓	=	=					
7	8	✓	✓	=	=					
8	9	✓	✓	=	=					
9	10	✓	✓	=	=					
10	11	✓	✓	=	=					
11	12	✓	✓	=	=					
12	13	✓	✓	=	=					
13	14				=					

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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J20/20; 041; 3028	02/25/2022	YC
B01D53/02	02/25/2022	YC
C02F1/283	02/25/2022	YC

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

/YONG L CHU/ Primary Examiner, Art Unit 1731	

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Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

Search Notes		
Search Notes	**Date**	**Examiner**
EAST	02/25/2022	YC
STN	02/25/2022	YC
Patent global Dossier of 16/839,862	02/25/2022	YC
Google scholar search--PFAS removal from wastewater Ca2+ Mg2+--02252022	02/25/2022	YC
The PCT search report "Y" references are not good prior art. Much better prior art references are found and cited by this examiner. A lot of search time spent	02/25/2022	YC
ODP search (PALM inventor name and assignee, EAST and STN search)	02/25/2022	YC
PE2E-search	10/24/2022	YC
ODP search (inventor name and assignee PE2E-search)	07/21/2023	YC
ODP search (inventor name and assignee PE2E-search)	10/06/2023	YC
PE2E-search	10/06/2023	YC

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
See search report	See search report	10/06/2023	YC

/YONG L CHU/ Primary Examiner, Art Unit 1731	

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Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

CPC						
Symbol					**Type**	**Version**
B01J	/	20	/	20	F	2013-01-01
B01J	/	20	/	041	I	2013-01-01
C02F	/	1	/	283	I	2013-01-01
B01D	/	53	/	02	I	2013-01-01
B01J	/	20	/	3028	I	2013-01-01
C02F	/	2101	/	36	A	2013-01-01

CPC Combination Sets							
Symbol					**Type**	**Set**	**Ranking**	**Version**
	/		/					

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 13	
/YONG L CHU/ Primary Examiner, Art Unit 1731 (Primary Examiner)	06 October 2023 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure None

U.S. Patent and Trademark Office — Part of Paper No.: 20231006

Exhibit 1042
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Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

INTERNATIONAL CLASSIFICATION				
CLAIMED				
B01J	/	20	/	20
B01J	/	20	/	04
B01J	/	20	/	30
B01D	/	53	/	02
C02F	/	1	/	28

NON-CLAIMED				
	/		/	

US ORIGINAL CLASSIFICATION	
CLASS	**SUBCLASS**
502	418

CROSS REFERENCES(S)						
CLASS	**SUBCLASS (ONE SUBCLASS PER BLOCK)**					

NONE (Assistant Examiner) (Date)	**Total Claims Allowed:** 13	
/YONG L CHU/ Primary Examiner, Art Unit 1731 (Primary Examiner) 06 October 2023 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure None

U.S. Patent and Trademark Office Part of Paper No.: 20231006

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00059

Issue Classification	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIMS

Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original	Final	Original

NONE (Assistant Examiner)	(Date)	**Total Claims Allowed:** 13	
/YONG L CHU/ Primary Examiner, Art Unit 1731 (Primary Examiner)	06 October 2023 (Date)	O.G. Print Claim(s) 1	O.G. Print Figure None

U.S. Patent and Trademark Office Part of Paper No.: 20231006

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
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Bibliographic Data

Application No: 16/839,862

Foreign Priority claimed: ○ Yes ◉ No

35 USC 119 (a-d) conditions met: ☐ Yes ☐ No ☐ Met After Allowance

Verified and Acknowledged: /YONG L CHU/ (Examiner's Signature) | (Initials)

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
04/03/2020	502	1731	123450-013001
RULE			

APPLICANTS

CALGON CARBON CORPORATION, Moon Township, PA, UNITED STATES

INVENTORS

Rebecca L. DISTEFANO, Oakdale, PA, UNITED STATES

Richard A. MIMNA, Oakdale, PA, UNITED STATES

CONTINUING DATA

This application has PRO of 62828790 04/03/2019

FOREIGN APPLICATIONS

IF REQUIRED, FOREIGN LICENSE GRANTED**

04/13/2020

STATE OR COUNTRY

UNITED STATES

ADDRESS

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348
UNITED STATES

FILING FEE RECEIVED

$1,880

PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L1	1	"20140112856".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:57 PM
L2	1	"20140336568".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:58 PM
L3	1	"20200179902".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L4	1	"20080283446".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L5	1	"20190270081".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L6	118	((("CALGON") near3 ("CARBON") near3 ("CORPORATION"))).AS,AANM.	(USPAT)	OR	ON	ON	2023/07/21 10:32 AM
L7	53	((("DISTEFANO") near3 ("Rebecca")) OR (("MIMNA") near3 ("Richard"))).INV.	(US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT)	OR	ON	ON	2023/07/21 10:32 AM
L8	17	L7 AND L6	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:32 AM
L9	50	(B01J20/20.cpc. OR B01J20/041.cpc. OR B01J20/3028.cpc.) AND B01D53/02.cpc. AND C02F1/283.cpc.	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:39 AM
L10	1	L9 AND (perfluoroalkyl OR polyfluoroalkyl OR PFAS)	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:41 AM
L11	17	"839862".ap.	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:41 PM
L12	18	l8	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L13	0	L12 NOT L8	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L14	51	L9	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM
L15	0	L14 NOT L9	(US-PGPUB; USPAT)	OR	ON	ON	2023/10/06 04:44 PM

PE2E SEARCH - Search History (Interference)

There are no Interference searches to show.

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OK to enter. /YONG CHU/ 10/06/2023

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1731
Confirmation No.	:	5111
Examiner	:	CHU, YONG LIANG

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RESPONSE TO *EX PARTE QUAYLE* ACTION

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This Response constitutes a reply to the issue raised in the *Ex Parte Quayle* Action mailed August 4, 2023 in the above-identified application. A two-month shortened statutory period for reply is set forth in the Office Action. Accordingly, this response is timely filed.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **4** of this paper.

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	DISTEFANO; Rebecca L.
Art Unit	1731
Examiner Name	CHU, YONG LIANG
Attorney Docket Number	123450-013001

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
/Y.L.C/	1	2018116842	WO	A1	2018-06-28	KURARAY CO	w/English Machine Translation	X

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	DISTEFANO; Rebecca L.
	Art Unit	1731
	Examiner Name	CHU, YONG LIANG
	Attorney Docket Number	123450-013001

	1	

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EXAMINER SIGNATURE

Examiner Signature	/YONG L CHU/	Date Considered	10/06/2023

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00065

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1731
Confirmation No.	:	5111
Examiner	:	CHU, YONG LIANG

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RESPONSE TO *EX PARTE QUAYLE* ACTION

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This Response constitutes a reply to the issue raised in the *Ex Parte Quayle* Action mailed August 4, 2023 in the above-identified application. A two-month shortened statutory period for reply is set forth in the Office Action. Accordingly, this response is timely filed.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **4** of this paper.

AMENDMENTS TO THE CLAIMS

The current listing of the claims replaces all prior versions and listings of the claims in the present application.

1. (Previously Presented) A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:
   providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and
   contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, and reactivated carbon.
2. (Canceled)
3. (Original) The method of claim 2, wherein the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.
4. (Original) The method of claim 2, wherein the first sorbent material is reactivated carbon.
5. (Original) The method of claim 2, wherein the first sorbent material is a reagglomerated activated carbon.
6. (Original) The method of claim 1, further comprising:
   providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and
   contacting the second sorbent material with the liquid or gas containing the PFAS.

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7. (Original) The method of claim 1, wherein the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium, an oxide of strontium, or an oxide of barium.
8. (Original) The method of claim 7, wherein the first sorbent material includes one or more of MgO or CaO.
9. (Previously Presented) The method of claim 1, wherein the salt, oxide, or hydroxide of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation, chemical vapor deposition, or physical vapor deposition.
10. (Previously Presented) The method of claim 1, wherein about 1 wt.% to about 20 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
11. (Previously Presented) The method of claim 10, wherein about 2 wt.% to about 8 wt.% of the first sorbent material comprises salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
12. (Previously Presented) The method of claim 1, wherein the first sorbent material is a reactivated carbon comprising oxides of calcium, magnesium, sodium, potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the oxides of calcium, magnesium, sodium, potassium and zinc.
13. (Previously Presented) The method of claim 12, wherein the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the oxides of calcium, magnesium, sodium, and zinc.
14. (Previously Presented) The method of claim 1, wherein the first sorbent material includes one or more of a carbonate of magnesium, a carbonate of calcium, a carbonate of strontium, or a carbonate of barium.

REMARKS

Applicant would like to thank the Examiner for the careful consideration given to the present application. Applicant also thanks the Examiner for the withdrawal of the rejections to the claims. Claims 1 and 3-14 are pending and have been allowed.

In order to correct the formal matters necessary to move the present application to issuance, the Applicant hereby submits the following action and remarks.

Objection to Amendment

In the *Ex parte Quayle* Action, the Examiner objected to the previous amendments made to claim 2 in the Response filed April 28, 2023 for being non-compliance under M.P.E.P. § 714(c)(4)(i). Applicant has removed the text from canceled claim 2 and submits that no new matter has been added.

There being no other objections or rejections, Applicant believes pending claims 1 and 3-14 are in condition for allowance and respectfully requests notice to such effect.

AUTHORIZATION

Should the Examiner have any questions or comments, or need any additional information from Applicant's representative, the Examiner is invited to contact the undersigned. The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to Deposit Account No. 60-4406.

Respectfully submitted,
DLA PIPER LLP

/Nicholas Kokkinos/

Nicholas C. Kokkinos
Registration No. 76,979

Date: October 2, 2023
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UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**10/02/2023 04:15:51 PM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	62912316	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Nicholas Kokkinos

Documents

TOTAL DOCUMENTS: 3

DOCUMENT		PAGES	DESCRIPTION	SIZE (KB)
123450.013001 Response to ex parte Quayle Action.pdf		4	-	176 KB
123450.013001 Response to ex parte Quayle Action-A.QU.pdf	(1-1)	1	Response after Ex Parte Quayle Action	165 KB
123450.013001 Response to ex parte Quayle Action-CLM.pdf	(2-3)	2	Claims	106 KB
123450.013001 Response to ex parte Quayle Action-REM.pdf	(4-4)	1	Applicant Arguments/Remarks Made in an Amendment	165 KB

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DOCUMENT	MESSAGE DIGEST(SHA-512)
123450.013001 Response to ex parte Quayle Action.pdf	F3F64F5810A6ED9F30EF18EFF49D30D5DD2A0FB48DE3594AE C6D135C78137885D618BBB7EE4F9CFB0DBFE0AE197072CE7 911F416E24480F20986A18E3CB349EC
123450.013001 Response to ex parte Quayle Action-A.QU.pdf	F1AEBE375EBA6B01343934CA13997BE74FEA11CB5A5463370 10F000C1F731FB30003796CA4CA2CAAE0AA702CB8F0A95B9E D7D663EF22F7F83CCD2259C32990FA
123450.013001 Response to ex parte Quayle Action-CLM.pdf	99ADFE73EA2939D17A0CEADE108F785DDBAC6C8212DCFDA A6B3C9674C32E973713E70F818E8AB3E6440B00DCFF9B2BC7 396D27B3253D492D3474090334577BFF
123450.013001 Response to ex parte Quayle Action-REM.pdf	E533ACFCD85520065E918D91242F69D077E13F2BA22B7DA29 4200D90550B38ACE1E1B8DDAC8B8F54D997E5593284CE199E 3FCA30C4A0DAD54AD39B73EF6BE0FA

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National Stage of an International Application under 35 U.S.C. 371

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New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	DISTEFANO; Rebecca L.
	Art Unit	1731
	Examiner Name	CHU, YONG LIANG
	Attorney Docket Number	123450-013001

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	1	2018116842	WO	A1	2018-06-28	KURARAY CO	w/English Machine Translation	X

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	Filing Date	2020-04-03
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	Attorney Docket Number	123450-013001

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	DISTEFANO; Rebecca L.
	Art Unit	1731
	Examiner Name	CHU, YONG LIANG
	Attorney Docket Number	123450-013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☒ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

X See attached certification statement.

X The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Emma K. Holland/	Date (YYYY-MM-DD)	2023-09-22
Name/Print	Emma K. Holland, Ph.D.	Registration Number	79,947

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

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Patents WO 2018116842 A1

Porous carbon material, method for producing same and use of same

Abstract

The present invention relates to a porous carbon material which has a nitrogen content of 0.5-2.0% by mass and an iron content of at least 400 mg/kg - the porous carbon material or more, while having an electrical conductivity of 10 S/cm or more as determined by powder resistance measurement.

Classifications

B01J37/084 Decomposition of carbon-containing compounds into carbon

View 15 more classifications

WO2018116842A1

WIPO (PCT)

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Other languages: French, Japanese

Inventor: 啓太 高橋, 貴行 香川, 人貴 吉岡, 克則 山田, 暢之

Worldwide applications

2017 EP WO JP CN KR AU US TW

Application PCT/JP2017/043947 events

	Priority claimed from JP2016-246202
2017-12-07	Application filed by 株式会社クラレ
2017-12-07	Priority to KR1020197020184A
2017-12-07	Priority to AU2017383796A
2017-12-07	Priority to EP17884810.7A
2017-12-07	Priority to US16/471,345
2017-12-07	Priority to JP2018557662A
2017-12-07	Priority to CN201780078351.6A
2018-06-28	Publication of WO2018116842A1

Info: Patent citations (23), Non-patent citations (1), Cited by (3), Legal events, Similar documents, Priority and Related Applications

External links: Espacenet, Global Dossier, PatentScope, Discuss

Claims (11)

Hide Dependent

1. The nitrogen content is 0.5-2.0 mass%,
The iron content is at least 400 mg / kg-more than the porous carbon material, and
A porous carbon material having an electrical conductivity of 10 S / cm or more obtained by powder resistance measurement.

2. 2. The porous carbon material according to claim 1, wherein the benzene adsorption performance is in the range of 25 to 50%.

3. A molded body containing the porous carbon material according to claim 1 or 2.

4. A cracking catalyst comprising the porous carbon material according to claim 1 or 2.

5. The decomposition catalyst according to claim 4, which is a decomposition catalyst for at least one of peroxide, chloramine and bromic acid.

6. A method for producing the porous carbon material according to claim 1, comprising:
Carbonaceous material is carbonized and heat-treated at a temperature of 1000 to 1200 ° C.,
Then, the method for producing a porous carbon material, comprising activating at a temperature of 850 to 1000 ° C. in a mixed gas atmosphere containing water vapor, nitrogen and carbon dioxide.

7. The method for producing a porous carbon material according to claim 6, wherein the carbonaceous material is a natural mineral as a raw material.

8. The method for producing a porous carbon material according to claim 7, wherein the nitrogen content of the natural mineral raw material is 1.0 to 2.0 mass%.

9. The porous carbon material according to claim 1 or 2 is used as a decomposition catalyst, and is brought into contact with an object, and from the object, at least one of peroxide, chloramine, bromic acid, hypobromous acid and hypochlorous acid. A method of disassembling and removing one.

10. A cracking catalyst device comprising the molded article according to claim 3.

11. A cracking catalyst device comprising the cracking catalyst according to claim 4.

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Description

Porous carbon material and production method and use thereof

The present invention relates to a porous carbon material that can be used as a decomposition catalyst, a production method thereof, and an application thereof.

It is well known that a porous carbon material itself such as activated carbon acts as a decomposition catalyst. For example, activated carbon is known to be useful for various oxidation reactions including oxidation of hydrogen sulfide and SO_2. Activated carbon has been observed to affect such reactions, activated carbon as a catalyst affects only the reaction rate, and activated carbon itself is hardly altered by the reaction.

活性炭 Activated carbon produced from raw materials rich in nitrogen effectively catalyzes in specific reactions such as decomposition of hydrogen peroxide, compared with activated carbon produced from raw materials low in nitrogen. Similarly, it is also known that when activated carbon produced from a raw material with low nitrogen content is exposed to a nitrogen-containing compound such as ammonia at a high temperature, the catalytic function of the activated carbon is enhanced. Recently, activated carbon having a high catalytic activity has been produced by carbonizing a nitrogen-rich substance such as polyacrylonitrile and polyamide at a low temperature or a high temperature and activating (activating) the carbonized material. In either case, the activated carbon is produced by heat treatment at a temperature exceeding 700 ° C. It is also known that it is advantageous to oxidize activated carbon produced from raw materials with low nitrogen content before or during exposure to nitrogen-containing compounds.

However, all of the prior art methods for producing catalytic activated carbon have certain drawbacks, which limit their overall usefulness and practicality. For example, raw materials with high nitrogen content such as polyacrylonitrile and polyamide are expensive and generate large amounts of cyanide and other toxic gases upon carbonization. Activated carbon obtained from a raw material with a low nitrogen content requires a vigorous chemical post-treatment in order to greatly change the catalytic ability. In so doing, it is achieved at the expense of carbon yield in order to obtain the desired catalytic activity, which is necessarily expensive. Furthermore, the chemical treatment method uses a large amount of toxic and dangerous chemicals such as nitric acid, sulfuric acid or ammonia, so that there are a significant amount of toxic and dangerous by-products such as SOx, NOx and cyanide. Arise.

Patent Document 1 reports a catalytically active carbonaceous char that rapidly decomposes hydrogen peroxide. In this document, raw materials are oxidized at low temperatures, exposed to nitrogen-containing compounds such as urea, heated at high temperatures in an inert atmosphere, activated at high temperatures in water vapor and / or carbon dioxide, and cooled in an inert atmosphere. The production of carbonaceous char is described. Patent Document 2 describes that activated carbon having catalytic activity can be produced by mixing and activating charcoal with one or more organic nitrogen-containing compounds.

However, methods using nitrogen-containing compounds as described in Patent Documents 1 and 2 have toxicity such as NOx and produce a large amount of dangerous by-products.

Patent Document 3 describes a method for producing catalytically active activated carbon using charcoal. This method involves the addition of ammonia to the steam. Such addition of ammonia is undesirable both from a health and environmental point of view.

Patent Document 4 describes a method for producing activated carbon using bituminous coal containing nitrogen. However, in this method, since high temperature heat treatment is not performed, the conductivity of activated carbon is low, and sufficient catalytic performance cannot be obtained. Further, since a raw material containing excessive nitrogen is used, harmful gases such as NOx are generated during production, which is not desirable from the viewpoints of both health and the environment.

An object of the present invention is to provide a porous carbon material that can be obtained without treatment with a nitrogen-containing compound and can be used as a decomposition catalyst for various compounds and substances, and a production method and use thereof.

Japanese Patent No. 2685356 Special table 2014-506529 gazette Japanese Patent No. 3955062 JP2013-163629A

The porous carbon material according to one aspect of the present invention has a nitrogen content of 0.5 to 2.0% by mass, an iron content of at least 400 mg / kg-more than the porous carbon material, and a powder. The electrical conductivity obtained by body resistance measurement is 10 S / cm or more.

As a result of intensive studies to solve the above problems, the present inventors have found that when a porous carbon material containing a nitrogen content at a predetermined concentration or higher and having a crystallinity increased by heat treatment is used as a decomposition catalyst, The inventors have found that the resolution of peroxides such as hydrogen is greatly improved, and that chloramine, bromic acid and the like are effectively decomposed, and the present invention has been completed by further research based on this finding.

The porous carbon material of the present invention exhibits high catalytic activity as a decomposition catalyst. Moreover, the porous carbon material of the present invention retains high catalytic activity even after repeated use. Therefore, the porous carbon material of the present invention can be used as a decomposition catalyst for various compounds and substances, and in particular, can effectively decompose peroxides (such as hydrogen peroxide) in an aqueous solution. Furthermore, the porous carbon material of the present invention is suitable for decomposing chloramine, bromic acid and the like.

Hereinafter, embodiments of the present invention will be described in detail, but the present invention is not limited thereto.

<Porous carbon material and decomposition catalyst>
The porous carbon material of the present invention has the following characteristics.
(A) the nitrogen content is 0.5 to 2.0 mass%,
(B) The electrical conductivity obtained by powder resistance measurement is 10 S / cm or more,
(C) The iron content is at least 400 mg / kg—more than the porous carbon material.

The catalytic activity of the porous carbon material of the present embodiment is, for example, when the decomposition target is hydrogen peroxide, proceeds by electron donation to hydrogen peroxide from a specific structural site containing nitrogen, and is subjected to heat treatment to produce crystals. It is considered that electron donation to hydrogen peroxide can be enhanced by increasing the conductivity and increasing the conductivity. Similarly, it is possible to promote the decomposition of a peroxide whose decomposition proceeds by electron donation.

Furthermore, the porous carbon material of the present invention preferably has the following characteristics.
(D) The benzene adsorption performance is 25 to 50%.

Regarding the physical properties (a), (b), (c), and (d) described above, the catalytic activity of the porous carbon material of the present embodiment is not a single physical property, but these physical properties are involved in a complex manner. Seems to be. Therefore, even if one of the physical properties (a) to (c) is within the above range, if the other physical properties are out of the above range, the catalytic activity of the decomposition catalyst is lowered.

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If the nitrogen content of the porous carbon material is too smaller than the above-mentioned specified range, the reaction sites having a catalytic function are reduced, so that the decomposition performance is lowered. On the other hand, if it is too large, a large amount of harmful gas such as NOx generated during the production of the catalyst is generated, which may be harmful to health and the environment, which is not preferable. Therefore, the nitrogen content of the porous carbon material in the present embodiment is 0.5 to 2.0% by mass. More preferably, it is 0.5 to 1.0% by mass.

If the electrical conductivity of the porous carbon material is too smaller than the specified range described above, the electron donating ability of the decomposition catalyst is lowered, and the decomposition performance is deteriorated. Therefore, the electrical conductivity of the porous carbon material in this embodiment is 10 S / cm or more. If the electrical conductivity is within this range, sufficient decomposition performance can be obtained, so the upper limit is not particularly limited. However, if the electrical conductivity is too large, the electron donating ability of the decomposition catalyst is improved, but the decomposition catalyst contains nitrogen. The amount may decrease and the decomposition performance of the catalyst may decrease. Therefore, the electrical conductivity of the porous carbon material in the present embodiment is preferably 10 to 20 S / cm, and more preferably 12 to 18 S / cm.

If the content of iron in the porous carbon material is too smaller than the above-mentioned specified range, it is presumed that the decomposition performance is lowered because the crystal structure of the decomposition catalyst is poorly developed. Therefore, the iron content of the porous carbon material in this embodiment is at least 400 mg / kg-porous carbon material or more. If the iron content is within this range, sufficient decomposition performance can be obtained, so the upper limit is not particularly limited. However, if the iron content is too high, the yield of the decomposition catalyst decreases, which is preferable from an economic viewpoint. Absent. Therefore, the iron content of the porous carbon material in the present embodiment is preferably 400 to 5000 mg / kg-porous carbon material, and more preferably 500 to 3000 mg / kg-porous carbon material. The unit "mg / kg-porous carbon material" means the iron content (mg) per kg of the porous carbon material.

The benzene adsorption performance of the porous carbon material in the present embodiment provides a sufficient specific surface area within the above specified range, so that excellent decomposition performance can be obtained more reliably. The upper limit of the benzene adsorption performance is not particularly limited, but if it is too large, the yield of the cracking catalyst is lowered, which is not preferable from an economical viewpoint. Therefore, the benzene adsorption performance in the present embodiment is preferably 20 to 50%, more preferably 30 to 45%. In addition, the benzene adsorption | suction performance in this specification points out what was measured based on JISK1474 (2014).

The catalytic activity of the porous carbon material of the present embodiment is presumed to proceed by electron donation from a specific structural site containing nitrogen to the compound to be decomposed, such as hydrogen peroxide described above. . Therefore, the porous carbon material of the present embodiment is useful as a decomposition catalyst that decomposes a compound that decomposes by electron donation. Among them, a compound that is easily electron donated to a compound from a specific structural site containing nitrogen is more easily decomposed.

For example, the porous carbon material of this embodiment is very useful for the decomposition of peroxides, chloramines, bromic acid, hypobromous acid and hypochlorous acid. Examples of the peroxide include inorganic peroxides such as hydrogen peroxide and organic peroxides such as peracetic acid.

The chloramine (chloroamine) in the present embodiment may be any of monochloroamine NH_2Cl, dichloroamine $NHCl_2$, and trichloroamine NCl_3. A typical chloramine widely used for disinfection of tap water or the like is monochloroamine, which has low volatility and high stability. Therefore, the remaining monochloroamine is treated with sodium thiosulfate or the like. The decomposition catalyst of the present invention efficiently decomposes such chloramine (monochloroamine and the like) to liberate chlorine.

The present embodiment also includes a cracking catalyst containing the porous carbon material as described above. The decomposition catalyst of this embodiment is useful for decomposing a compound whose decomposition proceeds by electron donation. Examples of the compound include the above-described peroxides, chloramines, bromic acid, hypobromous acid, and hypochlorous acid. In particular, it is useful as a decomposition catalyst for at least one of peroxide, chloramine and bromic acid. It is also useful as a decomposition catalyst for peroxides and / or chloramines.

<Method for producing porous carbon material>
Usually, the production of a porous carbon material used as a decomposition catalyst is carried out by bringing activated carbon into contact with a nitrogen-containing compound such as ammonia or by active carbonization from a nitrogen-rich raw material such as polyacrylonitrile.

In this embodiment, a cracking catalyst having high catalytic activity can be produced at low cost by managing parameters other than nitrogen.

That is, the porous carbon material of the present embodiment is obtained by carbonizing carbonaceous material and heat-treating the obtained carbonized product at a temperature of 1000 to 1200 ° C., more preferably 1000 to 1100 ° C., and then steam, nitrogen and carbon dioxide. Can be obtained by an activation treatment at a temperature of 850 to 1000 ° C. in a mixed gas atmosphere containing. In this activation treatment, the carbonized carbon material may be partially gasified.

The carbonaceous material can be selected from all known materials, such as plants (coconut husk, rice bran, potato pod, wood, etc.), natural polymers (starch, cellulose, lignins, etc.), semi-synthetic polymers (cellulose). Examples include esters, cellulose ethers, lignin resins, etc.), synthetic polymers (phenolic resins, furan resins, epoxy resins, etc.), bituminous substances, and the like. These raw materials can be used alone or in combination of two or more. A preferable raw material may be a plant raw material such as wood, but it is particularly preferable to use a natural mineral as a raw material. Specifically, coals containing nitrogen and iron, for example, coal selected from coals consisting of peat, lignite, sub-bituminous coal, bituminous coal, semi-anthracite coal, anthracite coal are preferably used, and in particular, contain a large amount of nitrogen. Therefore, bituminous coal is preferable. However, use of bituminous coal with too much nitrogen content is not preferable because a large amount of harmful substances such as NOx are generated and there is concern about the effects on health and the environment. Therefore, it is desirable that the nitrogen content of the carbonaceous material raw material is 1.0 to 2.0% by mass, preferably 1.5 to 2.0% by mass. In addition, if the content of iron contained as an ash content of a carbonaceous material raw material (for example, bituminous coal) is too small, the development of the crystal structure of the porous carbon material becomes poor and high decomposition performance cannot be obtained. On the other hand, if it is too large, the yield of the decomposition catalyst is lowered, which is not preferable from an economical viewpoint. Therefore, the iron content of the carbonaceous material is preferably 500 to 10,000 mg / kg, more preferably 500 to 2000 mg / kg.

The carbonaceous material of this embodiment can be produced using a fluidized bed, a multistage furnace, a rotary furnace, or the like, which is a general activated carbon production facility.

The dry distillation can be performed by a conventional method, for example, by heating the carbonaceous material at 400 to 800 ° C., preferably 500 to 800 ° C., more preferably 600 to 800 ° C. while blocking oxygen or air .

The heat treatment can be carried out at a temperature of 1000 ° C. or higher, preferably 1000 to 1200 ° C., more preferably 1000 to 1100 ° C. with oxygen or air blocked from the distillate. If this heat treatment temperature is too low, the degree of crystallinity of the porous carbon material will be poorly developed and sufficient electron donating ability will not be obtained. On the other hand, if the heat treatment temperature is too high, the crystallinity increases, but nitrogen is desorbed from the carbon structure, so that there is a possibility that sufficient decomposition performance cannot be obtained.

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In the production method of the present embodiment, the activation treatment is performed using a fluidized bed, a multistage furnace, a rotary furnace, etc., and the dried product is at a temperature of 850 ° C. or higher, preferably 850 to 1000 ° C. (for example, 850 to 950 ° C.) It can be carried out in an atmosphere of a mixture of water vapor, nitrogen and carbon dioxide. By activating in the atmosphere of the said mixture, a dry distillation thing is partially gasified and a porous carbon material (decomposition catalyst) is obtained. In addition, the gas (gas mixture consisting of water vapor, nitrogen, and carbon dioxide) for gasifying a part of the carbonaceous material is obtained by burning natural gas, petroleum, or other combustible materials including hydrocarbons. Can also be obtained. Note that the activation temperature usually varies in a range of about ± 25 ° C. in many cases.

The activation time is not particularly limited, but may be about 1 to 48 hours, preferably 4 to 24 hours, more preferably about 5 to 20 hours (for example, 6 to 12 hours). If the activation time is too short, the decomposition catalytic activity of the porous carbon material is lowered, and if it is too long, the productivity may be lowered.

The gas partial pressure is not particularly limited, but the water vapor partial pressure is 7.5 to 40%, preferably 10 to 35% (eg, 10 to 20%), the carbon dioxide partial pressure is 10 to 50%, preferably 15 to 45%. (For example, 20 to 40%), nitrogen partial pressure of 30 to 80%, preferably 40 to 70% (for example, 45 to 65%), and the gas partial pressure is water vapor partial pressure of 10 to 40%, carbon dioxide The partial pressure may be about 10 to 40% and the nitrogen partial pressure is about 40 to 80%. The total pressure of the gas is usually 1 atmosphere (about 0.1 MPa).

Further, the total gas supply amount (flow rate) is about 1 to 50 L / min, preferably about 1 to 20 L / min, with respect to 100 g of the dry-distilled product raw material. If the flow rate is too low, activation is not sufficient, and if it is too high, the decomposition catalytic activity of the porous carbon material decreases.

It is considered that a porous carbon material having a target nitrogen content, electrical conductivity, and iron content can be obtained by combining such conditions. In addition, you may refer the below-mentioned Example for the detail of the manufacturing method of the porous carbon material of this embodiment.

Note that the porous carbon material obtained by the production method of the present embodiment may be powdery, granular, or granulated, and may be formed into a honeycomb-like form if necessary.

<Method for Producing Porous Carbon Material-Containing Molded Body>
Next, the manufacturing method of the molded object (henceforth a porous carbon material containing molded object) containing the porous carbon material of this embodiment is demonstrated. The porous carbon material-containing molded body of the present embodiment includes a slurry preparation step of preparing a slurry by dispersing a mixture obtained by mixing a granular or powdered porous carbon material and a fibrous binder in water, and the slurry. It is obtained by a production method including a suction filtration step of obtaining a preform by filtering while sucking, and a drying step of obtaining a dried compact by drying the preform.

{Slurry preparation process}
In the slurry preparation step, the granular or powdery porous carbon material and the fibrous binder were dispersed in water so that the solid content concentration was 0.1 to 10% by mass (particularly 1 to 5% by mass). Prepare a slurry. When the solid content concentration of the slurry is too high, dispersion tends to be non-uniform, and spots are easily formed on the molded product. On the other hand, if the solid content concentration is too low, not only the molding time is prolonged and the productivity is lowered, but also the density of the molded body is increased and clogging due to trapping of turbid components is likely to occur.

{Suction filtration process}
In the suction filtration step, molding is performed by putting a molding mold having a large number of holes in the slurry and filtering while suctioning from the inside of the mold. As the mold for molding, for example, a conventional mold can be used. For example, the mold described in FIG. 1 of Japanese Patent No. 3516811 can be used. As a suction method, a conventional method, for example, a suction method using a suction pump or the like can be used. Moreover, you may perform the process of adjusting the shape of an outer surface by compressing a preform on a shaping stand after suction filtration

{Drying process}
In the drying step, the preform can be obtained by removing the preform from the mold and drying with a dryer or the like. The drying temperature is, for example, about 100 to 150 ° C. (particularly 110 to 130 ° C.), and the drying time is, for example, about 4 to 24 hours (particularly 8 to 16 hours). If the drying temperature is too high, the fibrous binder may be altered or melted to reduce the filtration performance or the strength of the molded body. If the drying temperature is too low, the drying time tends to be long or drying tends to be insufficient. Moreover, you may perform the process of grinding (or polishing) the outer surface of the dry molded object.

The porous carbon material-containing molded body of the present embodiment is used as, for example, a water purification filter or an artificial dialysis filter. When the porous carbon material-containing molded body of this embodiment is used as a water purification filter or an artificial dialysis filter, it is preferably a cylindrical shape, and if necessary, a cap is attached to the cylindrical top portion. Alternatively, a reinforcing material such as a netron pipe, a ceramic filter, or a nonwoven fabric may be inserted into the cylindrical hollow portion, or a nonwoven fabric may be attached to the surface. By adopting the cylindrical shape, the water flow resistance can be lowered, and when the housing is used as a cartridge, the cartridge can be easily loaded and replaced in the water purifier.

<Method for removing peroxide and / or chloramine>

Using the porous carbon material of this embodiment as a decomposition catalyst, decomposes at least one of peroxide, chloramine, bromic acid, hypobromite and hypochlorous acid (peroxide and / or chloramine, etc.). And can be removed. That is, in the present invention, the porous carbon material is used as a decomposition catalyst, and is brought into contact with an object, and from the object, at least one of peroxide, chloramine, bromic acid, hypobromite and hypochlorous acid is used. A method of decomposing and removing one, preferably peroxide and / or chloramine from the object, more preferably peroxide, chloramine and bromic acid, more preferably peroxide, chloramine, bromic acid, hypochlorous acid. A method of decomposing and removing bromic acid and hypochlorous acid is included.

Here, the object is not particularly limited as long as it is an object for which peroxide and / or chloramine or the like is to be removed or various media including peroxide and / or chloramine. Examples thereof include water containing peroxide and / or chloramine, fluidized water, mist, and the like. Among these, the porous carbon material of the present embodiment is suitable for removing peroxide and / or chloramine from an object made of a liquid medium such as water or fluidized water.

Decomposition of the above-mentioned peroxide, chloramine, etc. (at least one of peroxide, chloramine, bromic acid, hypobromous acid and hypochlorous acid) can be carried out in an aqueous solvent, and an excess amount of solvent The decomposition reaction is often performed in the presence of. The concentration of the substrate such as peroxide and chloramine is not particularly limited. For example, the concentration of peroxide in the reaction system is 0.1 to 50% by mass, preferably 0.5 to 30% by mass, and more preferably. May be about 1 to 20% by mass. If the porous carbon material of the present embodiment is used, the substrate can be effectively decomposed or oxidized. Therefore, the porous carbon material of the present invention includes a trace amount of peroxide (such as hydrogen peroxide) and chloramine (such as monochloroamine). It is useful for removing substrates such as When processing a trace amount of remaining substrate, for example, the concentration of the substrate may be about 0.1 ppb to 1000 ppm.

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The amount of the porous carbon material used as a decomposition catalyst is not particularly limited. For example, it is 0.1 to 500 parts by mass, preferably 1 to 250 parts by mass with respect to 100 parts by mass of a substrate such as peroxide or chloramine. Part, more preferably about 5 to 100 parts by mass (for example, 10 to 50 parts by mass).

The decomposition (removal) reaction can be performed, for example, at about 10 to 70 ° C., preferably about 20 to 50 ° C. The decomposition reaction can be performed, for example, in air or in an oxygen-containing atmosphere, or in an inert gas atmosphere.

The porous carbon material of the present embodiment can maintain a high catalytic ability without reducing the catalytic activity even when it is repeatedly used as a decomposition catalyst. For example, in the test method described in the examples (evaluation of hydrogen peroxide decomposition performance in aqueous solution and measurement of hydrogen peroxide decomposition rate), the decomposition rate of hydrogen peroxide per 1 g of decomposition catalyst is 1000 mg-H_2O_2 / g-porous carbon material / hr or more (for example, 2000 to 100,000 mg-H_2O_2 / g-porous carbon material / hr, preferably 3000 to 75000 mg-H_2O_2 / g - porous carbon material / hr, more preferably from $_{5000\sim50000mg\text{-}H_2O_2}$ / g- porous carbon material / hr). Moreover, even if such a test method (the hydrogen peroxide decomposition test in a batch type aqueous solution) is repeatedly used 15 times or more (for example, 15 to 25 times, preferably about 15 to 30 times), high catalytic activity is obtained. maintain. That is, the porous carbon material of the present invention is repeatedly used 15 times or more while maintaining the hydrogen peroxide decomposition performance in an aqueous solution of 1000 mg-H_2O_2 / g-porous carbon material / hr or more in the test method. it can. "1000 mg-H_2O_2 / g-porous carbon material / hr" means that 1000 mg of hydrogen peroxide (H_2O_2) is decomposed per 1 g of porous carbon material per hour. To do.

Since the porous carbon material of the present embodiment is very useful as a decomposition catalyst for peroxide and / or chloramine, for example, decomposition of peroxide in industrial wastewater or decomposition removal of chloramine contained in tap water. Excellent effect in applications such as. Therefore, the porous carbon material of this embodiment is very useful as, for example, a water purifier and a decomposition catalyst for industrial wastewater treatment.

This specification discloses various modes of technology as described above, and the main technologies are summarized below.

The porous carbon material according to one aspect of the present invention has a nitrogen content of 0.5 to 2.0% by mass, an iron content of at least 400 mg / kg-more than the porous carbon material, and a powder. The electrical conductivity obtained by body resistance measurement is 10 S / cm or more.

With such a configuration, the porous carbon material of the present invention exhibits high catalytic activity as a decomposition catalyst, and retains high catalytic activity even when used repeatedly. Therefore, the porous carbon material of the present invention is effective as a decomposition catalyst for various compounds and substances.

In the porous carbon material, the benzene adsorption performance is preferably in the range of 25 to 50%.

Furthermore, a molded body according to another aspect of the present invention is characterized by containing the above-described porous carbon material. The molded body can be suitably used as, for example, a water purification filter or an artificial dialysis filter.

Furthermore, a cracking catalyst according to another aspect of the present invention is characterized by including the above-described porous carbon material. In addition, the decomposition catalyst is preferably a decomposition catalyst for at least one of peroxide, chloramine, and bromic acid.

Further, the method for producing a porous carbon material according to a further aspect of the present invention comprises carbonizing the carbonaceous material, heat-treating it at a temperature of 1000 to 1200 ° C., and then under a mixed gas atmosphere containing water vapor, nitrogen and carbon dioxide. , And activation at a temperature of 850 to 1000 ° C.

In the method for producing a porous carbon material, it is preferable that the carbonaceous material is a natural mineral.

Furthermore, the nitrogen content of the natural mineral raw material is preferably 1.0 to 2.0% by mass.

A method for decomposing and removing peroxide and / or chloramine and the like according to a further aspect of the present invention is to use the above-mentioned porous carbon material as a decomposition catalyst, and contact the object with the peroxide, chloramine, It is characterized by decomposing and removing at least one of bromic acid, hypobromous acid and hypochlorous acid.

Furthermore, the present invention provides a cracking catalyst device comprising the above-described molded body or the above-described cracking catalyst. Are also included.

Hereinafter, the present invention will be described in more detail based on examples. However, the following examples do not limit the present invention

(Test Example 1)
In Examples and Comparative Examples described later, the decomposition catalyst performance of the porous carbon material was evaluated as follows.

[Measurement of nitrogen content of porous carbon material]
After the pulverized porous carbon material was dried at 120 ° C. for 2 hours, the nitrogen content of the porous carbon material was measured using Vario EL III manufactured by ELEMENTAR and using sulfanilic acid as a reference substance.

[Measurement of conductivity of porous carbon material]
The electrical conductivity of the porous carbon material was measured using a powder resistivity measuring unit MCP-PD51 manufactured by Mitsubishi Chemical Analytech. Since the particle size of the measurement sample greatly affects the measurement of conductivity, the 10% particle diameter (D10) of the volume-based cumulative distribution of the porous carbon material is about 1 to 3 μm, and 50% of the volume-based cumulative distribution. Conductivity of porous carbon material pellets when pulverized so that particle diameter (D50) is about 5-8 μm and 90% particle diameter (D90) of volume-based cumulative distribution is about 10-20 μm and a load of 12 kN is applied. Was measured. The particle size of the pulverized porous carbon material was measured by a laser diffraction measurement method. That is, the porous carbon material to be measured was placed in ion-exchanged water together with a surfactant, ultrasonic vibration was applied to prepare a uniform dispersion, and measurement was performed using Microtrac MT3000EX-II manufactured by Microtrac Bell. "Polyoxyethylene (10) octylphenyl ether" manufactured by Wako Pure Chemical Industries, Ltd. was used as the surfactant. The analysis conditions are shown below.
(Analysis conditions)
Number of measurements: 3 times Measurement time: 30 seconds Distribution display: Volume Particle size classification: Standard Calculation mode: MT3000II Solvent name: WATER

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Measurement upper limit: 2000 μm, measurement lower limit: 0.021 μm
Residual ratio: 0.00
Passage ratio: 0.00
Residual ratio setting: Invalid Particle permeability: Absorption Particle refractive index: N / A
Particle shape: N / A
Solvent refractive index: 1.333
QV value: 0.0100 to 0.0500
Transmittance (TR): 0.750 to 0.920

[Measurement of benzene adsorption performance of porous carbon materials]
Based on the activated carbon test method JISK1474 in Japanese Industrial Standard, the benzene adsorption performance of the porous carbon material was measured.

[Measurement of iron content of porous carbon material]
First, a calibration curve for iron content was prepared from a standard solution of known concentration. Next, the pulverized measurement sample was dried at 120 ° C. for 2 hours, then 0.1 g was put into a decomposition container, 10 ml of nitric acid was added and mixed, and then a microwave sample pretreatment apparatus (CEM, Discover SP-D80) was used. The sample was dissolved. The dissolved solution was taken out and made up to 25 ml to prepare a measurement solution, which was then analyzed with an ICP emission spectroscopic analyzer (Thermo Fisher Scientific, iCAP 6200). The iron content was determined from the obtained value and the calibration curve created earlier.

[Evaluation of hydrogen peroxide decomposition performance in aqueous solution and measurement of hydrogen peroxide decomposition rate]
To 400 mL of an aqueous solution having a concentration of 3000 mg / L hydrogen peroxide at 25 ° C., 0.1 g of a porous carbon material pulverized to a D50 of 5 to 8 μm and dried at 120 ° C. is added. The hydrogen oxide concentration was measured, and the change over time was evaluated until the residual amount became zero. The residual hydrogen peroxide concentration in the degradation performance evaluation was measured using QUANTOFIX Peroxide manufactured by MACHEREY-NAGEL.

Hydrogen peroxide decomposition rate = (Co-C) x 0.4 / A / T
Co = hydrogen peroxide initial concentration (mg / L), C = hydrogen peroxide concentration after arbitrary time (mg / L), A = porous carbon material amount (g), T = arbitrary time (hr)
The hydrogen peroxide decomposition performance evaluation at the time of repetition was performed by adding a 30% by mass hydrogen peroxide aqueous solution to the solution in which the residual amount became zero to 3000 mg / L and again remaining in the aqueous solution. The hydrogen oxide concentration is measured, and the change over time is evaluated until the residual amount becomes zero. This operation is $_{1000mg\text{-}H_2O_2}$ / g-porous carbon material / hr or more hydrogen peroxide decomposition rate was repeated until no obtained. It evaluated by the repetition frequency. In this embodiment, the number of repetitions is 15 or more.

[Example 1]
The carbonaceous raw material was bituminous coal (raw material nitrogen content: 1.91% by mass), and after carbonization at 650 ° C., the obtained carbonization product was heat-treated at 1100 ° C. Thereafter, 400 g of the heat-treated product is put into the furnace, and a mixed gas having a water vapor partial pressure of 15%, a carbon dioxide partial pressure of 11%, and a nitrogen partial pressure of 74% is supplied at a total gas pressure of 1 atm and a flow rate of 5.5 L / min. The porous carbon material (decomposition catalyst) was produced by supplying into the furnace and treating the benzene adsorption performance to be 20.6% under the condition of the activation temperature of 900 ° C. It was confirmed that the obtained decomposition catalyst had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within a predetermined range, and the number of repetitions as a catalyst was as high as 16 times.

[Example 2]
A porous carbon material (decomposition catalyst) was produced in the same manner as in Example 1 except that the carbonaceous raw material was bituminous coal and the activation treatment was performed under conditions such that the benzene adsorption performance was 25.1%. It was confirmed that the obtained decomposition catalyst had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within a predetermined range, and the number of repetitions as a catalyst was as high as 21 times.

[Example 3]
A porous carbon material (decomposition catalyst) was produced in the same manner as in Example 1 except that the carbonaceous raw material was bituminous coal and the activation treatment was performed under conditions such that the benzene adsorption performance was 30.8%. The obtained cracking catalyst was confirmed that the nitrogen content, conductivity, benzene adsorption performance and iron content were all within the predetermined ranges, and the number of repetitions as a catalyst was as high as 25 times.

[Example 4]
A porous carbon material (decomposition catalyst) was produced in the same manner as in Example 1 except that the carbonaceous raw material was bituminous coal and the activation treatment was performed under conditions such that the benzene adsorption performance was 41.7%. The obtained decomposition catalyst had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within predetermined ranges. When the hydrogen peroxide decomposition performance of the obtained decomposition catalyst was evaluated, the hydrogen peroxide decomposition rate at the 31st repetition was 800 mg-H_2O_2 / g-porous carbon material / hr. Was 30 times.

[Example 5]
Porous carbon was used in the same manner as in Example 1 except that bituminous coal was used as the carbonaceous raw material, heat treatment of the dry distillation product was performed under conditions of 1200 ° C., and activation treatment was performed under conditions such that the benzene adsorption performance was 29.7%. A material (decomposition catalyst) was prepared. It was confirmed that the obtained decomposition catalyst had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within a predetermined range, and the number of repetitions as a catalyst was as high as 22 times.

[Example 6]
Porous carbon was used in the same manner as in Example 1 except that the carbonaceous raw material was bituminous coal, the heat treatment of the dry-distilled product was performed at 1000 ° C., and the activation treatment was performed under such a condition that the benzene adsorption performance was 30.9%. A material (decomposition catalyst) was prepared. It was confirmed that the obtained cracking catalyst had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within a predetermined range, and the number of repetitions as a catalyst was as high as 23 times.

[Example 7]
The porous carbon material obtained in Example 4 was washed in 1N hydrochloric acid, desalted using ion-exchanged water, and then dried at 120 ° C. It was confirmed that the obtained porous carbon material had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within the predetermined ranges, and the number of repetitions as a catalyst was as high as 25 times.

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[Example 8]
The porous carbon material obtained in Example 4 was washed in 0.5N hydrochloric acid, desalted with ion-exchanged water, and dried at 120 ° C. It was confirmed that the obtained porous carbon material had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within a predetermined range, and the number of repetitions as a catalyst was as high as 28 times.

[Example 9]
A porous carbon material (decomposition catalyst) was produced in the same manner as in Example 5 except that the carbonaceous raw material was bituminous coal and the activation treatment was performed under conditions such that the benzene adsorption performance was 39.4%. It was confirmed that the obtained decomposition catalyst had a nitrogen content, electrical conductivity, benzene adsorption performance and iron content all within the predetermined ranges, and the number of repetitions as a catalyst was as high as 30 times.

[Comparative Example 1]
The porous carbon material (the same as in Example 1) except that the carbonaceous raw material was bituminous coal and the activation treatment was performed under the conditions that the benzene adsorption performance was 29.5% without performing the heat treatment after the carbonization treatment. Decomposition catalyst) was prepared. It was confirmed that the obtained decomposition catalyst had an electric conductivity outside the predetermined range. When the hydrogen peroxide decomposition performance of the obtained decomposition catalyst was evaluated, the hydrogen peroxide decomposition rate at the 12th repetition was 930 mg-H_2O_2 / g-porous carbon material / hr. The number of repetitions was 11 times. As a factor of low decomposition performance, it is conceivable that the electron donating ability of the catalyst is low because the conductivity is not increased.

[Comparative Example 2]
Porous carbon was used in the same manner as in Example 1 except that the carbonaceous raw material was bituminous coal, the heat treatment of the dry distillation product was performed at 1300 ° C., and the activation treatment was performed under the condition that the benzene adsorption performance was 29.8%. A material (decomposition catalyst) was prepared. It was confirmed that the obtained cracking catalyst had a nitrogen content outside the predetermined range, and the number of repetitions as a catalyst was as low as 13 times. It is conceivable that the content of nitrogen contributing to the catalytic reaction is small as a factor of low decomposition performance.

[Comparative Example 3]
The carbonaceous raw material is anthracite (raw material nitrogen content: 0.72% by mass) and activated under the conditions that the benzene adsorption performance is 32.6% at an activation temperature of 950 ° C. without performing heat treatment after carbonization. A porous carbon material (decomposition catalyst) was produced in the same manner as in Example 1 except for the treatment. It was confirmed that the obtained decomposition catalyst had a nitrogen content outside the predetermined range and the number of repetitions as a catalyst was as low as one. It is conceivable that the content of nitrogen contributing to the catalytic reaction is small as a factor of low decomposition performance.

[Comparative Example 4]
Similar to Example 1 except that the carbonaceous raw material was anthracite, the heat treatment of the dry distillation product was performed under the condition of 1100 ° C., and the activation treatment was performed under the condition that the benzene adsorption performance was 31.4% at the activation temperature of 950 ° C. Thus, a porous carbon material (decomposition catalyst) was produced. It was confirmed that the obtained cracking catalyst had a nitrogen content outside the predetermined range and the number of repetitions as a catalyst was as low as 5 times. It is conceivable that the content of nitrogen contributing to the catalytic reaction is small as a factor of low decomposition performance.

[Comparative Example 5]
Activated under the condition that the carbonaceous raw material is coconut shell (raw material nitrogen content: 0.30% by mass) and the benzene adsorption performance is 31.6% at an activation temperature of 950 ° C. without performing heat treatment after dry distillation treatment. A porous carbon material (decomposition catalyst) was produced in the same manner as in Example 1 except for the treatment. It was confirmed that the obtained cracking catalyst had a nitrogen content and conductivity that were out of the predetermined ranges, and the number of repetitions as a catalyst was as low as one. As a factor of low decomposition performance, it is conceivable that the electron donating ability of the catalyst is low because the conductivity is low in addition to the low content of nitrogen contributing to the catalytic reaction.

[Comparative Example 6]
Similar to Example 1, except that the carbonaceous raw material is coconut shell, heat treatment of the dry distillation product is performed under the condition of 1100 ° C., and the activation treatment is performed under the condition that the benzene adsorption performance is 33.1% at the activation temperature of 950 ° C. Thus, a porous carbon material (decomposition catalyst) was produced. It was confirmed that the obtained cracking catalyst had a nitrogen content and conductivity that were out of the predetermined ranges, and the number of repetitions as a catalyst was as low as one. As a factor of low decomposition performance, it is conceivable that the electron donating ability of the catalyst is low because the conductivity is low in addition to the low content of nitrogen contributing to the catalytic reaction.

[Comparative Example 7]
Polyacrylonitrile fiber tow (PAN) (raw material nitrogen content: 26.42% by mass) was oxidized in air at 260 ° C. for 2 hours. The obtained oxidized fiber was staple-spun to obtain a single yarn. A plain plain fabric of the obtained single yarn was produced, and this fabric was mixed gas having a water vapor partial pressure of 15%, a carbon dioxide partial pressure of 11% and a nitrogen partial pressure of 74%, and a benzene adsorption performance of 31.2% at 950 ° C. The activation treatment was performed under such conditions. It was confirmed that the obtained decomposition catalyst had a nitrogen content, electrical conductivity, and iron content outside the predetermined ranges, and the number of repetitions as a catalyst was as low as one Since the raw material PAN does not contain iron, the crystal structure of the catalyst is poorly developed. As a result, the electron donation of the catalyst is low and the decomposition performance is considered to be low.

[Comparative Example 8]
The porous carbon material obtained in Example 4 was heat-treated at 1900 ° C. under a mixed gas flow of hydrogen chloride and nitrogen. Thereafter, deoxidation treatment was performed for 20 minutes with a mixed gas having a water vapor partial pressure of 15%, a carbon dioxide partial pressure of 11%, and a nitrogen partial pressure of 74% under the condition of 600 ° C. The obtained decomposition catalyst confirmed that the iron content was out of the predetermined range and the number of repetitions as a catalyst was as low as one. Although it is not clear why the catalyst performance is low, it seems that iron contributes to the catalyst performance in addition to developing the crystal structure. Therefore, it is considered that the decomposition performance is lowered by removing most of the iron.

[Comparative Example 9]
Porous carbon was used in the same manner as in Example 1 except that the carbonaceous raw material was bituminous coal, the heat treatment of the dry distillation product was performed under the condition of 850 ° C., and the activation treatment was performed under the condition that the benzene adsorption performance was 29.6%. A material (decomposition catalyst) was prepared. It was confirmed that the obtained decomposition catalyst had a conductivity outside the predetermined range and the number of repetitions as a catalyst was as low as 12 times. As a factor of low decomposition performance, it is conceivable that the electron donating ability of the catalyst is low because the conductivity is not increased.

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Table 1 shows the evaluation results of the porous carbon materials obtained in Examples 1 to 9 and Comparative Examples 1 to 9. In the table, "N" represents nitrogen.

試料番号	原料	原料N含有量 (%)	熱処理	N含有量 (%)	導電率 (S／cm)	Bz吸着性能 (%)	鉄含有量 (mg／kg－多孔質炭素材料)	H_2O_2分解 繰り返し回数
実施例1	瀝青炭	1.91	1100℃	0.80	17.00	20.6	2051.5	16
実施例2	瀝青炭	1.91	1100℃	0.76	16.21	25.1	2136.9	21
実施例3	瀝青炭	1.91	1100℃	0.74	14.91	30.8	2388.4	25
実施例4	瀝青炭	1.91	1100℃	0.70	12.33	41.7	2878.9	30
実施例5	瀝青炭	1.91	1200℃	0.64	18.37	29.7	2792.1	22
実施例6	瀝青炭	1.91	1000℃	0.83	12.93	30.9	2342.4	23
実施例7	瀝青炭	1.91	1100℃	0.68	11.17	40.7	658.4	25
実施例8	瀝青炭	1.91	1100℃	0.68	10.96	39.6	1387.2	28
実施例9	瀝青炭	1.91	1000℃	0.80	13.08	39.4	2728.2	30
比較例1	瀝青炭	1.91	無	0.74	9.06	29.5	2705.2	11
比較例2	瀝青炭	1.91	1300℃	0.48	19.28	29.8	2921.4	13
比較例3	無煙炭	0.72	無	0.38	10.28	32.6	3415.6	1
比較例4	無煙炭	0.72	1100℃	0.41	14.77	31.4	3371.1	6
比較例5	ヤシガラ	0.3	無	0.19	6.01	31.6	1068.2	1
比較例6	ヤシガラ	0.3	1100℃	0.15	9.61	33.1	1047.5	1
比較例7	PAN	26.42	無	3.83	2.00	31.1	31.2	1
比較例8	瀝青炭	1.91	1100℃	0.68	11.09	40.4	22.1	1
比較例9	瀝青炭	1.91	850℃	0.73	9.21	29.6	2451.5	12

As is apparent from Table 1, the porous carbon materials obtained in Comparative Examples 1 to 9 have at least one physical property value among the nitrogen content, conductivity, benzene adsorption performance and iron content of the present invention. It is excessive or too small with respect to a predetermined range, and the number of times of repeated use as a catalyst is 1 to 14 times. The catalytic activity is greatly reduced by repeated use.

On the other hand, the porous carbon materials obtained in Examples 1 to 9 have nitrogen content, electrical conductivity, benzene adsorption performance and iron content within predetermined ranges, and the number of repeated uses as a catalyst is 15 It was revealed that it was greatly improved to ~30 times, and it can be used repeatedly while maintaining high catalytic activity.

Also, it was found from this example that heat treatment is important in obtaining the porous carbon material in the present invention. In Comparative Examples 1 and 7 in which heat treatment was not performed, the amount of nitrogen was sufficient, but the crystallinity (conductivity) was low, and the degradation performance was poor. In Comparative Example 2 in which the heat treatment temperature was too high, the crystallinity (conductivity) was high, but the amount of nitrogen decreased due to the high temperature heat treatment, and it was considered that the degradation performance was poor. Further, in Comparative Example 9 in which the heat treatment temperature was too low, the heat treatment temperature was not sufficient, and the crystallinity could not be sufficiently increased, resulting in poor decomposition performance.

On the other hand, in all the examples in which heat treatment was performed in an appropriate temperature range, the amount of nitrogen was appropriate and the crystallinity (conductivity) was sufficient, so that a porous carbon material having excellent decomposition performance was obtained. It was.

(Test Example 2)
[Degradation of chloramine]
Using the porous carbon materials obtained in Examples 1, 3, 4, 5, 7, and 9 and Comparative Examples 1, 2, 5, and 8, the amount of chloramine decomposition was measured as follows.

The porous carbon material of the above Example or Comparative Example was added in 100 mL of an aqueous solution of chloramine (monochloroamine) adjusted to about 100 ppm while changing the addition amount, shaken at 25 ° C. for 2 hours, and then filtered with a filter paper. The residual chloramine concentration of the filtrate was measured by the following DPD absorptiometry. Then, the relationship between the residual chloramine concentration and the chloramine decomposition amount

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(mg / g-porous carbon material) was obtained, and the chloramine decomposition amount (mg / g-porous carbon material) at the residual concentration of 3 ppm was calculated and used for comparison. It was. In this example, the amount of chloramine decomposition (mg / g-porous carbon material) at a residual concentration of 3 ppm is determined to be 50 mg / g-porous carbon material. The "mg / g-porous carbon material" means the amount (mg) of a substance decomposed per 1 g of the porous carbon material.

[Quantification method of chloramine: DPD spectrophotometry]
(1) Measurement of Free Residual Chlorine 2.5 mL of phosphate buffer solution was placed in a 50 mL colorimetric tube with a stopper, and 0.5 g of N, N-diethyl-p-phenylenediamine (DPD) reagent was added to this buffer solution. . Next, the filtrate is added to make a total volume of 50 mL. After mixing, an appropriate amount of the colored test solution is taken in an absorption cell, and the absorbance at a wavelength of 510 to 555 nm is measured using a photoelectric spectrophotometer.) To determine the free residual chlorine (mg / L) in 1 L of the sample.

(2) Preparation of free residual chlorine calibration curve Diluted water was prepared using the adjusted standard chlorine water to prepare a standard row of several stages. Next, the absorbance was measured for each standard column in the same manner as in (1) above to determine the concentration (mg / L) of each free residual chlorine, and a calibration curve was created based on the absorbance.

(3) Measurement of residual chlorine Add about 0.5 g of potassium iodide to the solution colored in (1) above, dissolve, leave it for about 2 minutes, and then measure in the same manner as in (1) above. Chlorine (mg / L) was determined.

(4) Measurement of bound residual chlorine (chloramine) The difference between the residual chlorine and free residual chlorine was measured as the combined residual chlorine (chloramine) concentration (mg / L).
The results are shown in Table 2.

試料番号	残留濃度3ppmでの クロラミン分解量 （mg／g－多孔質炭素材料）
実施例1	56
実施例3	82
実施例4	107
実施例5	63
実施例7	90
実施例9	137
比較例1	38
比較例2	40
比較例5	8
比較例8	28

From the results of Table 2, the decomposition catalysts of Examples 1, 3, 4, 5, 7 and 9 have higher decomposition amounts of chloramine than the porous carbon materials of Comparative Examples 1, 2, 5 and 8. Indicated.

(Test Example 3)
[Decomposition of bromic acid]
Using the porous carbon material obtained in Example 9 and Comparative Example 1, the amount of bromic acid decomposed was measured as follows.
After adding the porous carbon material of the said Example or a comparative example in 100 mL of raw | natural water (10 ppm bromate ion) which melt | dissolved sodium bromate in tap water, changing the addition amount, and shaking at 25 degreeC for 2 hours The solution was filtered through filter paper, and the filtrate was measured by ion chromatography analysis to determine the residual bromate ion concentration. Then, the relationship between the residual bromate concentration and the bromate decomposition amount (mg / g-porous carbon material) was determined, and the bromate decomposition amount (mg / g-porous carbon material) at a residual concentration of 1 ppm was calculated. Used for comparison.
The results are shown in Table 3.

試料番号	残留濃度1ppmでの 臭素酸分解量 （mg／g－多孔質炭素材料）
実施例9	6
比較例1	2

(Test Example 4)
[Decomposition of chloramine by a molded article containing a porous carbon material]
The porous carbon material of Example 9 was pulverized to have a center particle diameter of 150 μm, and 100 parts by mass of the pulverized porous carbon material and a fibrous binder were used. Acrylic fiber Bi-PUL / F manufactured by Nippon Exlan industry Co., Ltd. Was dispersed in water at a ratio of 5.5 parts by mass to prepare a slurry. Next, the obtained slurry was fitted with a cylindrical nonwoven fabric in a mold having an outer diameter of 63 mmφ having a large number of pores with a diameter of 3 mm, a median shaft diameter of 36 mmφ and a height of 245 mmH, and after the slurry was sucked, the surface was tumbled. After drying, a hollow cylindrical activated carbon molded body having an outer diameter of 63 mmφ, an inner diameter of 36 mmφ and a height of 245 mmH was obtained.
The obtained activated carbon molded body was filled in a standard housing of 10 inches, and chloramine could be removed when water passage evaluation was performed under the conditions of chloramine concentration 3 ppm, water temperature 20 ° C., flow rate 5 L / min, SV 600 / hr. It was.

This application is based on Japanese Patent Application No. 2016-246202 filed on Dec. 20, 2016, the contents of which are included in the present application.

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in order to express the present invention, the present invention has been described appropriately and sufficiently through the embodiments with reference to specific examples and the like. However, those skilled in the art can easily change and / or improve the above-described embodiments. It should be recognized that this is possible. Therefore, unless the modifications or improvements implemented by those skilled in the art are at a level that departs from the scope of the claims recited in the claims, the modifications or improvements are not limited to the scope of the claims. To be construed as inclusive.

The porous carbon material of the present invention is useful as a decomposition catalyst for peroxides (such as hydrogen peroxide) and chloramine. Moreover, since high catalytic activity can be maintained, the recyclability is high, the amount of decomposition catalyst waste can be reduced, and the cost can be reduced.

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Non-Patent Citations (1)

Title
See also references of EP3546425A4

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(54) Title: POROUS CARBON MATERIAL, METHOD FOR PRODUCING SAME AND USE OF SAME

(54) 発明の名称： 多孔質炭素材料並びにその製造方法と用途

(57) Abstract: The present invention relates to a porous carbon material which has a nitrogen content of 0.5-2.0% by mass and an iron content of at least 400 mg/kg - the porous carbon material or more, while having an electrical conductivity of 10 S/cm or more as determined by powder resistance measurement.

(57) 要約：本発明は、窒素含有量が０．５～２．０質量％であり、鉄の含有量が少なくとも４００ｍｇ／ｋｇ－多孔質炭素材料以上であり、かつ、粉体抵抗測定によって得られる導電率が１０Ｓ／ｃｍ以上である、多孔質炭素材料に関する。

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明　細　書

発明の名称 ： 多孔質炭素材料並びにその製造方法と用途

技術分野

[0001] 本発明は、分解触媒として使用できる多孔質炭素材料と、その製造方法及びその用途に関する。

背景技術

[0002] 活性炭等の多孔質炭素材料自体が分解触媒として作用することがよく知られており、例えば、活性炭は硫化水素及びSO_2の酸化を含む様々な酸化反応に有用であることが知られている。活性炭はそのような反応に影響することが観察されており、触媒としての活性炭は反応速度のみに影響し、活性炭自体は反応により殆ど変化しない。

[0003] 窒素分の多い原料から製造された活性炭は、窒素分の少ない原料から製造された活性炭に比べて、過酸化水素の分解などの特定の反応において効果的に触媒作用する。同様に、窒素分の少ない原料から製造された活性炭を、高温で、アンモニアなどの窒素含有化合物に曝すと、活性炭の触媒機能が高まることも知られている。最近では、ポリアクリロニトリルやポリアミドなどの窒素分の多い物質を低温又は高温で乾留し、この乾留物を活性（賦活）することにより、触媒活性の高い活性炭が製造されている。いずれの場合も、活性炭は７００℃を超える温度で熱処理することによって製造される。窒素分の少ない原料から製造された活性炭を、窒素含有化合物に曝す前、又は曝す最中に酸化するのが有利であることも知られている。

[0004] しかし、触媒活性を有する活性炭を製造する先行技術の方法は、すべてある種の欠点があり、そのために全体的な有用性や実用性が限られている。例えば、ポリアクリロニトリルやポリアミドなどの窒素分の多い原料は高価であり、炭素化に際し、大量のシアン化物および他の毒性ガスを発生する。窒素分の少ない原料から得られる活性炭では、触媒能力を大きく変化させるために激しい化学的な後処理が必要である。その際、所望の触媒活性を得るた

めに炭素収率を犠牲にして達成され、必然的に高価となる。さらに、化学的に処理する方法では、硝酸、硫酸またはアンモニアなどの毒性があり危険な薬品を大量に使用するため、ＳＯｘ、ＮＯｘ、シアン化物のような毒性があり危険な副生物が著しく大量に生じる。

[0005] 特許文献１には、過酸化水素を急速に分解する触媒活性の炭素質チャーが報告されている。この文献には、原料を低温で酸化し、尿素などの窒素含有化合物に曝し、不活性雰囲気中、高温で加熱し、水蒸気及び／又は二酸化炭素中、高温で活性化し、不活性雰囲気中で冷却する事により炭素質チャーを製造する事が記載されている。特許文献２には、炭を１種もしくは２種以上の有機系の窒素含有化合物と混合し、活性化することで、触媒活性を有する活性炭を製造できることが記載されている。

[0006] しかし、特許文献１や２に記載のような窒素含有化合物を使用する方法では、ＮＯｘ等の毒性を有し、危険な副生物を多量に生じる。

[0007] 特許文献３には、木炭を用いる触媒活性のある活性炭の製造方法が記載されている。この方法は、蒸気へのアンモニアの添加を含んでいる。アンモニアのこのような添加は、健康ならびに環境の観点からの両方で望ましくない。

[0008] 特許文献４には、窒素を含んだ瀝青炭を用いた活性炭の製造方法が記載されている。しかしながら、この方法では高温熱処理を行っていないため、活性炭の導電率が低く、十分な触媒性能が得られない。また、窒素を過剰に含んだ原料を用いるため、製造時にＮＯｘ等の有害ガスを発生し、健康ならびに環境の観点からの両方で望ましくない。

[0009] 本発明の目的は、窒素含有化合物によって処理することなく得られ、様々な化合物や物質の分解触媒として使用できる多孔質炭素材料、並びに、その製造方法とその用途を提供することにある。

先行技術文献

特許文献

[0010] 特許文献1：特許２６８５３５６号公報

特許文献2：特表２０１４－５０６５２９号公報

特許文献3：特許３９５５０６２号公報

特許文献4：特開２０１３－１６３６２９号公報

発明の概要

[0011] 本発明の一局面に係る多孔質炭素材料は、窒素含有量が０．５～２．０質量％であり、鉄の含有量が少なくとも４００ｍｇ／ｋｇ－多孔質炭素材料以上であり、かつ、粉体抵抗測定によって得られる導電率が１０Ｓ／ｃｍ以上であることを特徴とする。

発明を実施するための形態

[0012] 本発明者らは、前記課題を解決するため鋭意検討の結果、窒素含有量を所定の濃度以上含有し、かつ熱処理によって結晶化度を高めた多孔質炭素材料を分解触媒として用いると、過酸化水素等の過酸化物の分解能が大きく向上すること、並びに、クロラミン及び臭素酸等を有効に分解することを見出し、当該知見に基づきさらに研究を重ねて本発明を完成した。

[0013] 本発明の多孔質炭素材料は分解触媒として高い触媒活性を示す。また、本発明の多孔質炭素材料は繰り返し使用しても高い触媒活性を保持する。そのため、本発明の多孔質炭素材料は、様々な化合物や物質の分解触媒として使用でき、特に、水溶液中で過酸化物（過酸化水素など）を有効に分解できる。さらに本発明の多孔質炭素材料は、クロラミン及び臭素酸等を分解するのに適している。

[0014] 以下、本発明の実施形態について詳細に説明するが、本発明はこれらに限定されるものではない。

[0015] ＜多孔質炭素材料及び分解触媒＞

本発明の多孔質炭素材料は、以下の特徴を有する。

（ａ）窒素含有量が０．５～２．０質量％であり、

（ｂ）粉体抵抗測定によって得られる導電率が１０Ｓ／ｃｍ以上であり、

（ｃ）鉄の含有量が少なくとも４００ｍｇ／ｋｇ一多孔質炭素材料以上である。

[0016] 本実施形態の多孔質炭素材料が有する触媒活性は、例えば、分解対象が過酸化水素の場合、窒素を含む特定の構造部位からの過酸化水素への電子供与により進行し、熱処理を行って結晶性を高めて導電率を大きくすることで、過酸化水素への電子供与を高めることができると考えられる。同様に、電子供与により分解が進行する過酸化物の分解を促進することが可能である。

[0017] さらに、本発明の多孔質炭素材料は、以下の特徴を有することが好ましい。

（ｄ）ベンゼン吸着性能が２５～５０％である。

[0018] 上述の物性（ａ）、（ｂ）、（ｃ）、（ｄ）に関し、本実施形態の多孔質炭素材料の触媒活性には単一の物性ではなく、これらの物性が複合的に関与しているようである。そのため、特に上記（ａ）～（ｃ）の物性について一つの物性が上記範囲にあっても、その他の物性が上記範囲を外れると、分解触媒の触媒活性が低下する。

[0019] 多孔質炭素材料の窒素含有量が上述した規定範囲より小さすぎると、触媒機能を有する反応サイトが減少するため、分解性能が低下する。また、大きすぎると、触媒製造中に発生するＮＯｘ等の有害ガスが多量に発生し、健康ならびに環境への影響が懸念されるため、好ましくない。従って、本実施形態における多孔質炭素材料の窒素含有量は０．５～２．０質量％である。より好ましくは、０．５～１．０質量％である。

[0020] 多孔質炭素材料の導電率が上述した規定範囲より小さすぎると、分解触媒の電子供与能力が低下し、分解性能が低下する。従って、本実施形態における多孔質炭素材料の導電率は１０Ｓ／ｃｍ以上である。導電率がこの範囲であれば十分な分解性能が得られるため、特に上限値に限定はないが、導電率があまり大きすぎると、分解触媒の電子供与能力は向上するが、分解触媒の窒素含有量が減少し、触媒の分解性能が低下するおそれがある。よって、本実施形態における多孔質炭素材料の導電率は、好ましくは１０～２０Ｓ／ｃｍであり、さらに好ましくは１２～１８Ｓ／ｃｍである。

[0021] 多孔質炭素材料の鉄の含有量が上述した規定範囲より小さすぎると、分解

触媒の結晶構造の発達が乏しくなるため分解性能が低下すると推測される。従って、本実施形態における多孔質炭素材料の鉄含有量は、少なくとも、４００ｍｇ／ｋｇ－多孔質炭素材料以上とする。鉄含有量がこの範囲であれば十分な分解性能が得られるため、特に上限値に限定はないが、鉄含有量が多すぎると、分解触媒の収率が低下するため、経済的観点から好ましくない。従って、本実施形態における多孔質炭素材料の鉄含有量は、好ましくは４００～５０００ｍｇ／ｋｇ－多孔質炭素材料であり、より好ましくは、５００～３０００ｍｇ／ｋｇ－多孔質炭素材料である。なお、前記「ｍｇ／ｋｇ－多孔質炭素材料」との単位は、多孔質炭素材料１ｋｇあたりの鉄含有量（ｍｇ）を意味する。

[0022] 本実施形態における多孔質炭素材料のベンゼン吸着性能は、上述の規定範囲であれば、十分な比表面積が得られるため、優れた分解性能をより確実に得られる。前記ベンゼン吸着性能の上限は特に限定はされないが、あまり大きくなると、分解触媒の収率が低下するため、経済的観点から好ましくない。従って、本実施形態におけるベンゼン吸着性能は２０～５０％であることが好ましく、より好ましくは３０～４５％である。なお、本明細書におけるベンゼン吸着性能とは、ＪＩＳＫ１４７４（２０１４年）に準拠して測定されたものを指す。

[0023] 本実施形態の多孔質炭素材料が有する触媒活性は、上記した過酸化水素のように、分解対象の化合物に対し、窒素を含む特定の構造部位からの化合物への電子供与により進行すると推測される。したがって、本実施形態の多孔質炭素材料は、電子供与により分解が進行する化合物を分解する分解触媒として有用である。中でも、窒素を含む特定の構造部位から化合物への電子供与のされやすい化合物は、より分解されやすい。

[0024] 例えば、本実施形態の多孔質炭素材料は、過酸化物、クロラミン、臭素酸、次亜臭素酸や次亜塩素酸の分解などに非常に有用である。過酸化物としては、例えば、過酸化水素などの無機過酸化物、過酢酸などの有機過酸化物などが例示できる。

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
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[0025] 本実施形態におけるクロラミン（クロロアミン）としては、モノクロロアミンNH_2Cl、ジクロロアミン$NHCl_2$、トリクロロアミンNCl_3のいずれであってもよい。水道水などの消毒に汎用される代表的なクロラミンはモノクロロアミンであり、このモノクロロアミンは揮発性が低く、安定性が高い。そのため、残存するモノクロロアミンはチオ硫酸ナトリウムなどで処理されている。本発明の分解触媒は、このようなクロラミン（モノクロロアミンなど）を効率よく分解し、塩素を遊離化させる。

[0026] 本実施形態には、上述したような多孔質炭素材料を含む分解触媒も包含される。本実施形態の分解触媒は、電子供与により分解が進行する化合物を分解するのに有用である。前記化合物としては上記した過酸化物、クロラミン、臭素酸、次亜臭素酸、次亜塩素酸などが挙げられる。特に、過酸化物、クロラミン及び臭素酸のうち少なくともいずれかひとつのための分解触媒として有用である。また、過酸化物及び／又はクロラミンのための分解触媒としても有用である。

[0027] ＜多孔質炭素材料の製造方法＞

通常、分解触媒として用いる多孔質炭素材料の製造は、活性炭をアンモニアなどの窒素含有化合物と接触させるか、ポリアクリロニトリルなどの窒素を多く含む原料から活性炭化する方法で行われる。

[0028] 本実施形態では、窒素以外のパラメーターを管理することにより、高触媒活性を有する分解触媒を安価に製造できる。

[0029] すなわち、本実施形態の多孔質炭素材料は、炭素質材料を乾留し、得られた乾留品を１０００～１２００℃、より好ましくは１０００～１１００℃の温度で熱処理した後、水蒸気、窒素及び二酸化炭素を含む混合ガス雰囲気下、８５０～１０００℃の温度で賦活処理することにより得ることができる。この賦活処理において、乾留した炭素材は部分的にガス化してもよい。

[0030] 炭素質材料としては、公知の材料全てから選択でき、例えば、植物（ヤシガラ、籾ガラ、珈琲豆滓、木材など）、天然高分子（デンプン、セルロース、リグニン類など）、半合成高分子（セルロースエステル類、セルロースエ

ーテル類、リグニン樹脂など）、合成高分子（フェノール系樹脂、フラン系樹脂、エポキシ樹脂など）、瀝青質物質などで例示できる。これらの原料は単独で又は二種以上組み合わせて使用できる。好ましい原料は、木材などの植物原料であってもよいが、特に、天然鉱物を原料とすることが好ましい。具体的には、窒素や鉄を含む石炭類、例えば、泥炭、亜炭、亜瀝青炭、瀝青炭、半無煙炭、無煙炭からなる石炭類から選ばれる石炭が好ましく用いられ、中でも、窒素含有量を多く含むことから、瀝青炭が好ましい。しかし、窒素含有量が多すぎる瀝青炭を用いると、ＮＯｘ等の有害物質が多量に発生し、健康ならびに環境への影響が懸念されるため、好ましくない。従って、炭素質材料原料の窒素含有量は１．０～２．０質量％、好ましくは１．５～２．０質量％であることが望ましい。また、炭素質材料原料（例えば、瀝青炭）の灰分として含まれる鉄の含有量が少なすぎると、多孔質炭素材料の結晶構造の発達が乏しくなり、高い分解性能が得られない。一方で、大きすぎると、分解触媒の収率が低下するため経済的観点から好ましくない。従って、炭素質材料原料の鉄の含有量は５００～１００００ｍｇ／ｋｇであることが好ましく、５００～２０００ｍｇ／ｋｇがより好ましい。

[0031] 本実施形態の炭素質材料は、一般的な活性炭製造設備である流動層、多段炉、回転炉などを用いて作製することができる。

[0032] 乾留は、慣用の方法、例えば、炭素質材料を、酸素又は空気を遮断して、４００～８００℃、好ましくは５００～８００℃、さらに好ましくは６００～８００℃で加熱することにより行うことができる。

[0033] 前記熱処理は、乾留物を酸素又は空気を遮断して、１０００℃以上の温度、好ましくは１０００～１２００℃の温度、さらに好ましくは１０００～１１００℃で行うことができる。この熱処理温度が低すぎると、多孔質炭素材料の結晶化度の発達が乏しくなり、充分な電子供与能力が得られないため、分解性能も低くなると考えられる。また、熱処理温度が高すぎると、結晶化度は高まるが、炭素構造中から窒素が脱離するため、十分な分解性能が得られないおそれがある。

[0034] 本実施形態の製造方法において、賦活処理は、流動層、多段炉、回転炉などを用いて、乾留物を、８５０℃以上の温度、好ましくは８５０～１０００℃ （例えば８５０～９５０℃）で、水蒸気、窒素及び二酸化炭素の混合物の雰囲気下で行うことができる。前記混合物の雰囲気下で賦活することにより、乾留物が部分的にガス化し、多孔質炭素材料（分解触媒）が得られる。なお、炭素質材料の乾留物の一部をガス化させるためのガス（水蒸気、窒素及び二酸化炭素からなる混合ガス）は、天然ガス、石油、又は炭化水素を含む他の可燃物を燃焼させることによって得ることもできる。なお、賦活温度は、通常、±２５℃程度の範囲で変動する場合が多い。

[0035] 賦活時間は、特に限定はされないが、１～４８時間、好ましくは４～２４時間、さらに好ましくは５～２０時間（例えば、６～１２時間）程度であってもよい。賦活時間が短すぎると、多孔質炭素材料の分解触媒活性が低下し、長すぎると生産性が低下するおそれがある。

[0036] ガス分圧も特に限定はされないが、水蒸気分圧７．５～４０％、好ましくは１０～３０％（例えば、１０～２０％）、二酸化炭素分圧１０～５０％、好ましくは１５～４５％（例えば、２０～４０％）、窒素分圧３０～８０％、好ましくは４０～７０％（例えば、４５～６５％）程度であり、ガス分圧は、水蒸気分圧１０～４０％、二酸化炭素分圧１０～４０％及び窒素分圧４０～８０％程度であってもよい。なお、ガスの全圧は、通常、１気圧（約０．１ＭＰａ）である。

[0037] また、総ガス供給量（流量）は、乾留品原料１００ｇに対して、１～５０Ｌ／分、好ましくは１～２０Ｌ／分程度である。流量が少なすぎると、賦活が十分でなく、多すぎると、多孔質炭素材料の分解触媒活性が低下する。

[0038] このような条件を組み合わせることにより、目的とする窒素含有量、導電率及び鉄の含有量を有する多孔質炭素材料が得られると考えられる。なお、本実施形態の多孔質炭素材料の製造方法の詳細は、後述の実施例を参照してもよい。

[0039] なお、本実施形態の製造方法で得られる多孔質炭素材料は、粉末状、粒状

、造粒状であってもよく、必要であれば、ハニカム状などの形態に成形してもよい。

[0040] ＜多孔質炭素材料含有成形体の製造方法＞

次に、本実施形態の多孔質炭素材料を含有する成形体（以下、多孔質炭素材料含有成形体と称す）の製造方法について説明する。本実施形態の多孔質炭素材料含有成形体は、粒状または粉末状の多孔質炭素材料及び繊維状バインダーを混合して得た混合物を水中に分散させスラリーを調製するスラリー調製工程と、前記スラリーを吸引しながら濾過して予備成形体を得る吸引濾過工程と、前記予備成形体を乾燥して乾燥した成形体を得る乾燥工程とを含む製造方法により得られる。

[0041] （スラリー調製工程）

前記スラリー調製工程において、粒状または粉末状の多孔質炭素材料及び繊維状バインダーを、固形分濃度が０．１～１０質量％（特に１～５質量％）になるように、水に分散させたスラリーを調製する。前記スラリーの固形分濃度が高すぎると、分散が不均一になり易く、成形体に斑が生じ易い。一方、固形分濃度が低すぎると、成形時間が長くなり生産性が低下するだけではなく、成形体の密度が高くなり、濁り成分を捕捉することによる目詰まりが発生しやすい。

[0042] （吸引濾過工程）

吸引濾過工程では、前記スラリーに多数の穴を有する成形用の型枠を入れて、前記型枠の内側から吸引しながら濾過することにより成形する。成形用の型枠としては、例えば、慣用の型枠を利用でき、例えば、特許第３５１６８１１号公報の図１に記載の型枠などを使用できる。吸引方法としても、慣用の方法、例えば、吸引ポンプなどを用いて吸引する方法などを利用できる。また、吸引濾過後に、予備成形体を整形台上で圧縮することで、外表面の形状を整える工程を行っても良い。

[0043] （乾燥工程）

乾燥工程では、吸引濾過工程で得られた予備成形体を型枠から取り外し、

乾燥機などで乾燥することにより成形体を得ることができる。乾燥温度は、例えば、１００～１５０℃（特に１１０～１３０℃）程度であり、乾燥時間は、例えば、４～２４時間（特に８～１６時間）程度である。乾燥温度が高すぎると、繊維状バインダーが変質したり溶融して濾過性能が低下したり成形体の強度が低下し易い。乾燥温度が低すぎると、乾燥時間が長時間になったり、乾燥が不十分になり易い。また、乾燥した成形体の外表面を研削（又は研磨）する工程を行っても良い。

[0044] 本実施形態の多孔質炭素材料含有成形体は、例えば、浄水フィルターや人工透析用フィルターなどとして用いられる。本実施形態の多孔質炭素材料含有成形体を浄水フィルターや人工透析用フィルターとして使用する場合は、円筒形状にするのが好ましく、さらに必要に応じて、円筒形状の筒頂部分にキャップを装着したり、円筒形状の中空部にネトロンパイプやセラミックフィルター、不織布などの補強材を挿入したり、表面に不織布を装着させてもよい。円筒形状にすることによって、通水抵抗を低下することができ、さらに、ハウジングに充填してカートリッジとして使用する場合、浄水器へのカートリッジの装填・交換作業が簡単にできる。

[0045] ＜過酸化物及び／又はクロラミン等の除去方法＞

本実施形態の多孔質炭素材料を分解触媒として用いて、過酸化物、クロラミン、臭素酸、次亜臭素酸及び次亜塩素酸のうち少なくとも一つ（過酸化物及び／又はクロラミン等）を分解して除去することができる。すなわち、本発明には、多孔質炭素材料を分解触媒として用いて、対象物と接触させて該対象物から過酸化物、クロラミン、臭素酸、次亜臭素酸及び次亜塩素酸のうち少なくとも一つを分解し除去する方法、好ましくは該対象物から過酸化物及び／又はクロラミンを、より好ましくは過酸化物、クロラミン及び臭素酸を、さらに好ましくは過酸化物、クロラミン、臭素酸、次亜臭素酸及び次亜塩素酸を分解し除去する方法が包含される。

[0046] ここで、対象物とは、過酸化物及び／又はクロラミン等を除去したい物あるいは過酸化物及び／又はクロラミン等を含む各種媒体であれば特に限定は

されない。例えば、過酸化物及び／又はクロラミン等を含む水や流動水、ミスト等が挙げられる。中でも本実施形態の多孔質炭素材料は、水、流動水等の液体媒体からなる対象物から過酸化物及び／又はクロラミン等を除去することに適している。

[0047] 上記過酸化物、クロラミンなど（過酸化物、クロラミン、臭素酸、次亜臭素酸及び次亜塩素酸のうち少なくとも一つ）の基質の分解は水性溶媒中で行うことができ、過剰量の溶媒の存在下で、前記分解反応を行う場合が多い。なお、過酸化物、クロラミンなどの基質の濃度は特に制限されず、例えば、反応系での過酸化物の濃度は０．１～５０質量％、好ましくは０．５～３０質量％、さらに好ましくは１～２０質量％程度であってもよい。本実施形態の多孔質炭素材料を使用すれば、前記基質を有効に分解又は酸化できるため、本発明の多孔質炭素材料は、微量の過酸化物（過酸化水素など）、クロラミン（モノクロロアミンなど）などの基質を除去するのに有用である。残存する微量の基質を処理する場合、例えば、基質の濃度は、０．１ｐｐｂ～１０００ｐｐｍ程度であってもよい。

[0048] 多孔質炭素材料の分解触媒としての使用量は、特に限定はされないが、例えば、過酸化物、クロラミンなどの基質１００質量部に対して、０．１～５００質量部、好ましくは１～２５０質量部、さらに好ましくは５～１００質量部（例えば、１０～５０質量部）程度であってもよい。

[0049] 前記分解（除去）反応は、例えば、１０～７０℃、好ましくは２０～５０℃程度で行うことができる。前記分解反応は、例えば、空気中又は酸素含有雰囲気下で行うこともでき、不活性ガス雰囲気下で行うこともできる。

[0050] 本実施形態の多孔質炭素材料は、分解触媒として繰り返し使用しても触媒活性が低下せずに高い触媒能を維持することができる。例えば、実施例に記載の試験方法（水溶液中過酸化水素分解性能評価及び過酸化水素分解速度の測定）において、分解触媒１ｇ当たり１時間での過酸化水素の分解速度は、バッチ式の水溶液中で１０００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒ以上（例えば、２０００～１００００００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／

ｈｒ、好ましくは３０００～７５０００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒ、さらに好ましくは５０００～５００００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒ）である。しかも、このような試験方法（バッチ式の水溶液中該過酸化水素分解試験）に繰り返し１５回以上（例えば、１５～２５回、好ましくは１５～３０回程度）使用しても、高い触媒活性を維持する。すなわち、本発明の多孔質炭素材料は、前記試験方法において、１０００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒ以上の水溶液中の過酸化水素分解性能を維持しつつ繰り返し１５回以上使用できる。なお、「１０００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒ」とは、１時間あたり、多孔質炭素材料１ｇあたり１０００ｍｇの過酸化水素（H_2O_2）が分解されることを意味する。

[0051] 本実施形態の多孔質炭素材料は、過酸化物及び／又はクロラミンの分解触媒として非常に有用であるため、例えば、工業用排水中の過酸化物の分解や水道水中に含まれるクロラミンの分解除去等といった用途において優れた効果を発揮する。よって、本実施形態の多孔質炭素材料は、例えば、浄水器、工業用廃水処理用の分解触媒として非常に有用である。

[0052] 本明細書は、上述したように様々な態様の技術を開示しているが、そのうち主な技術を以下に纏める。

[0053] 本発明の一局面に係る多孔質炭素材料は、窒素含有量が０．５～２．０質量％であり、鉄の含有量が少なくとも４００ｍｇ／ｋｇ－多孔質炭素材料以上であり、かつ、粉体抵抗測定によって得られる導電率が１０Ｓ／ｃｍ以上であることを特徴とする。

[0054] このような構成により、本発明の多孔質炭素材料は分解触媒として高い触媒活性を示し、また、繰り返し使用しても高い触媒活性を保持する。そのため、本発明の多孔質炭素材料は、様々な化合物や物質の分解触媒として有効である。

[0055] また、前記多孔質炭素材料において、ベンゼン吸着性能が２５～５０％の範囲であることが好ましい。

[0056] さらに、本発明のもう一つの局面に係る成形体は、上述の多孔質炭素材料

を含有することを特徴とする。当該成形体は、例えば、浄水フィルターや人工透析用フィルターなどとして好適に使用できる。

[0057] さらに、本発明の他の局面に係る分解触媒は、上述の多孔質炭素材料を含むことを特徴とする。また、当該分解触媒が、過酸化物、クロラミン及び臭素酸のうち少なくともいずれかのための分解触媒であることが好ましい。

[0058] また、本発明のさらなる局面に係る多孔質炭素材料を製造する方法は、炭素質材料を乾留し、１０００～１２００℃の温度で熱処理し、その後、水蒸気、窒素及び二酸化炭素を含む混合ガス雰囲気下、８５０～１０００℃の温度で賦活することを含むことを特徴とする。

[0059] また、多孔質炭素材料の製造方法において、前記炭素質材料が天然鉱物を原料とすることが好ましい。

[0060] さらに、前記天然鉱物原料の窒素含有量が１．０～２．０質量％であることが好ましい。

[0061] 本発明のさらなる局面に関する過酸化物及び／又はクロラミン等を分解除去する方法は、上述の多孔質炭素材料を分解触媒として用いて、対象物と接触させて該対象物から過酸化物、クロラミン、臭素酸、次亜臭素酸及び次亜塩素酸のうち少なくとも一つを分解除去することを特徴とする。

[0062] さらに本発明には、上述の成形体又は上述の分解触媒を備える分解触媒装置。も包含される。

実施例

[0063] 以下に実施例に基づいて本発明をより詳細に述べるが、以下の実施例は、本発明を何ら限定するものではない。

[0064] （試験例１）

なお、後述の実施例及び比較例では、多孔質炭素材料の分解触媒性能を以下のようにして評価した。

[0065] ［多孔質炭素材料の窒素含有量の測定］

粉砕した多孔質炭素材料を１２０℃で２時間乾燥した後、ＥＬＥＭＥＮＴＡＲ社製Ｖａｒｉｏ　ＥＬ　ＩＩＩを使用し、基準物質にスルファニル酸を

用いて、多孔質炭素材料の窒素含有量を測定した。

[0066] ［多孔質炭素材料の導電率の測定］

三菱化学アナリテック社製、粉体抵抗率測定ユニットＭＣＰ－ＰＤ５１を使用し、多孔質炭素材料の導電率を測定した。導電率の測定には、測定試料の粒径が大きく影響するため、多孔質炭素材料の体積基準の累積分布の１０％粒子径（Ｄ１０）が１～３μｍ程度、体積基準の累積分布の５０％粒子径（Ｄ５０）が５～８μｍ程度、体積基準の累積分布の９０％粒子径（Ｄ９０）が１０～２０μｍ程度になるよう粉砕し、荷重を１２ｋＮかけた際の多孔質炭素材料ペレットの導電率を測定した。なお、粉砕した多孔質炭素材料の粒径はレーザー回折測定法により測定した。すなわち、測定対象である多孔質炭素材料を界面活性剤と共にイオン交換水中に入れ、超音波振動を与え均一分散液を作製し、マイクロトラック・ベル社製のＭｉｃｒｏｔｒａｃ ＭＴ３０００ＥＸ－IIを用いて測定した。界面活性剤には、和光純薬工業株式会社製の「ポリオキシエチレン（１０）オクチルフェニルエーテル」を用いた。分析条件を以下に示す。

（分析条件）

測定回数：３回

測定時間：３０秒

分布表示：体積

粒径区分；標準

計算モード：ＭＴ３０００II

溶媒名：ＷＡＴＥＲ

測定上限：２０００μｍ、測定下限：０．０２１μｍ

残分比：０．００

通過分比：０．００

残分比設定：無効

粒子透過性：吸収

粒子屈折率：Ｎ／Ａ

粒子形状：Ｎ／Ａ

溶媒屈折率：１．３３３

ＤＶ値：０．０１００～０．０５００

透過率（ＴＲ）：０．７５０～０．９２０

[0067] ［多孔質炭素材料のベンゼン吸着性能の測定］

日本工業規格における活性炭試験方法ＪＩＳＫ１４７４に準拠し、多孔質炭素材料のベンゼン吸着性能を測定した。

[0068] ［多孔質炭素材料の鉄含有量の測定］

まず、既知濃度の標準液から鉄含有量についての検量線を作成した。ついで、粉砕した測定試料を１２０℃で２時間乾燥した後、分解容器に０．１ｇ入れ、硝酸１０ｍｌを加え混ぜた後、マイクロウェーブ試料前処理装置（ＣＥＭ社製、ＤｉｓｃｏｖｅｒＳＰ－Ｄ８０）を用いて試料を溶解した。その溶解液を取り出し、２５ｍｌにメスアップして測定溶液を調製した後、ＩＣＰ発光分光分析装置（サーモフィッシャーサイエンティフィック社製、ｉＣＡＰ６２００）にて分析した。得られた値と先に作成した検量線より鉄含有量を求めた。

[0069] ［水溶液中過酸化水素分解性能評価及び過酸化水素分解速度の測定］

２５℃における３０００ｍｇ／Ｌ過酸化水素濃度の水溶液４００ｍＬに、Ｄ５０が５～８μｍになるよう粉砕し、１２０℃で乾燥した多孔質炭素材料０．１ｇを添加し、水溶液中に残留している過酸化水素濃度を測定し、経時変化を残留量がゼロになるまで評価した。なお、分解性能評価における残留過酸化水素濃度の測定は、ＭＡＣＨＥＲＥＹ－ＮＡＧＥＬ社製、ＱＵＡＮＴＯＦＩＸ　Ｐｅｒｏｘｉｄｅを用いて測定した。

[0070] 過酸化水素分解速度＝（Ｃｏ－Ｃ）×０．４／Ａ／Ｔ

Ｃｏ＝過酸化水素初濃度（ｍｇ／Ｌ），Ｃ＝任意時間経過後の過酸化水素濃度（ｍｇ／Ｌ），Ａ＝多孔質炭素材料量（ｇ），Ｔ＝任意時間（ｈｒ）

繰り返し時における過酸化水素分解性能評価は、残留量がゼロになった溶液に、３０質量％濃度の過酸化水素水溶液を３０００ｍｇ／Ｌになるように

添加し、再び水溶液中に残留している過酸化水素濃度を測定し、経時変化を残留量がゼロになるまで評価する。この操作を１０００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒ以上の過酸化水素分解速度が得られなくなるまで繰り返した。その繰り返し回数で評価した。本実施例では、この繰り返し回数が１５回以上を合格とする。

[0071] ［実施例１］

炭素質原料を瀝青炭（原料窒素含有量：１．９１質量％）とし、６５０℃で乾留した後、得られた乾留品を１１００℃の条件下で熱処理した。その後に、熱処理品４００ｇを炉に投入し、水蒸気分圧１５％、二酸化炭素分圧１１％、窒素分圧７４％の混合ガスを、ガスの全圧１気圧でかつ流量５．５Ｌ／ｍｉｎで炉内に供給し、賦活温度９００℃の条件下で、ベンゼン吸着性能が２０．６％となるように処理して多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も１６回と高いことを確認した。

[0072] ［実施例２］

炭素質原料を瀝青炭とし、ベンゼン吸着性能が２５．１％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も２１回と高いことを確認した。

[0073] ［実施例３］

炭素質原料を瀝青炭とし、ベンゼン吸着性能が３０．８％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も２５回と高いことを確認した。

[0074] ［実施例４］

炭素質原料を瀝青炭とし、ベンゼン吸着性能が４１．７％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であった。得られた分解触媒の過酸化水素分解性能を評価したところ、繰り返し回数３１回目における過酸化水素分解速度が８００ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒであったため分解触媒の繰り返し回数を３０回とした。

[0075] ［実施例５］

炭素質原料を瀝青炭とし、乾留品の熱処理を１２００℃の条件下で行い、ベンゼン吸着性能が２９．７％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も２２回と高いことを確認した。

[0076] ［実施例６］

炭素質原料を瀝青炭とし、乾留品の熱処理を１０００℃の条件下で行い、ベンゼン吸着性能が３０．９％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も２３回と高いことを確認した。

[0077] ［実施例７］

実施例４で得られた多孔質炭素材料を、１Ｎの塩酸中で洗浄後、イオン交換水を用いて脱塩し、その後１２０℃で乾燥した。得られた多孔質炭素材料は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も２５回と高いことを確認した。

[0078] ［実施例８］

実施例４で得られた多孔質炭素材料を、０．５Ｎの塩酸中で洗浄後、イオ

ン交換水を用いて脱塩し、１２０℃で乾燥した。得られた多孔質炭素材料は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も２８回と高いことを確認した。

[0079] ［実施例９］

炭素質原料を瀝青炭とし、ベンゼン吸着性能が３９．４％となるような条件で賦活処理した以外は、実施例６と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が全て所定範囲内であり、触媒としての繰り返し回数も３０回と高いことを確認した。

[0080] ［比較例１］

炭素質原料を瀝青炭とし、乾留処理した後の熱処理を行わずに、ベンゼン吸着性能が２９．５％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、導電率が所定範囲から外れることを確認した。得られた分解触媒の過酸化水素分解性能を評価したところ、繰り返し回数１２回目における過酸化水素分解速度が９３０ｍｇ－H_2O_2／ｇ－多孔質炭素材料／ｈｒであったため、分解触媒としての繰り返し回数を１１回とした。分解性能が低い要因として、導電率が高められていないことにより、触媒の電子供与能力が低いことが考えられる。

[0081] ［比較例２］

炭素質原料を瀝青炭とし、乾留品の熱処理を１３００℃の条件下で行い、ベンゼン吸着性能が２９．８％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量が所定範囲から外れており、触媒としての繰り返し回数も１３回と低いことを確認した。分解性能が低い要因として、触媒反応に寄与する窒素の含有量が少ないことが考えられる。

[0082] ［比較例３］

炭素質原料を無煙炭（原料窒素含有量：０．７２質量％）とし、乾留処理

した後の熱処理を行わずに、賦活温度９５０℃でベンゼン吸着性能が３２．６％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量が所定範囲から外れ、触媒としての繰り返し回数も１回と低いことを確認した。分解性能が低い要因として、触媒反応に寄与する窒素の含有量が少ないことが考えられる。

[0083] ［比較例４］

炭素質原料を無煙炭とし、乾留品の熱処理を１１００℃の条件下で行い、賦活温度９５０℃でベンゼン吸着性能が３１．４％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量が所定範囲から外れ、触媒としての繰り返し回数も６回と低いことを確認した。分解性能が低い要因として、触媒反応に寄与する窒素の含有量が少ないことが考えられる。

[0084] ［比較例５］

炭素質原料をヤシガラ（原料窒素含有量：０．３０質量%）とし、乾留処理した後の熱処理を行わずに、賦活温度９５０℃でベンゼン吸着性能が３１．６％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量および導電率が所定範囲から外れ、触媒としての繰り返し回数も１回と低いことを確認した。分解性能が低い要因として、触媒反応に寄与する窒素の含有量が少ないことに加えて、導電率が低いことから、触媒の電子供与能力が低いことが考えられる。

[0085] ［比較例６］

炭素質原料をヤシガラとし、乾留品の熱処理を１１００℃の条件下で行い、賦活温度９５０℃でベンゼン吸着性能が３３．１％となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、窒素含有量および導電率が所定範囲から外れ、触媒としての繰り返し回数も１回と低いことを確認した。分解性能が低い

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要因として、触媒反応に寄与する窒素の含有量が少ないことに加えて、導電率が低いことから、触媒の電子供与能力が低いことが考えられる。

[0086] ［比較例７］

ポリアクリロニトリル系繊維トウ（ＰＡＮ）（原料窒素含有量：２６．４２質量%）を空気中２６０℃で２時間酸化処理した。得られた酸化繊維をステープル紡績して単糸を得た。得られた単糸の平織物を作製し、この織物を水蒸気分圧１５%、二酸化炭素分圧１１%、窒素分圧７４%の混合ガスにて、９５０℃でベンゼン吸着性能が３１．２%となるような条件で賦活処理した。得られた分解触媒は、窒素含有量、導電率および鉄の含有量が所定範囲から外れ、触媒としての繰り返し回数も１回と低いことを確認した。原料のＰＡＮには鉄が含有されていないため、触媒の結晶構造の発達が乏しくなった結果、触媒の電子供与が低く、分解性能が低くなったと考えられる。

[0087] ［比較例８］

実施例４で得られた多孔質炭素材料に、塩化水素と窒素の混合ガス流通下、１０００℃の条件で熱処理を行った。その後、６００℃の条件下、水蒸気分圧１５%、二酸化炭素分圧１１%、窒素分圧７４%の混合ガスにて２０分脱酸処理した。得られた分解触媒は、鉄の含有量が所定範囲から外れ、触媒としての繰り返し回数も１回と低いことを確認した。触媒性能が低い要因については定かではないが、鉄は結晶構造を発達させることに加えて、触媒性能にも何らかの寄与をしていると思われる。従って、鉄の大部分を除去することによっても分解性能は低下すると考えられる。

[0088] ［比較例９］

炭素質原料を瀝青炭とし、乾留品の熱処理を８５０℃の条件下で行い、ベンゼン吸着性能が２９．６%となるような条件で賦活処理した以外は、実施例１と同様にして多孔質炭素材料（分解触媒）を作製した。得られた分解触媒は、導電率が所定範囲から外れており、触媒としての繰り返し回数も１２回と低いことを確認した。分解性能が低い要因として、導電率が高められていないことにより、触媒の電子供与能力が低いことが考えられる。

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[0089] 実施例１～９及び比較例１～９で得られた多孔質炭素材料の評価結果を表１に示す。なお、表中の「Ｎ」は窒素を示す。

[0090]

[表1]

試料番号	原料	原料N含有量 (%)	熱処理	N含有量 (%)	導電率 (S／cm)	Bz吸着性能 (%)	鉄含有量 (mg／kg－多孔質炭素材料)	H_2O_2分解 繰り返し回数
実施例1	瀝青炭	1.91	1100℃	0.80	17.00	20.6	2051.5	16
実施例2	瀝青炭	1.91	1100℃	0.76	16.21	25.1	2136.9	21
実施例3	瀝青炭	1.91	1100℃	0.74	14.91	30.8	2388.4	25
実施例4	瀝青炭	1.91	1100℃	0.70	12.33	41.7	2878.9	30
実施例5	瀝青炭	1.91	1200℃	0.64	18.37	29.7	2792.1	22
実施例6	瀝青炭	1.91	1000℃	0.83	12.93	30.9	2342.4	23
実施例7	瀝青炭	1.91	1100℃	0.68	11.17	40.7	658.4	25
実施例8	瀝青炭	1.91	1100℃	0.68	10.96	39.6	1387.2	28
実施例9	瀝青炭	1.91	1000℃	0.80	13.08	39.4	2728.2	30
比較例1	瀝青炭	1.91	無	0.74	9.06	29.5	2705.2	11
比較例2	瀝青炭	1.91	1300℃	0.48	19.28	29.8	2921.4	13
比較例3	無煙炭	0.72	無	0.38	10.28	32.6	3415.6	1
比較例4	無煙炭	0.72	1100℃	0.41	14.77	31.4	3371.1	6
比較例5	ヤシガラ	0.3	無	0.19	6.01	31.6	1068.2	1
比較例6	ヤシガラ	0.3	1100℃	0.15	9.61	33.1	1047.5	1
比較例7	PAN	26.42	無	3.83	2.00	31.1	31.2	1
比較例8	瀝青炭	1.91	1100℃	0.68	11.09	40.4	22.1	1
比較例9	瀝青炭	1.91	850℃	0.73	9.21	29.6	2451.5	12

[0091] 表１から明らかなように、比較例１～９で得られた多孔質炭素材料は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量の内、少なくとも１つの物性値が本発明の所定の範囲に対して過剰又は過小であり、触媒としての繰り返し使用回数も１～１４回であり、繰り返し使用により触媒活性が大きく低下する。

[0092] これらに対して、実施例１～９で得られた多孔質炭素材料は、窒素含有量、導電率、ベンゼン吸着性能および鉄の含有量が所定の範囲にあり、触媒としての繰り返し使用回数も１５～３０回と大きく向上し、高い触媒活性を維持し繰り返し使用できることが明らかとなった。

[0093] また、本発明における多孔質炭素材料を得るにあたり、熱処理が重要であることも本実施例からわかった。熱処理を行わなかった比較例１および７では、窒素量は十分であったものの結晶性（導電率）が低くなったため分解性能に劣る結果となった。また、熱処理温度が高すぎた比較例２においては、結晶性（導電率）は高かったが、高温熱処理のために窒素量が減少してしまい、分解性能に劣る結果となったと考えられる。また、熱処理温度が低すぎた比較例９では、熱処理温度が十分でなく、結晶性を十分に高めることができなかったため、分解性能に劣る結果となった。

[0094] これに対し、適度な温度範囲で熱処理を行った実施例ではいずれにおいても、窒素量が適切であり、結晶性（導電率）も十分であるために分解性能に優れた多孔質炭素材料が得られた。

[0095] （試験例２）

［クロラミンの分解］

実施例１、３、４、５、７及び９と比較例１、２、５及び８で得られた多孔質炭素材料を用いて、以下のようにして、クロラミンの分解量を測定した。

[0096] 約１００ｐｐｍに調整したクロラミン（モノクロロアミン）水溶液１００ｍＬ中に、上記実施例または比較例の多孔質炭素材料を、添加量を変えて投入し、２５℃で２時間振とうした後、ろ紙で濾過し、濾液を下記のＤＰＤ吸

光光度法で残留クロラミン濃度を測定した。そして、残存するクロラミン濃度とクロラミン分解量（ｍｇ／ｇ－多孔質炭素材料）の関係を求め、残存濃度３ｐｐｍでのクロラミン分解量（ｍｇ／ｇ－多孔質炭素材料）を算出し、比較に用いた。なお、本実施例では、残留濃度３ｐｐｍでのクロラミン分解量（ｍｇ／ｇ－多孔質炭素材料）が、５０ｍｇ／ｇ－多孔質炭素材料であることを合格とする。なお、前記「ｍｇ／ｇ－多孔質炭素材料」とは、多孔質炭素材料１ｇあたり分解される物質の量（ｍｇ）を意味する。

[0097] ［クロラミンの定量方法：ＤＰＤ吸光光度法］

（１）遊離残留塩素の測定

リン酸緩衝液２．５ｍＬを共栓付き比色管５０ｍＬに採り、この緩衝液にＮ，Ｎ－ジエチル－ｐ－フェニレンジアミン（ＤＰＤ）試薬０．５ｇを加えた。次に、前記濾液を加えて全量を５０ｍＬとし、混和後、呈色した検液の適量を吸収セルに採り、光電分光光度計を用いて波長５１０～５５５ｎｍ付近における吸光度を測定し、下記（２）で作成した検量線によって試料１Ｌ中の遊離残留塩素（ｍｇ／Ｌ）を求めた。

[0098] （２）遊離残留塩素検量線の作成

調整した標準塩素水を用いて希釈水で希釈し、数段階の標準列を調製した。次に、直ちに各標準列について上記（１）と同様に操作して吸光度を測定し、それぞれの遊離残留塩素の濃度（ｍｇ／Ｌ）を求め、それらの吸光度を基準として検量線を作成した。

[0099] （３）残留塩素の測定

上記（１）で発色させた溶液にヨウ化カリウム約０．５ｇを加えて溶解し、約２分間静置後、上記（１）と同様に測定して試料の残留塩素（ｍｇ／Ｌ）を求めた。

[0100] （４）結合残留塩素（クロラミン）の測定

上記残留塩素と遊離残留塩素の差を結合残留塩素（クロラミン）濃度（ｍｇ／Ｌ）として測定した。

結果を表２に示す。

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[0101] [表2]

試料番号	残留濃度3ppmでのクロラミン分解量（mg／g－多孔質炭素材料）
実施例1	56
実施例3	82
実施例4	107
実施例5	63
実施例7	90
実施例9	137
比較例1	38
比較例2	40
比較例5	8
比較例8	28

[0102] 表２の結果より、実施例１、３、４、５、７及び９の分解触媒は、比較例１、２、５及び８の多孔質炭素材料に比べて、クロラミンの分解量が高いことが示された。

[0103] （試験例３）

［臭素酸の分解］

実施例９及び比較例１で得られた多孔質炭素材料を用いて、以下のようにして、臭素酸の分解量を測定した。

臭素酸ナトリウムを水道水に溶解した原水（臭素酸イオン１０ｐｐｍ）１００ｍＬ中に、上記実施例または比較例の多孔質炭素材料を、添加量を変えて投入し、２５℃で２時間振とうした後、ろ紙で濾過し、濾液をイオンクロマト分析にて測定し、残留臭素酸イオン濃度を求めた。そして、残存する臭素酸濃度と臭素酸分解量（ｍｇ／ｇ－多孔質炭素材料）の関係を求め、残存濃度１ｐｐｍでの臭素酸分解量（ｍｇ／ｇ－多孔質炭素材料）を算出し、比較に用いた。

結果を表３に示す。

[0104] [表3]

試料番号	残留濃度1ppmでの 臭素酸分解量 （mg／g－多孔質炭素材料）
実施例9	6
比較例1	2

[0105] （試験例４）

［多孔質炭素材料含有成形体によるクロラミンの分解］

実施例９の多孔質炭素材料を中心粒子径が１５０μｍとなるよう粉砕し、粉砕した多孔質炭素材料を１００質量部、および繊維状バインダーとして、日本エクスラン工業株式会社製アクリル繊維Ｂｉ－ＰＵＬ／Ｆを５．５質量部の割合で水に分散させてスラリーを調製した。次いで、得られたスラリーを、直径３ｍｍの多数の細孔を有する外径６３ｍｍφ、中軸径３６ｍｍφおよび高さ２４５ｍｍＨの金型に円筒状不織布を装着し、スラリーを吸引後、表面を転動成型し、乾燥後、外径６３ｍｍφ、内径３６ｍｍφおよび高さ２４５ｍｍＨの中空型円筒状の活性炭成形体を得た。

得られた活性炭成形体を１０インチの標準ハウジングに充填し、クロラミン濃度３ｐｐｍ、水温２０℃、流量５Ｌ／分、ＳＶ６００／ｈｒの条件で通水評価を行った所、クロラミンを除去することができた。

[0106] この出願は、２０１６年１２月２０日に出願された日本国特許出願特願２０１６－２４６２０２を基礎とするものであり、その内容は、本願に含まれるものである。

[0107] 本発明を表現するために、前述において具体例等を参照しながら実施形態を通して本発明を適切かつ十分に説明したが、当業者であれば前述の実施形態を変更及び／又は改良することは容易になし得ることであると認識すべきである。したがって、当業者が実施する変更形態又は改良形態が、請求の範囲に記載された請求項の権利範囲を離脱するレベルのものでない限り、当該変更形態又は当該改良形態は、当該請求項の権利範囲に包括されると解釈さ

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れる。

産業上の利用可能性

[0108] 本発明の多孔質炭素材料は、過酸化物（過酸化水素など）、クロラミンの分解触媒として有用である。しかも、高い触媒活性を維持できるため、リサイクル性が高く、分解触媒廃棄物の少量化が図れ、コスト低減を行うことができる。

請求の範囲

[請求項1] 窒素含有量が０．５～２．０質量％であり、

鉄の含有量が少なくとも４００ｍｇ／ｋｇ－多孔質炭素材料以上であり、かつ、

粉体抵抗測定によって得られる導電率が１０Ｓ／ｃｍ以上である、多孔質炭素材料。

[請求項2] ベンゼン吸着性能が２５～５０％の範囲である、請求項１記載の多孔質炭素材料。

[請求項3] 請求項１又は２に記載の多孔質炭素材料を含有する成形体。

[請求項4] 請求項１又は２に記載の多孔質炭素材料を含む分解触媒。

[請求項5] 過酸化物、クロラミン及び臭素酸のうち少なくともいずれかのための分解触媒である、請求項４に記載の分解触媒。

[請求項6] 請求項１又は２に記載の多孔質炭素材料を製造する方法であって、

炭素質材料を乾留し、１０００～１２００℃の温度で熱処理し、

その後、水蒸気、窒素及び二酸化炭素を含む混合ガス雰囲気下、８５０～１０００℃の温度で賦活することを含む、多孔質炭素材料の製造方法。

[請求項7] 前記炭素質材料が天然鉱物を原料とする、請求項６に記載の多孔質炭素材料の製造方法。

[請求項8] 前記天然鉱物原料の窒素含有量が１．０～２．０質量％である請求項７に記載の多孔質炭素材料の製造方法。

[請求項9] 請求項１又は２に記載の多孔質炭素材料を分解触媒として用いて、対象物と接触させて該対象物から過酸化物、クロラミン、臭素酸、次亜臭素酸及び次亜塩素酸のうち少なくとも一つを分解除去する方法。

[請求項10] 請求項３に記載の成形体を備える分解触媒装置。

[請求項11] 請求項４に記載の分解触媒を備える分解触媒装置。

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00114

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/043947

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C01B32/30(2017.01)i, B01J23/745(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C01B32/30, B01J23/745

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JST7580 (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2013-163629 A (KURARAY CO., LTD.) 22 August 2013, example 2 (Family: none)	1-11
Y	JP 48-043555 B1 (AGENCY DIRECTOR OF INDUSTRIAL SCIENCE AND TECHNOLOGY) 19 December 1973, page 1, column 2, lines 23-25 (Family: none)	1-11
Y	WO 2015/194142 A1 (PANASONIC CORP.) 23 December 2015, paragraphs [0007], [0008] & US 2017/0149070 A1, paragraphs [0005], [0006] & EP 3159958 A1 & CN 106463735 A	1-11

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 January 2018 (30.01.2018)	13 February 2018 (13.02.2018)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

国際調査報告

国際出願番号　ＰＣＴ／ＪＰ２０１７／０４３９４７

Ａ．　発明の属する分野の分類（国際特許分類（ＩＰＣ））

Int.Cl.　C01B32/30(2017.01)i, B01J23/745(2006.01)i

Ｂ．　調査を行った分野

調査を行った最小限資料（国際特許分類（ＩＰＣ））

Int.Cl.　C01B32/30, B01J23/745

最小限資料以外の資料で調査を行った分野に含まれるもの

日本国実用新案公報	１９２２－１９９６年
日本国公開実用新案公報	１９７１－２０１８年
日本国実用新案登録公報	１９９６－２０１８年
日本国登録実用新案公報	１９９４－２０１８年

国際調査で使用した電子データベース（データベースの名称、調査に使用した用語）

JSTPlus /JST7580 (JDreamIII)

Ｃ．　関連すると認められる文献

引用文献のカテゴリー＊	引用文献名　及び一部の箇所が関連するときは、その関連する箇所の表示	関連する請求項の番号
Y	JP 2013-163629 A (クラレケミカル株式会社) 2013.08.22, 実施例2 (ファミリーなし)	1-11
Y	JP 48-043555 B1 (工業技術院長) 1973.12.19, 第1頁第2欄第23行-第25行 (ファミリーなし)	1-11
Y	WO 2015/194142 A1 (パナソニック株式会社) 2015.12.23, 段落0007,0008 & US 2017/0149070 A1 [0005], [0006] & EP 3159958 A1 & CN 106463735 A	1-11

☐　Ｃ欄の続きにも文献が列挙されている。

☐　パテントファミリーに関する別紙を参照。

＊　引用文献のカテゴリー
「Ａ」特に関連のある文献ではなく、一般的技術水準を示すもの
「Ｅ」国際出願日前の出願または特許であるが、国際出願日以後に公表されたもの
「Ｌ」優先権主張に疑義を提起する文献又は他の文献の発行日若しくは他の特別な理由を確立するために引用する文献（理由を付す）
「Ｏ」口頭による開示、使用、展示等に言及する文献
「Ｐ」国際出願日前で、かつ優先権の主張の基礎となる出願の日の後に公表された文献
「Ｔ」国際出願日又は優先日後に公表された文献であって出願と矛盾するものではなく、発明の原理又は理論の理解のために引用するもの
「Ｘ」特に関連のある文献であって、当該文献のみで発明の新規性又は進歩性がないと考えられるもの
「Ｙ」特に関連のある文献であって、当該文献と他の１以上の文献との、当業者にとって自明である組合せによって進歩性がないと考えられるもの
「＆」同一パテントファミリー文献

国際調査を完了した日	国際調査報告の発送日
３０．０１．２０１８	１３．０２．２０１８

国際調査機関の名称及びあて先
日本国特許庁（ＩＳＡ／ＪＰ）
郵便番号１００－８９１５
東京都千代田区霞が関三丁目４番３号

特許庁審査官（権限のある職員）　４Ｇ　４６６５
塩谷　領大
電話番号　０３－３５８１－１１０１　内線　３４１６

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00116

Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(d) and C.F.R. §1.97(e)(2) / Fee Authorization

This Information Disclosure Statement is being filed under 37 C.F.R. §1.97(d) after the mailing date of a Final Office Action or Notice of Allowance, but before the payment of the issue fee. The undersigned asserts in accordance with 37 CFR 1.97(e)(2), that no item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the Information Disclosure Statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the Information Disclosure Statement under 37 C.F.R. §1.97(e)(2). Accordingly, the Information Disclosure Statement Fee of $260.00 is submitted herewith under 37 C.F.R. § 1.17(p). However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00117

Statement under 37 C.F.R. §1.704(d)(i) / Patent Term Adjustment

Applicant states that each item of information contained in the Information Disclosure Statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in § 1.56 (c) more than thirty days prior to the filing of the Information Disclosure Statement. Thus, Applicant holds that the submission of this Statement does not affect any Patent Term Adjustment.

Respectfully submitted,

DLA PIPER LLP (US)

/ Emma K. Holland /

Emma K. Holland
Reg. No. 79,947

DLA PIPER LLP (US)
1650 Market Street, Suite 5000
Philadelphia, PA 19103-7348
Telephone: (215) 656-3300
Date: September 22, 2023

Doc Code: PTA.IDS
Document Description: Patent Term Adjustment Stmt Under 37 CFR 1.704(d)

PTO/SB/133 (10-21)

PATENT TERM ADJUSTMENT STATEMENT UNDER 37 CFR 1.704(d)		
	Application Number	16/839,862
	Filing Date	April 3, 2020
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Practitioner Docket No.	123450-013001

APPLICANT HEREBY STATES THE FOLLOWING (please review 37 CFR 1.704(d) before filing this form):

☑ Each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

AND/OR

☐ Each item of information contained in the information disclosure statement is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

INSTRUCTIONS:

- **This form will not satisfy the requirement of 37 CFR 1.97(e).** The present statement is filed under 37 CFR 1.704(d) and will not substitute for compliance with any of the requirements of 37 CFR 1.97 and 1.98. For an information disclosure statement to comply with 37 CFR 1.97(c) or (d), the information disclosure statement must be accompanied by a statement under 37 CFR 1.97(e) notwithstanding any statement filed under 37 CFR 1.704(d).
- The present form (PTO/SB/133) should be filed concurrently with the information disclosure statement to derive benefit under 37 CFR 1.704(d).

Signature	/Emma K. Holland/	Date	September 22, 2023
Typed or Printed Name	Emma K. Holland	Practitioner Registration Number	79,947

***Note**: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature. If necessary, submit multiple forms for more than one signature, see below*.*

☑ *Total of 1 forms are submitted.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Patent Application Fee Transmittal

Application Number:	16839862
Filing Date:	03-Apr-2020
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Filer:	Emma Holland/Paula Watson
Attorney Docket Number:	123450-013001

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Miscellaneous:				
SUBMISSION- INFORMATION DISCLOSURE STMT	1806	1	260	260
		Total in USD ($)		**260**

Electronic Acknowledgement Receipt

EFS ID:	48627488
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Emma Holland/Paula Watson
Filer Authorized By:	Emma Holland
Attorney Docket Number:	123450-013001
Receipt Date:	22-SEP-2023
Filing Date:	03-APR-2020
Time Stamp:	15:22:51
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$260
RAM confirmation Number	E20239LF23389204
Deposit Account	604406
Authorized User	Paula Watson
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.19 (Document supply fees) 37 CFR 1.21 (Miscellaneous fees and charges)	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Information Disclosure Statement (IDS) Form (SB08)	123450-013001_0_IDS_SB08_20230921160833.pdf	1331613 121a2f4a105ad2087ff2ab81096de40ce5e80461	no	4
Warnings:					
Information:					
A U.S. Patent Number Citation or a U.S. Publication Number Citation is required in the Information Disclosure Statement (IDS) form for autoloading of data into USPTO systems. You may remove the form to add the required data in order to correct the Informational Message if you are citing U.S. References. If you chose not to include U.S. References, the image of the form will be processed and be made available within the Image File Wrapper (IFW) system. However, no data will be extracted from this form. Any additional data such as Foreign Patent Documents or Non Patent Literature will be manually reviewed and keyed into USPTO systems.					
2	Foreign Reference	WO2018116842A1_EFS.pdf	9146757 092a91ca88659e480625b14a2ca00c1d0a10b9eb	no	41
Warnings:					
Information:					
3	Letter specifying the conditions for filing under 37 CFR 1.97	123450-013001_Trransmittal-SIDS_9-22-2023.pdf	111945 acddcc4649e1d1dccbe446cf6580c107b4a761e4	no	2
Warnings:					
Information:					
4	Patent Term Adjustment Statement under 37 CFR 1.704(d) filed with an IDS	123450_013001_SafeHarbor_SIDS_09-22-2023.pdf	233130 da1d13cfb086799651f6033d12d9c717f094cf12	no	2
Warnings:					
Information:					
5	Fee Worksheet (SB06)	fee-info.pdf	38314 375b2a4507cdd7e35b7768bd1e2ab779d6dfaf3f	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	10861759		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

93724 7590 08/04/2023

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

EXAMINER	
CHU, YONG LIANG	

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
08/04/2023	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Office Action Summary	Application No. 16/839,862	Applicant(s) DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 2 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 04/28/2023.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☐ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☑ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1 and 3-14 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☑ Claim(s) 1 and 3-14 is/are allowed.

7) ☐ Claim(s) _____ is/are rejected.

8) ☑ Claim(s) 2 is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☑ The drawing(s) filed on 04/03/2020 is/are: a)☑ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00127

DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission on 04/28/2023 has been entered. Upon entering the submission, claim 1 has been amended. Claim 2 is cancelled. Claims 1, and 3-14 are pending, and are under examination on the merits.

Information Disclosure Statements

Applicants' Information Disclosure Statements, filed on 03/31/2023 and 05/16/2023, have been considered. Please refer to Applicant's copies of the PTO-1449 submitted herewith.

Response to RCE Submission

Object to Amendment

Applicant cancels claim 2. However, the amendment is objected to for non-compliance with MPEP§714(c), which states "In the claim listing, the status of every claim must be indicated after its claim number by using one of the following identifiers in a parenthetical expression: (Original), (Currently amended), (Canceled), (Withdrawn), (Previously presented), (New), and (Not entered)." Claim 2 indicates as "Cancelled". No claim texts shall be presented for any claim in the claim listing with the status of "canceled"." See MPEP§714(c)(4)(i). Appropriate correction is required.

Claim rejection under 35 U.S.C. §103(a)

Applicant's amendment and arguments have been fully considered. Specifically,

Applicant amends claim 1 by further limiting the first sorbent material used in the claimed method includes one or more of carbonaceous char, activated carbon, and reactivated carbon. In addition, Applicant argues that Wang teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS because Wang describes a decrease in the Kd value of the sludge that was burned at 300 °C for 1 hour compared to sludge that was not burned. Therefore, Wang discourages using a sorbent material including one or more of carbonaceous char, activated carbon, and reactivated carbon. Applicant's amendment and arguments are sufficient to overcome the rejection. The rejection is hereby **withdrawn**.

Reasons for Allowance

The present invention is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, and reactivated carbon according to claim 1. Applicant's specification [0050-0051] describes EXAMPLE 1 of producing the first sorbent material by reactivating exhausted or used absorbing filter for treating groundwater with elevated calcium level under elevated temperatures with steam in a rotating kiln to restore its surface activity and break down any organic compounds.

The closest prior art is Wang *et al.*, *Chemosphere*, (**2015)**, v.131, p.178-183. Wang *et al.* discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up

to 100 mM comprising a step of mixing 1g of sludge B1 (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration, see "2.3 *Aqueous solution composition*" at page 180. However, Wang *et al.* does not teach about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof., nor the sorbent material used in the claimed method includes one or more of carbonaceous char, activated carbon, and reactivated carbon. In addition, Wang teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS because Wang describes a decrease in the Kd value of the sludge that was burned at 300 °C for 1 hour compared to sludge that was not burned. Therefore, Wang discourages using a sorbent material including one or more of carbonaceous char, activated carbon, and reactivated carbon.
Therefore, Wang *et al.* neither anticipate nor render instant claims obvious because there is no motivation disclosed by Wang for further modification in the reference. Therefore, claims 1, and 3-14 are allowed.

Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Conclusions

- Claims 1, and 3-14 are allowed.
- The amendment of canceled claim 2 is objected to.

Prosecution on the merits is closed in accordance with the practice under *Ex parte Quayle*, 25 USPQ 74, 453 O.G. 213, (Comm'r Pat. 1935).

A shortened statutory period for reply to this action is set to expire **TWO MONTHS** from the mailing date of this letter.

Telephone Inquiry

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Yong Chu, whose telephone number is (571)272-5759. The examiner can normally be reached on M-F 8:30am-5:00pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Bryan D. Ripa can be reached on 571-270-7875. The fax phone number for the organization where this application or proceeding is assigned is (571) 273-8300.

/YONG L CHU/
Primary Examiner, Art Unit 1731

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☑ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/25/2022	10/24/2022	07/21/2023						
	1	✓	✓	=						
	2	✓	✓	-						
	3	✓	✓	=						
	4	✓	✓	=						
	5	✓	✓	=						
	6	✓	✓	=						
	7	✓	✓	=						
	8	✓	✓	=						
	9	✓	✓	=						
	10	✓	✓	=						
	11	✓	✓	=						
	12	✓	✓	=						
	13	✓	✓	=						

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00132

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J20/20; 041; 3028	02/25/2022	YC
B01D53/02	02/25/2022	YC
C02F1/283	02/25/2022	YC

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00133

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

Search Notes		
Search Notes	**Date**	**Examiner**
EAST	02/25/2022	YC
STN	02/25/2022	YC
Patent global Dossier of 16/839,862	02/25/2022	YC
Google scholar search--PFAS removal from wastewater Ca2+ Mg2+--02252022	02/25/2022	YC
The PCT search report "Y" references are not good prior art. Much better prior art references are found and cited by this examiner. A lot of search time spent	02/25/2022	YC
ODP search (PALM inventor name and assignee, EAST and STN search)	02/25/2022	YC
PE2E-search	10/24/2022	YC
ODP search (inventor name and assignee PE2E-search)	07/21/2023	YC

Interference Search			
US Class/CPC Symbol	**US Subclass/CPC Group**	**Date**	**Examiner**
See search report		07/21/2023	YC

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00134

Bibliographic Data

Application No: 16/839,862

Foreign Priority claimed: ○ Yes ◉ No

35 USC 119 (a-d) conditions met: ☐ Yes ☐ No ☐ Met After Allowance

Verified and Acknowledged: /YONG L CHU/ Examiner's Signature | Initials

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

FILING or 371(c) DATE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
04/03/2020	502	1731	123450-013001
RULE			

APPLICANTS

CALGON CARBON CORPORATION, Moon Township, PA, UNITED STATES

INVENTORS

Rebecca L. DISTEFANO, Oakdale, PA, UNITED STATES

Richard A. MIMNA, Oakdale, PA, UNITED STATES

CONTINUING DATA

This application has PRO of 62828790 04/03/2019

FOREIGN APPLICATIONS

IF REQUIRED, FOREIGN LICENSE GRANTED**

04/13/2020

STATE OR COUNTRY

UNITED STATES

ADDRESS

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348
UNITED STATES

FILING FEE RECEIVED

$1,880

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. DISTEFANO
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20160102019	A1	2016-04-14	Pollack et al.	

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	Attorney Docket Number	123450-013001

	1	BARRIOS-BERMUDEZ et al. "Fe-Cu Doped Multiwalled Carbon Nanotubes for Fenton-like Degradation of Paracetamol under Mild Conditions" April 14, 2020, Nanomaterials 10(749):1-18	
	2	SONTHEIMER et al. "Evaluation Methods Utilizing Aqueous Solutions, In Activated Carbon For Water Treatment" 1988, DVGW-Forschungsstelle Second Edition 100-105	

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EXAMINER SIGNATURE

Examiner Signature	/YONG L CHU/	Date Considered	07/20/2023

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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Norit Americas, Inc. v. Calgon Carbon Corporation
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PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L1	1	"20140112856".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:57 PM
L2	1	"20140336568".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:58 PM
L3	1	"20200179902".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L4	1	"20080283446".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L5	1	"20190270081".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L6	118	((("CALGON") near3 ("CARBON") near3 ("CORPORATION"))).AS,AANM.	(USPAT)	OR	ON	ON	2023/07/21 10:32 AM
L7	53	((("DISTEFANO") near3 ("Rebecca")) OR (("MIMNA") near3 ("Richard"))).INV.	(US-PGPUB; USPAT; USOCR; EPO; JPO; DERWENT)	OR	ON	ON	2023/07/21 10:32 AM
L8	17	L7 AND L6	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:32 AM
L9	50	(B01J20/20.cpc. OR B01J20/041.cpc. OR B01J20/3028.cpc.) AND B01D53/02.cpc. AND C02F1/283.cpc.	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:39 AM
L10	1	L9 AND (perfluoroalkyl OR polyfluoroalkyl OR PFAS)	(US-PGPUB; USPAT)	OR	ON	ON	2023/07/21 10:41 AM

PE2E SEARCH - Search History (Interference)

There are no Interference searches to show.

Exhibit 1042
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00138

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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	1	108940191	CN	A	2018-12-07	Univ Northwest A&F	With English abstract	X

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	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

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Examiner Signature	/YONG L CHU/	Date Considered	07/20/2023

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00140

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (01-22)
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	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

	1	BARRIOS-BERMUDEZ et al. "Fe-Cu Doped Multiwalled Carbon Nanotubes for Fenton-like Degradation of Paracetamol under Mild Conditions" April 14, 2020, Nanomaterials 10(749):1-18	
	2	SONTHEIMER et al. "Evaluation Methods Utilizing Aqueous Solutions, In Activated Carbon For Water Treatment" 1988, DVGW-Forschungsstelle Second Edition 100-105	

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Examiner Signature		Date Considered	

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	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Emma K. Holland/	Date (YYYY-MM-DD)	2023-05-16
Name/Print	Emma K. Holland	Registration Number	79947

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00144

Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(b)(4) / Fee Authorization

This Information Disclosure Statement is submitted under 37 C.F.R. §1.97(b)(4) before the mailing of a first Office Action on the merits after the filing of a Request for Continued Examination. Therefore, applicant holds that no fee is due. However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission or credit any overpayment to Deposit Account No. 60-4406.

Respectfully submitted,

DLA PIPER LLP (US)

/Emma Holland/

Emma Holland
Reg. No. 79,947

DLA PIPER LLP (US)
1650 Market Street, Suite 5000
Philadelphia, PA 19103-7348
Telephone: (215) 656-3300

Date: May 16, 2023

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**05/16/2023 06:52:15 PM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	62101109	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Emma Holland

Documents

TOTAL DOCUMENTS: 4

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
123450-013001 Transmittal for SIDS_5-16-2023.pdf	1	Letter specifying the conditions for filing under 37 CFR 1.97	103 KB
123450-013001 SB08_5-16-2023.pdf	4	Information Disclosure Statement (IDS) Form (SB08)	1243 KB
Sontheimer100_NPL.PDF	8	Non Patent Literature	1005 KB
BARRIOS_BERMUDEZ1_NPL.pdf	18	Non Patent Literature	1583 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450-013001 Transmittal for SIDS_5-16-2023.pdf	1DE9FAF16B1146B8E5508811851B18BF9EF396CC81F2562AD62C5B6A16EEFBFEDAFB41574B78D8A682D63BA19983DE2DDB70F8A316DBCE5EB812553C4A09FC00
123450-013001 SB08_5-16-2023.pdf	1F6EA08419EB10AC442582A783501017D63E06FE88D5A8EC29C8A7572F058ED281F10ECE79FACDAE44A83F61532216B61CD64D081AC962D568127C88E3FC47BE
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BARRIOS_BERMUDEZ1_NPL.pdf	750822DF046D20FA6EEAC626A08B82F61B1F1A66E010697ED52CCFFD84AE40CF3BE4F4DF122C02A0F2B1CECA7BF98D51EE108FBC7D54CE903D8E988EC4A6470D

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc code: RCEX
Doc description: Request for Continued Examination (RCE)

PTO/SB/30EFS (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

REQUEST FOR CONTINUED EXAMINATION(RCE)TRANSMITTAL
(Submitted Only via EFS-Web)

Application Number	16/839,862	Filing Date	2020-04-03	Docket Number (if applicable)	123450-013001	Art Unit	1731
First Named Inventor	Rebecca L. DISTEFANO			Examiner Name	YONG LIANG CHU		

This is a Request for Continued Examination (RCE) under 37 CFR 1.114 of the above-identified application.
Request for Continued Examination (RCE) practice under 37 CFR 1.114 does not apply to any utility or plant application filed prior to June 8, 1995, or to any design application. The Instruction Sheet for this form is located at WWW.USPTO.GOV

SUBMISSION REQUIRED UNDER 37 CFR 1.114

Note: If the RCE is proper, any previously filed unentered amendments and amendments enclosed with the RCE will be entered in the order in which they were filed unless applicant instructs otherwise. If applicant does not wish to have any previously filed unentered amendment(s) entered, applicant must request non-entry of such amendment(s).

☒ Previously submitted. If a final Office action is outstanding, any amendments filed after the final Office action may be considered as a submission even if this box is not checked.

☐ Consider the arguments in the Appeal Brief or Reply Brief previously filed on _____

☐ Other _____

☒ Enclosed

☒ Amendment/Reply

☐ Information Disclosure Statement (IDS)

☐ Affidavit(s)/ Declaration(s)

☒ Other PETITION FOR EXTENSION OF TIME UNDER 37 CFR 1.136(a)

MISCELLANEOUS

☐ Suspension of action on the above-identified application is requested under 37 CFR 1.103(c) for a period of months _____
(Period of suspension shall not exceed 3 months; Fee under 37 CFR 1.17(i) required)

☐ Other _____

FEES

☒ **The RCE fee under 37 CFR 1.17(e) is required by 37 CFR 1.114 when the RCE is filed.**
The Director is hereby authorized to charge any underpayment of fees, or credit any overpayments, to Deposit Account No 604406

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT REQUIRED

X Patent Practitioner Signature

Applicant Signature

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00148

PTO/SB/30EFS (01-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Signature of Registered U.S. Patent Practitioner			
Signature	/Douglas Kayuha/	Date (YYYY-MM-DD)	2023-04-28
Name	Douglas Kayuha	Registration Number	79855

This collection of information is required by 37 CFR 1.114. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these records.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00150

PTO/AIA/22 (12-22)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

PETITION FOR EXTENSION OF TIME UNDER 37 CFR 1.136(a)

Docket Number (Optional): 123450-013001

Application Number: 16/839,862

Filed: April 3, 2020

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Art Unit: 1731

Examiner: YONG LIANG CHU

This is a request under the provisions of 37 CFR 1.136(a) to extend the period for filing a reply in the above-identified application.

The requested extension and fee are as follows (check time period desired and enter the appropriate fee below):

		Fee	Small Entity Fee	Micro Entity Fee	
☐	One month (37 CFR 1.17(a)(1))	$220	$88	$44	$
☐	Two months (37 CFR 1.17(a)(2))	$640	$256	$128	$
☑	Three months (37 CFR 1.17(a)(3))	$1,480	$592	$296	$ 1480
☐	Four months (37 CFR 1.17(a)(4))	$2,320	$928	$464	$
☐	Five months (37 CFR 1.17(a)(5))	$3,160	$1,264	$632	$

☐ Applicant asserts small entity status. See 37 CFR 1.27.

☐ Applicant certifies micro entity status. See 37 CFR 1.29.
Form PTO/SB/15A or B or equivalent must either be enclosed or have been submitted previously.

☐ A check in the amount of the fee is enclosed.

☐ Payment by credit card. Form PTO-2038 is attached.

☐ The Director has already been authorized to charge fees in this application to a Deposit Account.

☑ The Director is hereby authorized to charge any fees which may be required, or credit any overpayment, to Deposit Account Number 60-4406.

☑ Payment made via USPTO's patent electronic filing system (Patent Center or EFS-Web).

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

I am the

☐ applicant.

☑ attorney or agent of record. Registration number 79855.

☐ attorney or agent acting under 37 CFR 1.34. Registration number _____.

/Douglas Kayuha/ — Signature

April 28, 2023 — Date

Douglas Kayuha — Typed or printed name

(215) 656-3300 — Telephone Number

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. Submit multiple forms if more than one signature is required, see below*.

☑ * Total of 1 forms are submitted.

A Federal agency may not conduct or sponsor, and a person is not required to respond to, nor shall a person be subject to a penalty for failure to comply with an information collection subject to the requirements of the Paperwork Reduction Act of 1995, unless the information collection has a currently valid OMB Control Number. The OMB Control Number for this information collection is 0651-0031. Public burden for this form is estimated to average 6 minutes per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the information collection. Send comments regarding this burden estimate or any other aspect of this information collection, including suggestions for reducing this burden to the Chief Administrative Officer, United States Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450 or email InformationCollection@uspto.gov. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS**. If filing this completed form by mail, send to: **Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. The United States Patent and Trademark Office (USPTO) collects the information in this record under authority of 35 U.S.C. 2. The USPTO's system of records is used to manage all applicant and owner information including name, citizenship, residence, post office address, and other information with respect to inventors and their legal representatives pertaining to the applicant's/owner's activities in connection with the invention for which a patent is sought or has been granted. The applicable Privacy Act System of Records Notice for the information collected in this form is COMMERCE/PAT-TM-7 Patent Application Files, available in the Federal Register at 78 FR 19243 (March 29, 2013). https://www.govinfo.gov/content/pkg/FR-2013-03-29/pdf/2013-07341.pdf

Routine uses of the information in this record may include disclosure to: 1) law enforcement, in the event that the system of records indicates a violation or potential violation of law; 2) a Federal, state, local, or international agency, in response to its request; 3) a contractor of the USPTO having need for the information in order to perform a contract; 4) the Department of Justice for determination of whether the Freedom of Information Act (FOIA) requires disclosure of the record; 5) a Member of Congress submitting a request involving an individual to whom the record pertains, when the individual has requested the Member's assistance with respect to the subject matter of the record; 6) a court, magistrate, or administrative tribunal, in the course of presenting evidence, including disclosures to opposing counsel in the course of settlement negotiations; 7) the Administrator, General Services Administration (GSA), or their designee, during an inspection of records conducted by GSA under authority of 44 U.S.C. 2904 and 2906, in accordance with the GSA regulations and any other relevant (i.e., GSA or Commerce) directive, where such disclosure shall not be used to make determinations about individuals; 8) another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)); 9) the Office of Personnel Management (OPM) for personnel research purposes; and 9) the Office of Management and Budget (OMB) for legislative coordination and clearance.

If you do not furnish the information requested on this form, the USPTO may not be able to process and/or examine your submission, which may result in termination of proceedings, abandonment of the application, and/or expiration of the patent.

Additional Uses

Additional USPTO uses of the information in this record may include disclosure to: 1) the International Bureau of the World Intellectual Property Organization, if the record is related to an international application filed under the Patent Cooperation Treaty; 2) the public i) after publication of the application pursuant to 35 U.S.C. 122(b), ii) after issuance of a patent pursuant to 35 U.S.C. 151, iii) if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections, or an issued patent, or iv) without publication of the application or patent under the specific circumstances provided for by 37 CFR 1.14(a)(1)(v)-(vii); and/or 3) the National Archives and Records Administration, for inspection of records.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**04/28/2023 04:10:30 PM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	62006441	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Douglas Kayuha

Documents

TOTAL DOCUMENTS: 5

DOCUMENT		PAGES	DESCRIPTION	SIZE (KB)
123450-013001_Response after Advisory Action-RCE.pdf		6	-	188 KB
123450-013001_Response after Advisory Action-RCE-AMSB.pdf	(1-1)	1	Amendment Submitted/Entered with Filing of Continued Prosecution Application (CPA)/Request for Continued Examination(RCE)	103 KB
123450-013001_Response after Advisory Action-RCE-CLM.pdf	(2-3)	2	Claims	107 KB
123450-013001_Response after Advisory Action-RCE-	(4-6)	3	Applicant Arguments/Remarks Made in an Amendment	178 KB

REM.pdf			
123450-013001_Extension.pdf	2	Extension of Time	272 KB
123450-013001_RCE.pdf	3	Request for Continued Examination (RCE)	1631 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450-013001_Response after Advisory Action-RCE.pdf	0F1EDA927D11D908C7CA851765DAF3442082784269BCA48EBCFC54C6657E490E21C103354A14D2BCE2E45CE80306DC29B95CDA22E1332C0853EB3BEB11E40318
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123450-013001_RCE.pdf	B6C34AB6F1F366FCBA55DC8EA02FB41C51472146A41554FDD21ED20758AF15A547FB8543BF4A80CFFE621BDFE663B5C34B65558D5523DEFAFF8A9B6558E7B24B

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as

described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1731
Confirmation No.	:	5111
Examiner	:	CHU, YONG LIANG

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RESPONSE TO ADVISORY ACTION

Mail Stop RCE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This paper is filed in response to the Advisory Action mailed March 3, 2023. A Request for Continued Examination (RCE) is being filed concurrently herewith, along with the requisite fees. The Office Action sets forth a period for reply expiring 6 months from the mailing date of the Final Rejection. Accordingly, this response is timely filed.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **4** of this paper.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00156

AMENDMENTS TO THE CLAIMS

The current listing of the claims replaces all prior versions and listings of the claims in the present application.

1. (Currently Amended) A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:
   providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and
   contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, and reactivated carbon.
2. (Canceled) ~~The method of claim 1, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, reactivated carbon, and carbon black~~.
3. (Original) The method of claim 2, wherein the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.
4. (Original) The method of claim 2, wherein the first sorbent material is reactivated carbon.
5. (Original) The method of claim 2, wherein the first sorbent material is a reagglomerated activated carbon.
6. (Original) The method of claim 1, further comprising:
   providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and

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contacting the second sorbent material with the liquid or gas containing the PFAS.

7. (Original) The method of claim 1, wherein the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium, an oxide of strontium, or an oxide of barium.
8. (Original) The method of claim 7, wherein the first sorbent material includes one or more of MgO or CaO.
9. (Previously Presented) The method of claim 1, wherein the salt, oxide, or hydroxide of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation, chemical vapor deposition, or physical vapor deposition.
10. (Previously Presented) The method of claim 1, wherein about 1 wt.% to about 20 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
11. (Previously Presented) The method of claim 10, wherein about 2 wt.% to about 8 wt.% of the first sorbent material comprises salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
12. (Previously Presented) The method of claim 1, wherein the first sorbent material is a reactivated carbon comprising oxides of calcium, magnesium, sodium, potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the oxides of calcium, magnesium, sodium, potassium and zinc.
13. (Previously Presented) The method of claim 12, wherein the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the oxides of calcium, magnesium, sodium, and zinc.
14. (Previously Presented) The method of claim 1, wherein the first sorbent material includes one or more of a carbonate of magnesium, a carbonate of calcium, a carbonate of strontium, or a carbonate of barium.

REMARKS

Applicant would like to thank the Examiner for the careful consideration given to the present application. Claims 1-14 are pending. The Office has rejected claims 1-14. Claim 1 has been amended and claim 2 has been canceled. The amendments to claim 1 include adding the material of canceled claim 2. Therefore, Applicant submits that no new matter has been added.

Rejection under 35 U.S.C. § 103

In the Advisory Action dated March 3, 2023, the Office states that claims 1-13 are allegedly obvious over Wang *et al., Chemosphere* ("Wang") in view of Appleman *et al., Water Research* ("Appleman"). In response, Applicant amends claim 1, cancels claim 2, and submits the following remarks. Claim 1 has been included below for convenience:

> A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:
> providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and
> contacting the first sorbent material with a liquid or gas containing the PFAS, wherein
> ***the first sorbent material includes one or more of carbonaceous char, activated carbon, and reactivated carbon***.
> ***(Emphasis added)***

Notably, claim 1 requires a method of removing PFAS from liquid or gas comprising providing a first sorbent material including "one or more of carbonaceous char, activated carbon, and reactivated carbon." *Wang* is directed towards a method of adsorbing PFAS on wastewater sludge through the use of cations. *Wang* at Abstract. *Wang* discloses the use of a sludge burned in an oven under 300° C for 1 hour to partially remove organic matter. *Wang* at page 179 section 2.2. However, *Wang* further describes a decrease in the K_d value of the sludge that was burned at 300° C for 1 hour compared to sludge that was not burned. *Wang* teaches "In this study, the surface area of sludge B was 2.5 m^2g^{-1} before thermal treatment and 16.5 m^2g^{-1} of sludge B1 after thermal treatment. However, even the surface area increase, the K_d value still decreased.

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These data strongly suggest that sorption to organic matter is more important for anionic PFASs than adsorption to mineral surfaces." *Wang* at page 182 section 3.4. In fact, *Wang* teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS. Furthermore, *Wang* fails to teach or disclose the use of a sorbent material including activated carbon or reactivated carbon for the removal of PFAS from liquid or gas. Therefore, one of skill in the art would not be motivated by *Wang* to method of removing PFAS from liquid or gas comprising providing a first sorbent material including one or more of carbonaceous char, activated carbon, and reactivated carbon.

Appleman is directed towards the removal of PFAS from water using activated carbon treatment. *Appleman* at abstract. *Appleman* is directed towards methods of removing PFAS from drinking water sources and wastewater sources using specific treatment processes such as the use of anion exchange, granular activated carbon, nanofiltration, and reverse osmosis. *Appleman* at page 248 section 2.1. As stated above, *Wang* teaches away from the use of any thermal treatment on a sorbent material for the removal of PFAS. Therefore, *Wang* teaches away from the teachings of *Appleman,* and the combination of the references is improper.

Additionally, *Wang* is directed towards the removal of PFAS from wastewater in wastewater treatment plants using sludge present in the wastewater. *Wang* at Abstract and page 179 section 1. Therefore, the teachings of *Wang* are not applicable to the teaching of *Appleman* and the methods of removing PFAS from drinking water sources and wastewater sources using specific treatment processes such as the use of anion exchange, granular activated carbon, nanofiltration, and reverse osmosis. Thus, one of ordinary skill in the art would not be motivated to combine the teachings of *Wang* and *Appleman*. Additionally, *Appleman* fails to teach a method of removing PFAS from a liquid or gas using a first sorbent material comprising a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium or combination or compound thereof. Therefore, *Appleman* fails to teach or disclose all aspects of claim 1. Thus, Applicant submits that claim 1, and claims 3-14 which are dependent on claim 1, are not obvious over *Wang* or *Appleman* and requests that rejections under 35 U.S.C. § 103 be withdrawn.

All of the stated grounds of rejection have been properly traversed, accommodated, or rendered moot. It is therefore respectfully requested that the Office reconsider and withdraw all

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presently outstanding rejections. There being no other rejections, it is respectfully requested that the current application be allowed and passed to issue.

If the Examiner believes for any reason that personal communication will expedite prosecution of this application, I invite the Examiner to telephone me directly.

AUTHORIZATION

Should the Examiner have any questions or comments, or need any additional information from Applicant's representative, the Examiner is invited to contact the undersigned. The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to Deposit Account No. 60-4406.

Respectfully submitted,
DLA PIPER LLP

/Douglas Kayuha/

Douglas E. Kayuha
Registration No. 79,855

Date: April 28, 2023
DLA Piper LLP
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Norit Americas, Inc. v. Calgon Carbon Corporation
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UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	04/28/2023 04:10:30 PM ET	123450-013001

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	62006441	AUTHORIZED BY	Douglas Kayuha
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	E20234RG12545235	Paula Watson

PRE-AUTHORIZED ACCOUNT	PRE-AUTHORIZED CATEGORY
604406	37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.20 (Post Issuance fees); 37 CFR 1.21 (Miscellaneous fees and charges)

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1253	EXTENSION FOR RESPONSE WITHIN THIRD MONTH	1260.00	1	1260.00
1801	REQUEST FOR CONTINUED EXAMINATION (RCE) - 1ST REQUEST (SEE 37 CFR 1.114)	1360.00	1	1360.00
			TOTAL AMOUNT:	$2,620.00

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (09-11)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 16/839,862	Filing Date 04/03/2020	☐ To be Mailed

ENTITY: ☑ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $100 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $460 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	04/28/2023	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 13	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	*** 3	= 0		x $480 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/TERESA J JACKSON WOODRUFF/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. DISTEFANO
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

	1	

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Exhibit 1042
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☒ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

X See attached certification statement.

X The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Emma K. Holland/	Date (YYYY-MM-DD)	2023-03-31
Name/Print	Emma K. Holland	Registration Number	79,947

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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Norit Americas, Inc. v. Calgon Carbon Corporation
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UNITED STATES
PATENT AND TRADEMARK OFFICE

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ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	03/31/2023 03:52:18 PM ET	123450-013001

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Kevin Malesic
PATENT CENTER #	61850155	AUTHORIZED BY	Emma Holland
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	E20233UF54155442	Kevin Malesic

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1806	SUBMISSION OF AN INFORMATION DISCLOSURE STATEMENT	260.00	1	260.00
			TOTAL AMOUNT:	$260.00

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: PTA.IDS
Document Description: Patent Term Adjustment Stmt Under 37 CFR 1.704(d)

PTO/SB/133 (10-21)

PATENT TERM ADJUSTMENT STATEMENT UNDER 37 CFR 1.704(d)		
	Application Number	16/839,862
	Filing Date	April 3, 2020
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Practitioner Docket No.	123450-013001

APPLICANT HEREBY STATES THE FOLLOWING (please review 37 CFR 1.704(d) before filing this form):

☑ Each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

AND/OR

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INSTRUCTIONS:

- **This form will not satisfy the requirement of 37 CFR 1.97(e).** The present statement is filed under 37 CFR 1.704(d) and will not substitute for compliance with any of the requirements of 37 CFR 1.97 and 1.98. For an information disclosure statement to comply with 37 CFR 1.97(c) or (d), the information disclosure statement must be accompanied by a statement under 37 CFR 1.97(e) notwithstanding any statement filed under 37 CFR 1.704(d).
- The present form (PTO/SB/133) should be filed concurrently with the information disclosure statement to derive benefit under 37 CFR 1.704(d).

Signature	/Emma K. Holland/	Date	March 31, 2023
Typed or Printed Name	Emma K. Holland	Practitioner Registration Number	79,947

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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**03/31/2023 03:52:18 PM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Kevin Malesic
PATENT CENTER #	61850155	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Emma Holland

Documents

TOTAL DOCUMENTS: 4

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
123450_013001_SIDS_Transmittal_31Mar23.pdf	2	Transmittal Letter	22 KB
123450_013001_SafeHarbor_SIDS_31Mar23.pdf	2	Patent Term Adjustment Statement under 37 CFR 1.704(d) filed with an IDS	231 KB
CN108940191AwEngAbs.pdf	13	Foreign Reference	2046 KB
123450_013001_SIDS_31Mar23.pdf	4	Information Disclosure Statement (IDS) Form (SB08)	1020 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450_013001_SIDS_Transmittal_31Mar23.pdf	FA201ED1E0130969BEFC8C0AAAD0B96ED243457333C50217D5FE77C6DB6D85E5ACBFE516FD521D67AE759CBDC97B3FE96A2D07E4C93909DB35B9335EF2136856
123450_013001_SafeHarbor_SIDS_31Mar23.pdf	3B9B7A1811C9853A288272BD676EEA17A26A96707F89F913FADE762F805D9291084B0BA80BC43A4790D4B85D04F53C4012C24489C9EAA96607924CECC5A02AE7
CN108940191AwEngAbs.pdf	31DEF3BFAD43E9F37A996A2C50024C55857172141F24ABC7F9BD620F2A31A290265366B41BAA19CFCB5F8C229AA86877E0BDC354CBC2E888FD0C79C3B27D3AAD
123450_013001_SIDS_31Mar23.pdf	9E5E9CA0E8B122AAE4CF645C93A8ACC3F7DA8A861524070E6873C529D11A272DA281B5EB2D363D3D79D416EF95E4291B6570690B73B90FA33E2C8B8FE92FA3BA

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New International Application Filed with the USPTO as a Receiving Office

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Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

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In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(d) and C.F.R. §1.97(e)(2) / Fee Authorization

This Information Disclosure Statement is being filed under 37 C.F.R. §1.97(d) after the mailing date of a Final Office Action or Notice of Allowance, but before the payment of the issue fee. The undersigned asserts in accordance with 37 CFR 1.97(e)(2), that no item of information contained in the Information Disclosure Statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the Information Disclosure Statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the Information Disclosure Statement under 37 C.F.R. §1.97(e)(2). Accordingly, the Information Disclosure Statement Fee of $260.00 is submitted herewith under 37 C.F.R. § 1.17(p). However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

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Statement under 37 C.F.R. §1.704(d)(i) / Patent Term Adjustment

Applicant states that each item of information contained in the Information Disclosure Statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in § 1.56 (c) more than thirty days prior to the filing of the Information Disclosure Statement. Thus, Applicant holds that the submission of this Statement does not affect any Patent Term Adjustment.

Respectfully submitted,

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Espacenet

CN108940191A Sulfur-nitrogen-doped porous biochar, preparation method and application

Applicants: UNIV NORTHWEST A&F

Inventors: WANG JIANLONG,WANG JING,YANG QINGFENG,YANG WEIXIA,ZHANG LIANG,ZHANG TIANSHU,ZHANG DAOHONG,LI ZHONGHONG

Classifications:

IPC ***B01J20/20; B01J20/28; B01J20/30; B01J27/24; B01J35/10; C02F1/28; C02F1/72;*** *C02F101/20; C02F101/30;*

CPC **B01J20/0274 (CN); B01J20/0285 (CN); B01J20/20 (CN); B01J20/28045 (CN); B01J20/28054 (CN); B01J27/24 (CN); B01J35/10 (CN); C02F1/281 (CN); C02F1/283 (CN); C02F1/725 (CN);** C02F2101/20 (CN); C02F2101/308 (CN);

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Published as: CN108940191A;**CN108940191B**

Sulfur-nitrogen-doped porous biochar, preparation method and application

Abstract

The invention discloses a sulfur-nitrogen-doped porous biochar, a preparation method and an application. The preparation method uses calcium sulfate as a template, potassium oxalate as an activator and bean fibers as a carbon source, and employs calcination to prepare the sulfur-nitrogen-doped porous biochar. The sulfur-nitrogen-doped biochar is an environment-friendly adsorbent for treating heavymetal wastewaters with low cost and high efficiency, adsorption capacities for Cu<2+> and Ni<2+> ions are substantially superior to other biochars. At the same time, the sulfur-nitrogen-doped biocharcontaining adsorbed heavy metals can be subjected to a reduction treatment, and then the reduction-treated sulfur-nitrogen-doped biochar can be further used for catalytic degradation of pollutants inwater to realize recovery and application of the heavy metals.

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(19)中华人民共和国国家知识产权局

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权利要求书1页 说明书5页 附图5页

(54)发明名称

一种硫氮掺杂多孔生物炭、制备方法及应用

(57)摘要

本发明公开了一种硫氮掺杂多孔生物炭、制备方法及应用，包括硫酸钙为模板，草酸钾为活化剂，豆类纤维为碳源，采用煅烧进行硫氮掺杂多孔生物炭的制备。本发明制备的硫氮掺杂生物炭是一种低成本、高效率处理重金属废水的环境友好型吸附剂，对Cu^{2+}和Ni^{2+}离子的吸附能力显著优于其他生物炭，同时通过还原处理可进一步用于水中污染物的催化降解，实现重金属的回收应用。

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1.一种硫氮掺杂多孔生物炭的制备方法，其特征在于，制备原料包括模板、活化剂和碳源，制备方法采用煅烧；

所述的碳源为豆类纤维。

2.根据权利要求1所述的硫氮掺杂多孔生物炭的制备方法，其特征在于，所述的模板为硫酸钙，所述的活化剂为草酸钾；模板、活化剂和碳源的质量比是1:1:1。

3.根据权利要求1或2所述的硫氮掺杂多孔生物炭的制备方法，其特征在于，所述煅烧的温度为800℃，时间为1h。

4.根据权利要求1或2所述的硫氮掺杂多孔生物炭的制备方法，其特征在于，所述的豆类纤维包括黄豆豆渣，黄豆豆渣为黄豆经食品加工后产生的废渣经脱脂后得到的渣体。

5.一种硫氮掺杂多孔生物炭，其特征在于，所述的硫氮掺杂多孔生物炭采用权利要求1-4任一权利要求所述的制备方法制备得到。

6.根据权利要求5所述的硫氮掺杂多孔生物炭，其特征在于，所述的硫氮掺杂多孔生物炭中，氮元素掺杂量为4.56at.%，硫元素掺杂量为10.73at.%，其中吡咯氮占氮元素掺杂量的0.54%，石墨氮占氮元素掺杂量的1.3%。

7.权利要求5或6所述的硫氮掺杂多孔生物炭用于吸附水中重金属离了的应用；

所述的重金属离子为铜离子、镍离子和或/铅离子。

8.一种生物炭-金属纳米颗粒复合催化剂，其特征在于，所述的生物炭为权利要求5或6所述的硫氮掺杂多孔生物炭。

9.根据权利要求8所述的生物炭-金属纳米颗粒复合催化剂，其特征在于，所述的硫氮掺杂多孔生物炭在吸附重金属铜离子和/或镍离子之后经过硼氢化钠进行原位还原，即得生物炭-金属纳米颗粒复合催化剂；

所述的生物炭-金属纳米颗粒复合催化剂用于催化降解镉离子或亚甲基蓝。

10.根据权利要求8或9所述的生物炭-金属纳米颗粒复合催化剂，其特征在于，所述的生物炭-金属纳米颗粒复合催化剂对水体中亚甲基蓝催化降解的条件包括：生物炭-金属纳米颗粒复合催化剂＝50mg/L，过硫酸钾＝0.10g/L，T＝25℃；

所述生物炭-金属纳米颗粒复合催化剂对水体中高价铬离子催化降解的条件包括：生物炭-金属纳米颗粒复合催化剂＝50mg/L，T＝25℃，甲酸＝0.1M。

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一种硫氮掺杂多孔生物炭、制备方法及应用

技术领域

[0001] 本发明属生物炭制备领域，具体涉及一种硫氮掺杂多孔生物炭、制备方法及应用。

背景技术

[0002] 生物炭是一种难溶的、稳定的、高度芳香化的、富含碳素的黑色蓬松状固态物质，是属于黑炭范畴的一种，组成元素主要是碳、氢、氧、氮等，含碳量在70％以上。生物炭具有致密的微孔结构和巨大的比表面积，吸附能力强，能吸附铅、铬、汞、镉、铜、锌等重金属。除此之外，生物炭还具有生产成本低、生态安全、无污染、可大面积推广等显著特点。这些显著特点，使其可作为一种高效、廉价的重金属离子吸附剂。

[0003] 豆渣是生产豆奶或豆腐过程中的副产品，具有蛋白质，脂肪，钙，磷，铁等多种营养物质。中国是豆腐生产的发源地，具有悠久的豆腐生产历史，豆腐的生产、销售量都较大，相应的豆渣产量也很大。除少部分豆渣供食用外，主要用作饲料或肥料使用，绝大部分并未被得到良好的开发利用。

发明内容

[0004] 本发明采用的一种硫氮掺杂多孔生物炭的制备方法，采用硫酸钙作硬模板，草酸钾作活化剂将食品废料脱脂大豆豆渣作为碳源进行800℃高温煅烧得到硫氮掺杂多孔生物炭。该制备方法简单，不需要添加其他化学物质或有机溶剂，制备过程环境友好，易于工业化生产。所得生物炭产物对重金属铜和镍具有良好的选择和吸附能力，且在吸附重金属离子后通过硼氢化钠原位还原可进一步应用于水体中污染物的催化降解，实现重金属的回收再利用。

[0005] 为达到上述技术效果，本发明采取的技术方案为：

[0006] 一种硫氮掺杂多孔生物炭的制备方法，制备原料包括模板、活化剂和碳源，制备方法采用煅烧；所述的碳源为豆类纤维。

[0007] 可选的，所述的模板为硫酸钙，所述的活化剂为草酸钾；模板、活化剂和碳源的质量比是1:1:1。

[0008] 可选的，所述煅烧的温度为800℃，时间为1h。

[0009] 可选的，所述的豆类纤维包括黄豆豆渣，黄豆豆渣为黄豆经食品加工后产生的废渣经脱脂后得到的渣体。

[0010] 一种硫氮掺杂多孔生物炭，所述的硫氮掺杂多孔生物炭采用本发明所述的制备方法制备得到。

[0011] 可选的，所述的硫氮掺杂多孔生物炭中，氮元素掺杂量为4.56at.％，硫元素掺杂量为10.73at.％，其中吡咯氮占氮元素掺杂量的0.54％，石墨氮占氮元素掺杂量的1.3％。

[0012] 所述的硫氮掺杂多孔生物炭用于吸附水中重金属离子的应用；

[0013] 所述的重金属离子为铜离子、镍离子和或/铅离子，对Cu^{2+}吸附量可达1366.67mg/g，对Ni^{2+}吸附量可达1250.21mg/g，对Pb^{2+}吸附量可达619.23mg/g。

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[0014] 一种生物炭-金属纳米颗粒复合催化剂，所述的生物炭为本发明所述的硫氮掺杂多孔生物炭。

[0015] 可选的，所述的硫氮掺杂多孔生物炭在吸附重金属铜离子和/或镍离子之后经过硼氢化钠进行原位还原，即得生物炭-金属纳米颗粒复合催化剂；

[0016] 所述的生物炭-金属纳米颗粒复合催化剂用于催化降解镉离子或亚甲基蓝。

[0017] 可选的，所述的生物炭-金属纳米颗粒复合催化剂对水体中亚甲基蓝催化降解的条件包括：生物炭-金属纳米颗粒复合催化剂＝50mg/L，过硫酸钾＝0.10g/L，T＝25℃；

[0018] 所述生物炭-金属纳米颗粒复合催化剂对水体中高价铬离子催化降解的条件包括：生物炭-金属纳米颗粒复合催化剂＝50mg/L，T＝25℃，甲酸＝0.1M。

[0019] 由于采用上述技术方案，具有以下有益效果：

[0020] (1)操作方法简单。本发明提供的硫氮掺杂多孔生物炭的制备方法制备方法简单，不需要添加其他化学物质或有机溶剂，制备过程环境友好，且不需要复杂的化学反应、特殊设备和严酷反应条件。其作用条件温和、无二次污染。

[0021] (2)高选择性。本发明提供的硫氮掺杂多孔生物炭结构为多孔海绵状，且具有较高的氮硫掺杂量，因而具有较高的重金属离子选择吸附能力，尤其对重金属铜和镍具有较强的选择性。

[0022] (3)高吸附性。本发明提供的硫氮掺杂多孔生物炭对重金属离子铜、镍、铅具有优异的吸附能力。

[0023] (4)低成本。该发明所用试剂硫酸钙，草酸钾，以及以食品废料脱脂大豆豆渣作为碳源所得氮硫掺杂多孔生物炭成本低($0.041/g)，适用于工业化生产和实际应用。

[0024] (5)进一步重金属的回收利用。本发明所得氮硫掺杂多孔生物炭在吸附重金属后可经过硼氢化钠进行原位还原，烘干所得产物可作为生物炭-金属纳米颗粒复合催化剂，并应用于水溶液中污染物的催化降解。

附图说明

[0025] 图1为本发明的硫氮掺杂多孔生物炭的电镜图；a为大豆豆渣800℃烧结后的不同放大倍数的电镜图，b为掺杂硫酸钙和草酸钾后600℃烧结后的不同放大倍数的电镜图，c为掺杂硫酸钙和草酸钾后700℃烧结后的不同放大倍数的电镜图，d为掺杂硫酸钙和草酸钾后800℃烧结后的不同放大倍数的电镜图；

[0026] 图2为实施例2的结果图；

[0027] 图3为实施例3的结果图；

[0028] 图4为实施例4的结果图；

[0029] 图5为实施例5的结果图；

[0030] 以下结合说明书附图和具体实施方式对本发明做具体说明。

具体实施方式

[0031] 经研究证明，大豆中有一部分营养成分残留在豆渣中，一般豆渣含水份85％，蛋白质3.0％，脂肪0.5％，碳水化合物(纤维素、多糖等)8.0％，此外，还含有钙、磷、铁等矿物质。将豆渣回收并利用是满足循环经济、变废为宝的处理处置方法。目前，将豆渣应用于重金属

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吸附剂的研究主要集中于直接使用或经过物理或化学方法进行表明处理来对其改性，使得生物炭具有更好的孔隙结构，更大的比表面积和更多的官能团来提升吸附性能。然而，直接使用豆渣由于功能基团的缺失和比表面积的不足往往导致较低的重金属吸附量，抑制其在实际废水处理中的应用。因此，借助有效的物理改性或化学改性(酸碱氧化，有机物和无机物负载)进行表面处理可有效增强其作为一种低成本且具有环境效益的新型生物吸附剂方面的研究意义。然而该类方法主要面临合成成本高、无法大规模制备以及仅限于实验室操作等缺陷。因此开发一种简便，低成本且可大规模合成的生物吸附剂的方法显得尤为重要。

[0032] 本发明制备的生物炭与传统生物炭相比，具有较高的重金属离子选择性吸附能力，并且吸附能力相比一般生物炭性能优异，是一种低成本、高效率处理重金属废水的环境友好型吸附剂。该生物炭在吸附重金属后可通过还原处理可进一步用于水中污染物的催化降解，并可循环多次使用，实现重金属的回收应用，适合应用于实际污水处理。

[0033] 本发明的工作原理为：将硫酸钙作硬模板，草酸钾作活化剂，以豆类纤维作为碳源进行高温煅烧条件下得到杂原子掺杂的生物炭。最好的，豆类纤维选用食品废料脱脂大豆豆渣，由于大豆豆渣本身的具有蛋白质等含氮物质，并且高温加热条件下硫酸钙高温分解产生的SO_2气体氛围，使得所得生物炭具有较高的氮硫掺杂量，同时产生致密的多孔结构。根据Lewis酸碱理论，由于含硫物质可作为Lewis碱，可与Lewis酸特性的重金属发生特异性结合，并且对于不同的重金属具有不同的结合能力，从而使得该氮硫掺杂的多孔生物炭具有较好的金属离子选择性吸附能力。同时由于其较大的比表面积和表面的含氧基团作用，使得该生物炭对重金属铜、镍、铅具有较高的吸附能力。进一步的，将吸附重金属后的生物炭通过硼氢化钠进行原位还原，所得产物可作为生物炭-金属纳米颗粒复合催化剂进一步应用于水溶液中污染物的催化降解，可用于水中污染物的催化降解，并可循环多次使用，实现重金属的回收应用，适合应用于实际污水处理。

[0034] 具体的制备过程包括，硫酸钙，草酸钾和脱脂大豆豆渣以质量比为1:1:1比例进行混合，煅烧条件为：氩气条件下以5℃/min升温速度升温至800℃，加热时间1h，并自然冷却至室温，所得产物用稀盐酸洗涤三次，60℃烘干过夜得到最终产物。

[0035] 再具体的，将所得硫氮掺杂的生物炭以0.5g/L添加于重金属溶液中，通过搅拌使得吸附剂均匀分散于水溶液中，同时吸附120min直至达到吸附平衡，通过离心分离的方式将吸附材料与溶液进行分离，将分离所得的材料利用1M硼氢化钠进行表面重金属的原位还原处理，得到生物炭-金属纳米颗粒复合催化剂。

[0036] 具体的，催化剂对水体中有机污染物亚甲基蓝可进行氧化催化降解，其催化条件包括：[MB]＝20mg/L，[生物炭-金属纳米颗粒复合催化剂]＝50mg/L，[过硫酸钾]＝0.10g/L，T＝25℃。

[0037] 详细的，催化剂对水体中高价铬离子可进行还原催化降解，由高毒性Cr^{VI}降解为低毒性Cr^{III}，催化条件包括：[Cr^{VI}]＝10mg/L，[生物炭-金属纳米颗粒复合催化剂]＝50mg/L，T＝25℃，[甲酸]＝0.1M。

[0038] 生物炭-金属纳米颗粒复合催化剂可重复使用于水体中高价铬离子的还原催化降解，循环使用四次仍可保持90％以上的催化活性。

[0039] 硫氮掺杂多孔生物炭用于污水中的重金属铜、镍、铅的去除，所得生物炭-金属纳米颗粒复合催化剂可应用于水体中污染物的催化降解应用。

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[0040] 实施例1:硫氮掺杂多孔生物炭的制备条件优化

[0041] 硫氮掺杂多孔生物炭的制备过程主要是将硫酸钙、草酸钾与脱脂大豆豆渣均匀混合并进行高温煅烧,本次实验使用脱脂大豆豆渣含水份85%,蛋白质3.0%,脂肪0.5%,碳水化合物(纤维素、多糖等)8.0%。

[0042] 具体煅烧条件为:氩气条件下以5℃/min升温速度升温至800℃,加热时间1h,并自然冷却至室温,所得产物用稀盐酸洗涤三次,60℃烘干过夜得到最终产物。

[0043] 硫氮掺杂多孔生物炭的制备方法的制备条件优化,包括以下步骤:

[0044] 1)辅助添加剂

[0045] 本实验例通过调整辅助添加剂的配比,比较不同添加剂下烧制的生物炭的微观形貌。结果发现,如图1a和1d所示,相比于未添加硫酸钙和草酸钾的生物炭,将硫酸钙和草酸钾以1:1:1比例与大豆豆渣混合并在800℃下无氧烧制1小时得到的生物炭,其扫描电镜观察下微观结构具有较为致密的多孔结构。因此,综合来看,该方法包括的硫酸钙和草酸钾在该生物炭合成的过程中起到调节其多孔结构增加比表面积的作用。

[0046] 2)煅烧温度

[0047] 本实验例通过调整煅烧温度,比较不同煅烧温度下烧制的生物炭的微观形貌,硫元素掺杂程度。如图1中的b、c和d所示,随着煅烧温度从600℃上升至800℃,烧制的生物炭微观形貌呈现多孔结构,并且多孔程度随着温度升高而呈现更为致密的效果。图2中a-d的X射线光电子能谱显示800℃合成的生物炭具有较高的硫元素掺杂量,具有4.56%氮掺杂量和10.73%硫掺杂量,其中吡咯氮占氮元素比例的0.54%,石墨氮占1.3%。并且通过拉曼光谱表征显示(如图2中的e和f),生物炭中硫元素掺杂程度随着温度升高而增加。因此,综合来看,该方法提供的生物炭合成方法在800℃条件下煅烧能够得到较高杂元素掺杂的多孔生物炭材料。

[0048] 下述实施例2-4使用的硫氮掺杂多孔生物炭为实施例1筛选后的最优的制备条件制备得到。

[0049] 实施例2:硫氮掺杂多孔生物炭对不同重金属吸附能力

[0050] 1)硫氮掺杂多孔生物炭在混合重金属离子溶液的竞争吸附能力

[0051] 将生物炭吸附剂以0.5mg/L的添加量加入重金属离子混合液中测试其竞争吸附能力,该混合液包括七种重金属离子铅,铜,镍,铬,锌,锰,铁且每种离子浓度分别为10ppm,吸附反应10h。反应完成后将材料与反应液通过离心操作进行分离,并用火焰原子吸收测量其上清溶液,利用公式计算该生物炭材料对每种离子的分配系数,判断其选择吸附能力。结果如图3中的a表明,该生物炭吸附材料对重金属铜和镍的分配系数分别为6.7×10^5和9.8×10^4mL/g,表明对重金属铜,镍离子具有较好的选择性。

[0052] 2)硫氮掺杂多孔生物炭对重金属铜、镍、铅离子的吸附

[0053] 将生物炭吸附剂以0.5mg/L的添加量分别加入铅,镍以及铜离子的溶液中进行动力学和等温线研究,其中,动力学研究的重金属离子初始浓度为100ppm,等温线研究的初始浓度范围为10-1000ppm,吸附反应10h。反应完成后将材料与反应液通过离心操作进行分离,并用火焰原子吸收测量其上清溶液,得到的吸附数据分别利用不同的动力学模型(如图3中的b)和等温线(如图3中的c)进行模拟分析。结果表明,该生物炭吸附材料对重金属的吸附过程较好的拟合伪二级动力学模型(图3中的b虚线所示),说明该过程为化学反应过程;

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同时，其吸附过程较好的拟合Langmuir吸附等温模型(如图3中的c所示，实线为Langmuir线性拟合图，虚线为Freundlich线性拟合图)，且对重金属铅，铜，镍的理论最大吸附量可达619.23，1356.62，1250.21mg/g，具有优异的吸附效果。与其他常见重金属吸附剂吸附效果和成本对比如图3中的d所示，结果表明该硫氮掺杂多孔生物炭具有较优的吸附效果和较低的合成成本。

[0054] 实施例3：回收使用硫氮掺杂多孔生物炭于有机污染物亚甲基蓝的高级氧化催化降解

[0055] 回收处理硫氮掺杂多孔生物炭：将吸附重金属铜和镍的硫氮掺杂多孔生物炭于0.1M的硼氢化钠溶液中浸泡1h，并将所得材料于60摄氏度烘箱中烘干备用。将回收的硫氮掺杂多孔生物炭以50mg/L添加量添加于20mg/L的亚甲基蓝溶液中，同时加入0.1g/L过硫酸钾溶液1mL，室温条件下反应0.5小时，离心处理后利用紫外分光光度计测量其上清液吸光度值。图4中的a结果表明，硫氮掺杂程度较高的多孔生物炭具有较好的催化氧化能力，并且由于回收处理后的硫氮掺杂多孔生物炭表明负载有纳米镍和纳米铜，因此其催化降解亚甲基蓝的效果最优。图4中的b-d表明该过程主要是由于催化产生活性$^1O_2$，SO_4^-和OH自由基参与染料降解反应。以上结果表明该回收处理的硫氮掺杂多孔生物炭可进一步应用于污染水体中有机污染物的净化降解。

[0056] 实施例4：回收使用硫氮掺杂多孔生物炭于六价铬的还原催化降解

[0057] 回收处理硫氮掺杂多孔生物炭(同实例3)：将吸附重金属铜和镍的硫氮掺杂多孔生物炭于0.1M的硼氢化钠溶液中浸泡1h，并将所得材料于60摄氏度烘箱中烘干备用。将回收的硫氮掺杂多孔生物炭以50mg/L添加量添加于10mg/L的六价铬溶液中，同时加入0.1mol/L甲酸溶液1mL，室温条件下反应0.5小时，离心处理后利用紫外分光光度计测量其上清液吸光度值。如图5中的a和b所示，硫氮掺杂程度较高的多孔生物炭具有较好的催化还原能力，由于回收处理后的硫氮掺杂多孔生物炭表明负载有镍纳米颗粒和铜纳米颗粒，因此其催化还原六价铬的效果最优。X射线光电子能谱(图5中的c)的XPS结果表明该材料能够有效将高毒性六价铬还原降解为低毒性的三价铬。循环利用结果(图5中的d)表明负载铜纳米颗粒的硫氮掺杂多孔生物炭可重复利用4次，并仍保持90％以上的催化效率。

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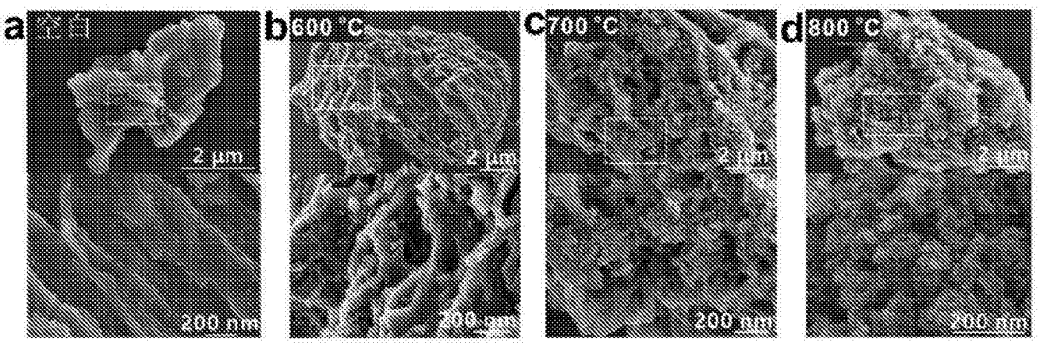


图1

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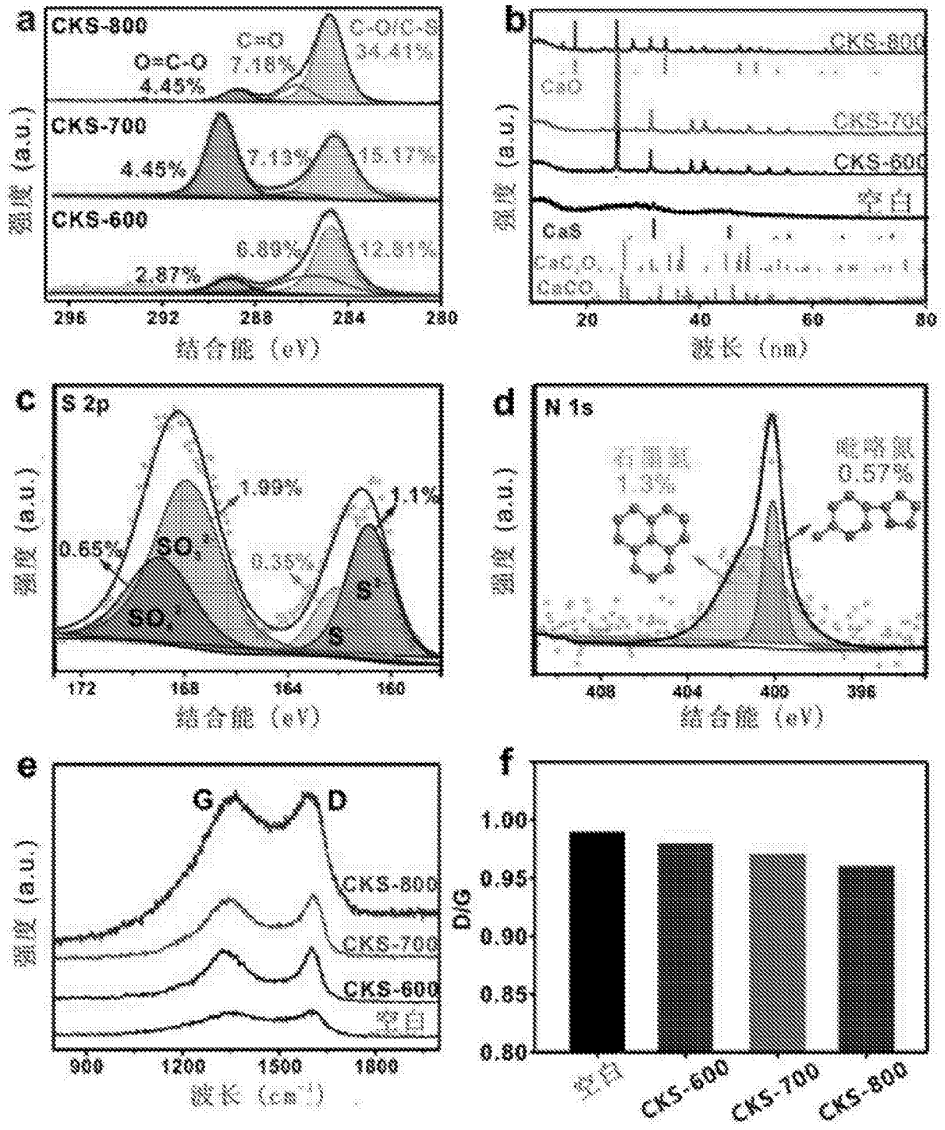


图2

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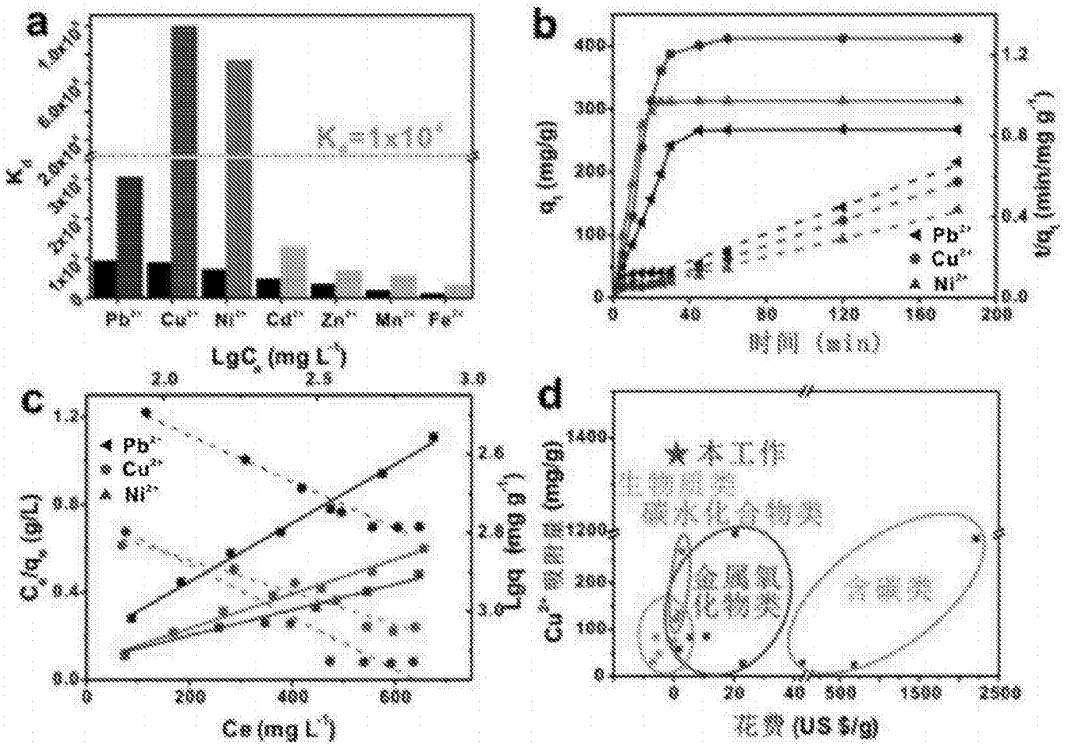


图3

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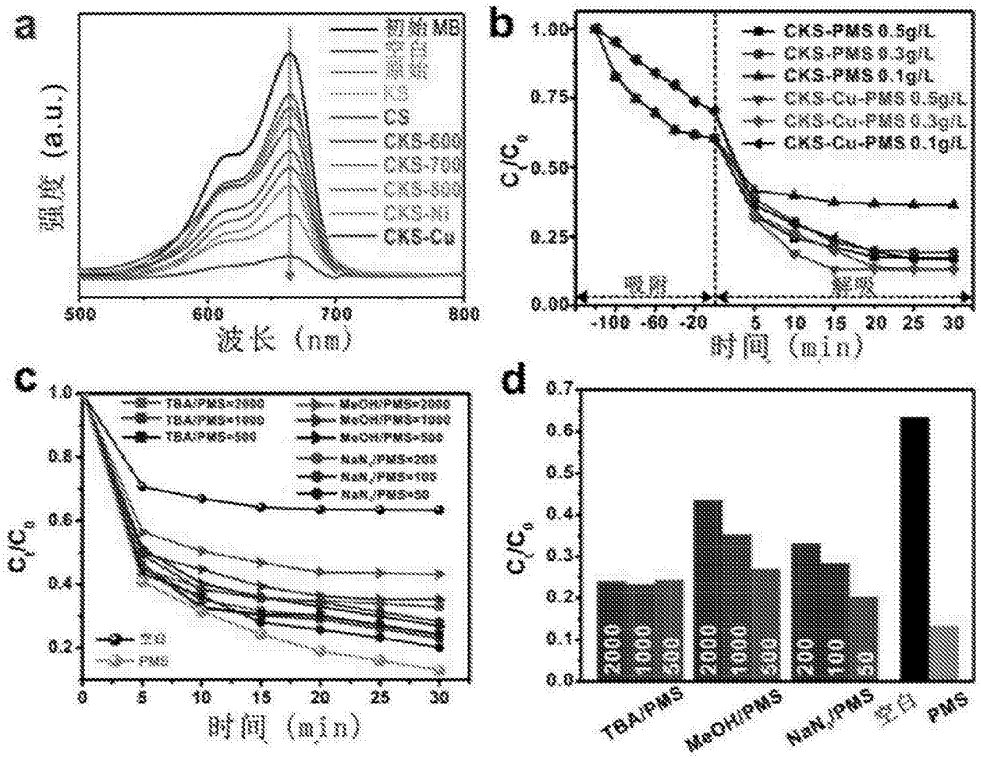


图4

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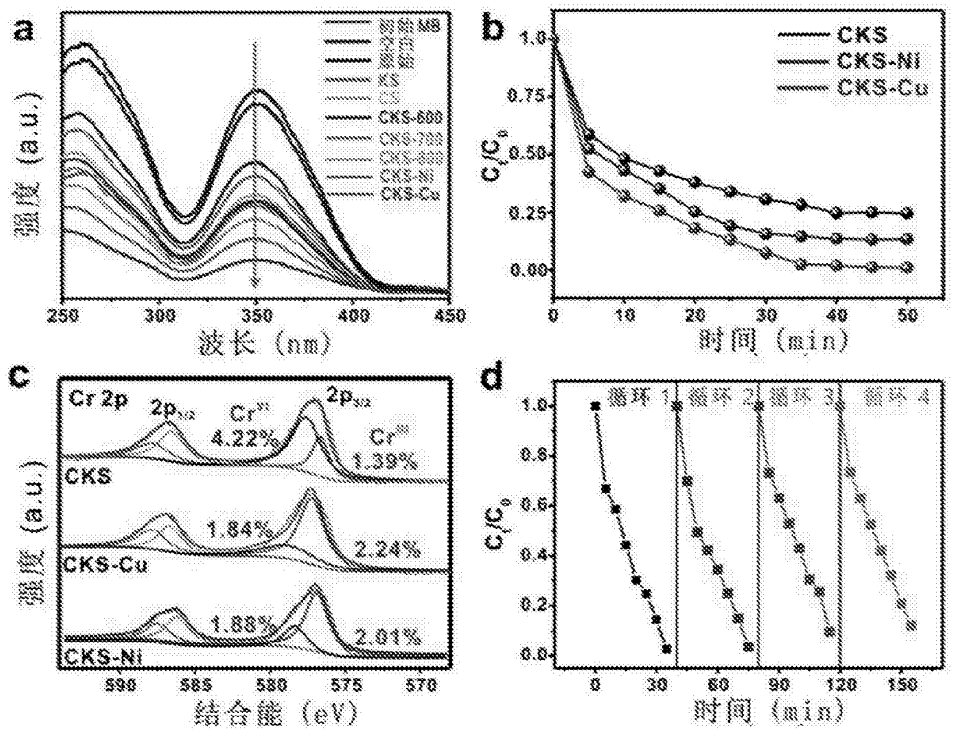


图5

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
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EXAMINER	
CHU, YONG LIANG	

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
03/03/2023	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Advisory Action Before the Filing of an Appeal Brief	**Application No.** 16/839,862	**Applicant(s)** DISTEFANO et al.	
	Examiner YONG L CHU	**Art Unit** 1731	**AIA (FITF) Status** Yes

--The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

THE REPLY FILED 23 February 2023 FAILS TO PLACE THIS APPLICATION IN CONDITION FOR ALLOWANCE.

NO NOTICE OF APPEAL FILED

1. ☑ The reply was filed after a final rejection. No Notice of Appeal has been filed. To avoid abandonment of this application, applicant must timely file one of the following replies: (1) an amendment, affidavit, or other evidence, which places the application in condition for allowance; (2) a Notice of Appeal (with appeal fee) in compliance with 37 CFR 41.31; or (3) a Request for Continued Examination (RCE) in compliance with 37 CFR 1.114 if this is a utility or plant application. Note that RCEs are not permitted in design applications. The reply must be filed within one of the following time periods:
   a) ☑ The period for reply expires 6 months from the mailing date of the final rejection.
   b) ☐ The period for reply expires on: (1) the mailing date of this Advisory Action; or (2) the date set forth in the final rejection, whichever is later. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the mailing date of the final rejection.
   c) ☐ A prior Advisory Action was mailed more than 3 months after the mailing date of the final rejection in response to a first after-final reply filed within 2 months of the mailing date of the final rejection.The current period for reply expires ____ months from the mailing date of *the prior Advisory Action* or SIX MONTHS from the mailing date of the final rejection, whichever is earlier.
   Examiner Note: If box 1 is checked, check either box (a), (b) or (c). ONLY CHECK BOX (b) WHEN THIS ADVISORY ACTION IS THE FIRST RESPONSE TO APPLICANTS FIRST AFTER-FINAL REPLY WHICH WAS FILED WITHIN TWO MONTHS OF THE FINAL REJECTION. ONLY CHECK BOX (c) IN THE LIMITED SITUATION SET FORTH UNDER BOX (c). See MPEP 706.07(f).

Extensions of time may be obtained under 37 CFR 1.136(a). The date on which the petition under 37 CFR 1.136(a) and the appropriate extension fee have been filed is the date for purposes of determining the period of extension and the corresponding amount of the fee. The appropriate extension fee under 37 CFR 1.17(a) is calculated from: (1) the expiration date of the shortened statutory period for reply originally set in the final Office action; or (2) as set forth in (b) or (c) above, if checked. Any reply received by the Office later than three months after the mailing date of the final rejection, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

NOTICE OF APPEAL

2. ☐ The Notice of Appeal was filed on _____. A brief in compliance with 37 CFR 41.37 must be filed within two months of the date of filing the Notice of Appeal (37 CFR 41.37(a)), or any extension thereof (37 CFR 41.37(e)), to avoid dismissal of the appeal. Since a Notice of Appeal has been filed, any reply must be filed within the time period set forth in 37CFR 41.37(a).

AMENDMENTS

3. ☐ The proposed amendments filed after a final rejection, but prior to the date of filing a brief, will not be entered because
   a) ☐ They raise new issues that would require further consideration and/or search (see NOTE below);
   b) ☐ They raise the issue of new matter (see NOTE below);
   c) ☐ They are not deemed to place the application in better form for appeal by materially reducing or simplifying the issues for appeal; and/or
   d) ☐ They present additional claims without canceling a corresponding number of finally rejected claims.
   NOTE: _____ (See 37 CFR 1.116 and 41.33(a)).
4. ☐ The amendments are not in compliance with 37 CFR 1.121. See attached Notice of Non-Compliant Amendment (PTOL-324).
5. ☑ Applicant's reply has overcome the following rejection(s): 112(b) rejection of claims 1-13
6. ☐ Newly proposed or amended claim(s) _____ would be allowable if submitted in a separate, timely filed amendment canceling the non-allowable claim(s).
7. ☑ For purposes of appeal, the proposed amendment(s):(a)☐ will not be entered, or (b)☑ will be entered, and an explanation of how the new or amended claims would be rejected is provided below or appended.

AFFIDAVIT OR OTHER EVIDENCE

8. ☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____
9. ☐ The affidavit or other evidence filed after final action, but before or on the date of filing a Notice of Appeal will not be entered because applicant failed to provide a showing of good and sufficient reasons why the affidavit or other evidence is necessary and was not earlier presented. See 37 CFR 1.116(e).
10. ☐ The affidavit or other evidence filed after the date of filing the Notice of Appeal, but prior to the date of filing a brief, will not be entered because the affidavit or other evidence failed to overcome all rejections under appeal and/or appellant fails to provide a showing of good and sufficient reasons why it is necessary and was not earlier presented. See 37 CFR 41.33(d)(1).
11. ☐ The affidavit or other evidence is entered. An explanation of the status of the claims after entry is below or attached.

REQUEST FOR RECONSIDERATION/OTHER

12. ☑ The request for reconsideration has been considered but does NOT place the application in condition for allowance because: See Continuation Sheet.
13. ☑ Note the attached Information *Disclosure Statement*(s). (PTO/SB/08) Paper No(s). _____
14. ☐ Other: _____.

STATUS OF CLAIMS

15. The status of the claim(s) is (or will be) as follows:
    Claim(s) allowed:_____.
    Claim(s) objected to:_____.
    Claim(s) rejected:1-14.
    Claim(s) withdrawn from consideration:_____.

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00191

Continuation of REQUEST FOR RECONSIDERATION/OTHER 12. The request for reconsideration has been considered but does NOT place the application in condition for allowance because: Applicant's argument that Wang fails to teach or disclose the use of any salt, oxide, or hydroxide for the removal of PFAS is not persuasive because Wang teaches using cations of Ca2+ and Mg2+ treated wastewater sludge (absorbent) burned under 300C to enhance PFAS absorbency. Wang discloses the Ca-salt is calcium chloride (CaCl2), and Mg-salt is magnesium chloride (MgCl2), see "2.1. Chemicals" at page 179. Since Wang teaches that Ca2+ cation and Mg2+ cation play important roll for enhancing absorbent's PFAS absorbency, selection of different counter-anions of magnesium and calcium salts such as chloride ion (Cl-) or carbonate would have been obvious selection to one ordinary skilled in the art, because the salts in aqueous liquid would result in the same cations Mg2+ and Ca2+ no matter which anions (i.e. chloride and carbonate) had been selected. Therefore, the cited prior art Wang and Appleman considered as a whole would have rendered claims 1-14 obvious.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. DISTEFANO
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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	1	1521723	EP	A1	2005-04-13	Remediation Products, Inc.		
	2	20120074080	KR	A	2012-07-05	Research Institute of Industrial Science & Technol	w/English Abstract	X

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
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EXAMINER SIGNATURE

Examiner Signature	/YONG L CHU/	Date Considered	02/27/2023

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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(Not for submission under 37 CFR 1.99)

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Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	198100399	WO	A1	1981-02-19	The Carborundum Company		

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Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
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	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

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EXAMINER SIGNATURE

Examiner Signature	/YONG L CHU/	Date Considered	02/27/2023

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

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** OK to enter.** /YONG CHU/ 02/27/2023

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1731
Confirmation No.	:	5111
Examiner	:	CHU, YONG LIANG

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RESPONSE TO FINAL OFFICE ACTION

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This paper is filed in response to the Final Office Action mailed October 28, 2022. The Office Action sets forth a 3-month shortened statutory period for reply. Accordingly, this response is timely filed with a 1-month extension of time.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **4** of this paper.

AMENDMENTS TO THE CLAIMS

The current listing of the claims replaces all prior versions and listings of the claims in the present application.

1. (Currently Amended) A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:
   providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises ~~an ion,~~ a salt, oxide, or hydroxide[[,]] ~~or carbonate~~ of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ~~ion,~~ salt, oxide, or hydroxide~~, or carbonate~~; and
   contacting the first sorbent material with a liquid or gas containing the PFAS.
2. (Original) The method of claim 1, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, reactivated carbon, and carbon black.
3. (Original) The method of claim 2, wherein the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.
4. (Original) The method of claim 2, wherein the first sorbent material is reactivated carbon.
5. (Original) The method of claim 2, wherein the first sorbent material is a reagglomerated activated carbon.
6. (Original) The method of claim 1, further comprising:
   providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and
   contacting the second sorbent material with the liquid or gas containing the PFAS.

7. (Original) The method of claim 1, wherein the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium, an oxide of strontium, or an oxide of barium.
8. (Original) The method of claim 7, wherein the first sorbent material includes one or more of MgO or CaO.
9. (Currently Amended) The method of claim 1, wherein the ~~ion,~~ salt, oxide, or hydroxide[[,]] ~~or carbonate~~ of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation, chemical vapor deposition, or physical vapor deposition.
10. (Currently Amended) The method of claim 1, wherein about 1 wt.% to about 20 wt.% of the first sorbent material comprises ~~an ion,~~ a salt, oxide, or hydroxide[[,]] ~~or carbonate~~ of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
11. (Currently Amended) The method of claim 10, wherein about 2 wt.% to about 8 wt.% of the first sorbent material comprises ~~an ion,~~ salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
12. (Currently Amended) The method of claim 1, wherein the first sorbent material is a reactivated carbon comprising ~~ions,~~ oxides ~~or carbonates~~ of calcium, magnesium, sodium, potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the ~~ions,~~ oxides~~, or carbonates~~ of calcium, magnesium, sodium, potassium and zinc.
13. (Currently Amended) The method of claim 12, wherein the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the ~~ions,~~ oxides~~, or carbonates~~ of calcium, magnesium, sodium, and zinc.
14. (New) The method of claim 1, wherein the first sorbent material includes one or more of a carbonate of magnesium, a carbonate of calcium, a carbonate of strontium, or a carbonate of barium.

AUTHORIZATION

Should the Examiner have any questions or comments, or need any additional information from Applicant's representative, the Examiner is invited to contact the undersigned. The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to Deposit Account No. 60-4406.

Respectfully submitted,
DLA PIPER LLP

/Douglas Kayuha/

Douglas E. Kayuha
Registration No. 79,855

Date: February 23, 2023
DLA Piper LLP
1650 Market St, Suite 5000
Philadelphia, PA 19103
Telephone: (215) 656-3300
Facsimile: (215) 656-3301

REMARKS

Applicant would like to thank the Examiner for the careful consideration given to the present application. Claims 1-13 are pending. The Office has rejected claims 1-13. Claims 1 and 9-13 have been amended and claim 14 has been added. The amendments to claims 1 and 9-13 include the removal of material. New claim 14 contains material removed from original claim 1. Therefore, Applicant submits that no new matter has been added.

Rejection under 35 U.S.C. § 112

In the Office Action dated March 3, 2022, the Office states that claim 1 is allegedly indefinite for failing to particularly point out and distinctly claim the subject matter regarded as the invention. Specifically, the Office states that claim 1 defines both narrowly defined species in a carbonate of magnesium and broadly defined species in a species of magnesium salts. In response Applicant has amended claim 1 to remove the narrowly defined species and included the narrowly defined species in new claim 14. Thus, Applicant submits that claim 1 is not indefinite and requests that the rejections under 35 U.S.C. § 112 be removed.

Rejection under 35 U.S.C. § 103

In the Office Action dated March 3, 2022, the Office states that claims 1-13 are allegedly obvious over Wang *et al., Chemosphere* ("Wang") in view of Appleman *et al., Water Research* ("Appleman"). In response, Applicant amends claims 1 and 9-13 and submits the following remarks. Claim 1 has been included below for convenience:

> A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:
> providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material is comprised of a ***salt, oxide, or hydroxide of magnesium, calcium, strontium, barium*** or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the salt, oxide, or hydroxide; and
> contacting the first sorbent material with a liquid or gas containing the PFAS.
> ***(Emphasis added)***

Notably, claim 1 requires a method of removing PFAS from liquid or gas comprising providing a first sorbent material comprising "a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium." Wang is directed towards a method of adsorbing PFAS on wastewater sludge through the use of cations. Wang at Abstract. However, Wang fails to disclose the use of a sorbent material comprising a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium for the removal of PFAS. In fact, Wang fails to teach or disclose the use of any salt, oxide, or hydroxide for the removal of PFAS. Appleman is directed towards the removal of PFAS from water using activated carbon treatment. Appleman at abstract. Appleman fails to disclose the use of a sorbent material comprising a salt, oxide, or hydroxide of magnesium, calcium, strontium, barium for the removal of PFAS from water. Therefore, Appleman fails to remedy the deficiencies in Wang, and Wang and Appleman, alone or in combination, fail to disclose all aspects of claim 1. Thus, Applicant submits that claim 1, and claims 2-14 which are dependent on claim 1, are not obvious over Wang in view of Appleman and requests that rejections under 35 U.S.C. § 103 be removed.

All of the stated grounds of rejection have been properly traversed, accommodated, or rendered moot. It is therefore respectfully requested that the Office reconsider and withdraw all presently outstanding rejections. There being no other rejections, it is respectfully requested that the current application be allowed and passed to issue.

If the Examiner believes for any reason that personal communication will expedite prosecution of this application, I invite the Examiner to telephone me directly.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1731
Confirmation No.	:	5111
Examiner	:	CHU, YONG LIANG

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RESPONSE TO FINAL OFFICE ACTION

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This paper is filed in response to the Final Office Action mailed October 28, 2022. The Office Action sets forth a 3-month shortened statutory period for reply. Accordingly, this response is timely filed with a 1-month extension of time.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **4** of this paper.

UNITED STATES
PATENT AND TRADEMARK OFFICE

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ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	02/23/2023 05:41:36 PM ET	123450-013001

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	61642750	AUTHORIZED BY	Douglas Kayuha
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	E20232MH44079414	Paula Watson

PRE-AUTHORIZED ACCOUNT	PRE-AUTHORIZED CATEGORY
604406	37 CFR 1.16 (National application filing, search, and examination fees); 37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.20 (Post Issuance fees); 37 CFR 1.21 (Miscellaneous fees and charges)

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1251	EXTENSION FOR RESPONSE WITHIN FIRST MONTH	220.00	1	220.00
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If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

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New International Application Filed with the USPTO as a Receiving Office

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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**02/23/2023 05:41:36 PM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

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CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Douglas Kayuha

Documents

TOTAL DOCUMENTS: 3

DOCUMENT		PAGES	DESCRIPTION	SIZE (KB)
123450-013001_Response to FOA.pdf		6	-	185 KB
123450-013001_Response to FOA-A.NE.pdf	(1-1)	1	Response After Final Action	102 KB
123450-013001_Response to FOA-CLM.pdf	(2-4)	3	Claims	178 KB
123450-013001_Response to FOA-REM.pdf	(5-6)	2	Applicant Arguments/Remarks Made in an Amendment	104 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450-013001_Response to FOA.pdf	01D9B9D56D25E2FD29BD55B9AD4CA5EC19F923E03D82EA7E8621E59F10F605A3F877AB85206A9FF30AD428D7E8106FF2BAC5A1C9AA3210B1BA7FD9CBC2B38DD2
123450-013001_Response to FOA-A.NE.pdf	5DB6B6292E2A872F2F0A4A3801597F8FEF66498208D6AAA05C07066A9BC985AAF612A82D7B6235A10D0717FA17ED43B6880D95C1A1396A3243C132F6B716E871
123450-013001_Response to FOA-CLM.pdf	E450EFD01772382FBE146779CE4EE630605C6D7E1416BDAA21D81F908A56A42AD40E25F84CDF7660E040BB310F5F43F2E5691710A70CD3B5245EEB3467A81448
123450-013001_Response to FOA-REM.pdf	FD7D250009B4B86FE75675A1BD1E55B42247FD6E8E3E5ECE4E65EBB55757AEA893EC389158FED07599AA7773AA07880887DBCB097ADC6D77FBF036269894CD62

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PTO/SB/06 (09-11)
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PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 16/839,862	Filing Date 04/03/2020	☐ To be Mailed

ENTITY: ☑ LARGE ☐ SMALL ☐ MICRO

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A		N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $100 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $460 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	02/23/2023	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 14	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	*** 3	= 0		x $480 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/DORIS M BURNS/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. DISTEFANO
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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	1	1521723	EP	A1	2005-04-13	Remediation Products, Inc.		
	2	20120074080	KR	A	2012-07-05	Research Institute of Industrial Science & Technol	w/English Abstract	X

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
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Examiner Signature		Date Considered	

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[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00210

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

X That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

X See attached certification statement.

X The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2022-12-28
Name/Print	Nicholas C. Kokkinos	Registration Number	76,979

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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00212

Doc Code: PTA.IDS
Document Description: Patent Term Adjustment Stmt Under 37 CFR 1.704(d)

PTO/SB/133 (10-21)

PATENT TERM ADJUSTMENT STATEMENT UNDER 37 CFR 1.704(d)		
	Application Number	16/839,862
	Filing Date	April 3, 2020
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Practitioner Docket No.	123450-013001

APPLICANT HEREBY STATES THE FOLLOWING (please review 37 CFR 1.704(d) before filing this form):

☑ Each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

AND/OR

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INSTRUCTIONS:

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Signature	/Nicholas Kokkinos/	Date	December 28, 2022
Typed or Printed Name	Nicholas C. Kokkinos	Practitioner Registration Number	76,979

***Note**: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature. If necessary, submit multiple forms for more than one signature, see below*.*

☑ *Total of 1 forms are submitted.

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4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
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PATENT AND TRADEMARK OFFICE

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ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	12/28/2022 09:08:58 AM ET	123450-013001

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	61358286	AUTHORIZED BY	Nicholas Kokkinos
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	E2022BR009483754	Paula Watson

PRE-AUTHORIZED ACCOUNT	PRE-AUTHORIZED CATEGORY
604406	37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.21 (Miscellaneous fees and charges)

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1806	SUBMISSION OF AN INFORMATION DISCLOSURE STATEMENT	260.00	1	260.00
			TOTAL AMOUNT:	$260.00

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement

Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

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(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Veröffentlichungsnummer:
(11) Publication number: **EP 1 521 723 A0**
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Internationale Anmeldung veröffentlicht durch die Weltorganisation für geistiges Eigentum unter der Nummer:

WO 2004/007379 (Art. 158 des EPÜ).

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Demande internationale publiée par l'Organisation Mondiale de la Propriété Intellectuelle sous le numéro:

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00217

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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22 January 2004 (22.01.2004)

PCT

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WO 2004/007379 A1

(51) International Patent Classification[7]: C02F 3/00, B01J 21/18

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(30) Priority Data:
10/194,946 12 July 2002 (12.07.2002) US

(71) Applicant: **REMEDIATION PRODUCTS, INC.** [US/US]; 6390 Joyce Drive, Suite 150 West, Golden, CO 80403 (US).

(72) Inventors: **NOLAND, Scott**; 7305 W. 64th Avenue, Arvada, CO 80003 (US). **ELLIOTT, Bob**; 12560 E. Bates Circle, Aurora, CO 80014 (US).

(74) Agents: **BURTON, Carol W.** et al.; Hogan & Hartson, LLP, 1200 17th Street, Suite 1500, Denver, CO 80202 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/007379 A1

(54) Title: COMPOSITIONS FOR REMOVING HYDROCARBONS AND HALOGENATED HYDROCARBONS FROM CONTAMINATED ENVIRONMENTS

(57) Abstract: The present invention provides a supported catalyst for *in situ* remediation of soil and/or groundwater contaminated with a halogenated hydrocarbon comprising an adsorbent impregnated with zero valent iron, wherein the adsorbent is capable of adsorbing the halogenated hydrocarbon. This invention further provides a bioremediation composition for *in situ* bioremediation of soil and/or groundwater contaminated with hydrocarbons, comprising an adsorbent capable of adsorbing said hydrocarbons, a mixture of facultative anaerobes capable of metabolizing said hydrocarbons under sulfate-reduction conditions, a sulfate-containing compound that releases sulfate over a period of time, and a nutrient system for promoting growth of said anaerobes, wherein said nutrient system includes a sulfide scavenging agent.

COMPOSITIONS FOR REMOVING HYDROCARBONS AND HALOGENATED HYDROCARBONS FROM CONTAMINATED ENVIRONMENTS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to compositions and methods for *in situ* remediation of contaminated environments, and particularly to the remediation of soil and/or groundwater contaminated with halogenated hydrocarbons and bioremediation of soil and/or groundwater contaminated with hydrocarbons.

Description of the State of Art

With increased concerns over protecting the environment and public health and safety, the identification and removal of contaminant materials in the environment, and especially from the groundwater supply, has become one of the most important environmental concerns today. Years of unregulated dumping of hazardous materials have severely contaminated the groundwater in many areas, creating significant health concerns and causing extensive damage to the local ecosystem. As a result, in recent years significant emphasis has been placed upon the clean-up and remediation of contaminated groundwater and the environment surrounding dump sites, which has lead to the creation of a new industry of environmental clean-up and remediation. However, conventional technologies currently being used for remediation for contaminated sites often are very expensive, can require years to perform, and are not always effective.

Because of the widespread use of both chlorinated solvents and petroleum hydrocarbons, contaminated ground water has been found in many sites around the world. Chlorinated solvents, such as trichloroethane (TCE) and perchloroethylene (PCE), are used for such purposes as dry cleaning, and as degreasers and cleaners in a variety of industries. Petroleum hydrocarbons commonly found in ground water include the components of gasoline, such as benzene, toluene, ethylbenzene, and xylene. Other common contaminants of ground water include naphthalene and chlorinated

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solvents. Additional groundwater and soil contaminants comprise polycyclic aromatic hydrocarbons (PAHs) created from combustion, coal coking, petroleum refining and wood-treating operations; and polychlorinated biphenyls (PCBs), once widely used in electrical transformers and capacitors and for a variety of other industrial purposes, pesticides, and herbicides.

Various *ex situ* and *in situ* methods have been utilized for the treatment, remediation or disposal of contaminated soil. *Ex situ* methods generally include permanent removal of the contaminated soil to a secure landfill, incineration, indirect thermal treatment, aeration, venting, and air sparging. Removal of contaminated soil to landfills is no longer an attractive alternative on account of the high excavation, transportation and disposal costs, and because of the potential for residual liability. Incineration and indirect thermal treatment can be achieved either on-site or off-site, but in either case involves excavation, handling and treatment of substantially all of the contaminated soil as well as significant amounts of soil adjacent to the contaminated soil. The soil must then either be transported to the treatment facility or else the treatment apparatus must be installed on-site. Other elaborate and expensive techniques that have been utilized involve excavation and treatment of the contaminated soil using multistep unit operations for separating and recovering the soil from the contaminants.

Additional existing clean-up methods and technologies include "pump and treat" methods in which contaminated groundwater is pumped to the surface, cleaned chemically or by passing the groundwater through a bioreactor, and then reinjected into the groundwater. Such a process generally is carried out over a long period of time, typically one to ten years or more. A common remediation treatment for ground water contaminated with chlorinated hydrocarbons involves pumping the water out of the well or aquifer, volatizing the contaminants in an air stripping tower, and returning the decontaminated water to the ground site. A related type of environmental remediation is the "dig and haul" method in which contaminated soils are removed and then treated or land filled.

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The biggest problem with pump and treat systems is that, over time, they become more and more inefficient, so that stable residual concentrations become established. When this happens, the system is said to be "flat-lined" and very little further benefit is obtained. In addition, channeling often occurs so that large pockets of contamination are left behind, and rebound frequently occurs after the pumps are turned off.

A wide variety of materials and methods have been evaluated for *in situ* remediation chlorinated hydrocarbons, including zero valent iron (ZVI), potassium permanganate, and hydrogen peroxide. ZVI renders the chlorinated hydrocarbon less toxic by reductive dehalogenation, i.e., by replacement of chlorine substituents with hydrogen. In this method, reactive walls are constructed by digging a trench across the plume migration path and filling it with iron filings. Sheet piling or some other means of directing the flow of groundwater is used to direct contaminated groundwater through the filing wall. The chlorinated hydrocarbons react with the elemental iron as the groundwater flows through the wall, and ideally, clean water emerges on the down gradient side of the wall. The disadvantage of the wall method lies in the difficulty of introducing large volumes of solid reactive material, such as iron particles, at effective depths. Conventional excavation methods generally limit the practical working depth to about 30 feet, whereas ground water contaminants are found at depths as great as 300 feet.

Oxygen release materials (ORMs) are compositions such as intercalated magnesium peroxide that release oxygen slowly and facilitate the aerobic degradation of hydrocarbon contaminants *in situ*. ORM's are most effective when used to polish up after a mechanical system has flat-lined and are least effective at new sites where no other remedial measures had been implemented. They are disadvantaged in that ORMs are expensive, and large amounts are required for complete oxidation. Additionally, multiple treatments are often required in order to achieve targeted cleanup goals, and two or three years may be needed to complete the process.

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Hydrogen Release Compound® (HRC) is an alternative option for the *in situ* remediation of chlorinated hydrocarbons under anaerobic conditions via reductive dehalogenation. When in contact with subsurface moisture, HRC® is hydrolyzed, slowly releasing lactic acid. Indigenous anaerobic microbes (such as acetogens) metabolize the lactic acid producing consistent low concentrations of dissolved hydrogen. The resulting hydrogen is then used by other subsurface microbes (reductive dehalogenators) to strip the solvent molecules of their chlorine atoms and allow for further biological degradation. HRC® is injected into the affected environment under pressure and each treatment lasts for roughly six to nine months. Like ORMs, HRC® is expensive, and large amounts are required for complete degradation. Additionally, multiple treatments are often required in order to achieve targeted cleanup goals, and two or three years may be needed to complete the process.

Another emerging clean-up technology is "bioremediation," in which natural or genetically engineered microorganisms are applied to contaminated sites such as groundwater, soils or rocks. In this technique, specialized strains of bacteria are developed which metabolize various hydrocarbons such as gasoline, crude oil, or other hydrocarbon-based contaminates and gradually reduce them to carbon dioxide and water. However, such bacterial remediation requires that the bacteria and the hydrocarbon be brought into intimate contact under conditions in which the bacteria will act to metabolize the hydrocarbons. This requires extensive labor and effort to spread the bacteria on the soil and then to continually work and rework the contaminated area, turning and tilling the soil, until such time as the bacteria have been brought substantially into contact with all of the contaminated hydrocarbon particles. An additional drawback has been the ineffective spreading of injected bacteria due to clogging around the wells due to adsorption and growth of the bacteria about the wells.

The above-described technologies share one or more of the following drawbacks. (1) Long periods of time are required for sustained reduction in contaminant concentrations to be realized. (2) Although reductions can be

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realized, regulatory cleanup standards or goals for soil and groundwater are seldom attained. (3) Performance is inconsistent and highly dependent on site conditions and contaminant levels. (4) With respect to active systems, contaminants are often removed from one formation (groundwater for example) and then released into another, such as air. As a result, contaminants are not destroyed, just moved from one place to another. (5) With respect to passive systems for treatment of chlorinated solvents, by-products are often released that are more toxic than the original contaminants, creating a transient condition more egregious than what existed before treatment.

There is still a need for remediation processes to effectively clean up soil and/or groundwater contaminated with hydrocarbons, and/or halogenated hydrocarbons, that is rapid, cost effective, and does not release toxic by-products into the soil, air or groundwater.

SUMMARY OF THE INVENTION

The present invention provides compositions and methods for *in situ* soil and/or groundwater remediation that can reduce contaminant concentrations quickly to regulatory cleanup standards. The compositions and methods work in a variety of soil and groundwater conditions and are applicable for the remediation of a variety of contaminants. The methods and compositions of this invention do not release toxic by-products into the soil, groundwater or air, and have no impact on soil properties or groundwater quality. The compositions of this invention are cost effective in that they remain active for an extended period of time so that only a single treatment is required.

Accordingly, one aspect of this invention provides a composition which, when added to a site such as soil and/or groundwater contaminated with one or more halogenated hydrocarbon, adsorbs the halogenated hydrocarbons and reduces them to less innocuous by-products. More specifically, one embodiment of this invention provides a supported catalyst for *in situ* remediation of soil and/or groundwater contaminated with a halogenated hydrocarbon comprising an adsorbent impregnated with zero valent iron, wherein the adsorbent is capable of adsorbing the halogenated hydrocarbon

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contaminants as well as the intermediate by-products resulting from the degradation of the contaminants.

Another aspect of this invention provides a method for the remediation of an environment contaminated with halogenated hydrocarbons, comprising adding a supported catalyst of this invention to one or more sites of said contaminated environment, wherein reductive dehalogenation of the halogenated hydrocarbon compounds is achieved.

This invention further provides a bioremediation composition which, when added to water and/or soil contaminated with petroleum or other hydrocarbons, will adsorb hydrocarbons from the soil and/or water and degrade the hydrocarbons. More specifically, this invention provides a bioremediation composition comprising an adsorbent capable of adsorbing said hydrocarbons, a mixture of facultative anaerobes capable of metabolizing said hydrocarbons under sulfate-reduction conditions, a sulfate-containing compound that releases sulfate over a period of time, and a nutrient system for promoting growth of said anaerobes, wherein said nutrient system includes a sulfide scavenging agent.

Another aspect of this invention provides a method for the bioremediation of an environment contaminated with hydrocarbons, comprising adding a bioremediation composition of this invention to one or more sites of said contaminated environment, wherein the mixture of facultative anaerobes metabolizes the hydrocarbon contaminants.

Additional advantages and novel features of this invention shall be set forth in part in the description and examples that follow, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by the practice of the invention. The objects and the advantages of the invention may be realized and attained by means of the instrumentalities and in combinations particularly pointed out in the appended claims.

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DETAILED DESCRIPTION OF THE INVENTION

This invention relates to compositions and methods for *in situ* remediation of environments such as soil or groundwater contaminated with hydrocarbons or halogenated hydrocarbons. The compositions and methods of this invention can reduce contaminant concentrations quickly to regulatory cleanup standards and work in a variety of soil and groundwater conditions. The methods and compositions of this invention do not release toxic by-products into the soil, groundwater or air, and have no impact on soil properties or groundwater quality. The compositions of this invention remain active for an extended period of time so that only a single treatment is required. The methods and compositions of this invention are applicable for the remediation of a variety of contaminants, and are reasonably cost effective relative to existing remedies.

More specifically, one embodiment of this invention provides a supported catalyst for the reductive dehalogenation of halogenated hydrocarbons comprising an adsorbent impregnated with zero valent iron, wherein the adsorbent has an affinity for halogenated hydrocarbons. The adsorbent can be any material having an affinity for, and therefore capable of adsorbing, halogenated hydrocarbons. In addition, the adsorbent is capable of adsorbing toxic intermediate by-products produced by the reductive dehalogenation of the contaminants (e.g., intermediates such as dichloroethane and vinyl chloride intermediate by-products of trichloroethane decomposition). The adsorbent provides a means for concentrating contaminants into a new matrix where a high surface area of iron is available, as discussed hereinafter in detail. The supported catalysts of this invention accomplish treatment of halogenated hydrocarbons in soil and groundwater by degrading halogenated hydrocarbon contaminants and their toxic intermediate by-products into harmless by-products (e.g., ethane, ethyne, etc.).

The supported catalysts of this invention are prepared using an adsorbent having a high surface area per unit weight and a high affinity for halogenated hydrocarbons. Suitable adsorbents for purposes of this invention

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include, but are not limited to, activated carbon, vermiculite, alumina, and zeolites. Thus, while the method of preparing the supported catalysts of this invention is described utilizing activated carbon as the adsorbent, it is to be understood that the methods and supported catalysts of this invention are not limited to this adsorbent. The ability of activated carbon to adsorb organics from water enhances its utility as a support. However, while the carbon can trap hydrocarbon contaminants, carbon by itself is not stable over long periods, i.e., it is subject to erosion, etc., in which case the contaminants move with the carbon and are not truly trapped and removed.

In one non-limiting embodiment, the supported catalyst comprises activated carbon as the support impregnated with zero valent iron. Activated carbon provides an efficient matrix for adsorption of the chlorinated hydrocarbon contaminants. Impregnating the activated carbon with the zero valent iron provides sub-micron deposits of iron within the pore structure of the carbon, maximizing the metal's available surface area and placing the metal where the concentration of adsorbed contaminant molecules is the highest. Accordingly, the supported catalyst allows efficient contact of the iron with adsorbed chemicals contaminants, since the iron will be in close proximity to the contaminant. The supported catalysts of this invention accomplish treatment of chlorinated hydrocarbons in soil and groundwater by degrading these chemicals into harmless by-products.

Activated carbons are manufactured from a broad spectrum of material, including, but not limited to, coal, coconut shells, peat and wood. The supported catalysts of this invention may be produced with virtually any source of activated carbon. All that is needed are minor adjustments in system design parameters to account for the different forms of carbon. When the product is used for remediation of groundwater, acid-washed carbons are preferred, since the acid wash removes any extraneous metals that may be of environmental concern from the carbon.

When the adsorbent is activated carbon, available surface areas for adsorption range from about 800 m^2/gm to 1800 m^2/gm. Some loss of carbon

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surface area may occur during the impregnation process, but testing has shown that the loss is not significant when measured by adsorption isotherms. In one embodiment, the surface area of the zero valent iron in the supported catalyst of this invention ranges from about 50 to 400 m^2/(gm-deposited iron). The weight percent of iron deposited within the carbon matrix ranges from about 1% to 20% by weight of iron.

As described above, the contaminants are initially adsorbed by the activated carbon and then degraded through a reductive dechlorination mechanism. However, toxic reaction by-products such as vinyl chloride and *cis*-dichloroethene are formed during the treatment process. In conventional remediation systems, even though these by-products will react with the iron, they do so at a reduced rate, and concentrations can initially rise. In fact, fairly large accumulations can occur, creating a more acute risk to the environment than that which originally existed. One of the advantages of the supported catalyst of this invention is that these toxic by-products are also readily adsorbed by the activated carbon of the supported catalyst. As a result, little if any by-product escapes from the carbon matrix and groundwater quality is protected throughout the cleanup lifecycle. Further, the supported catalyst degrades the intermediate by-products to non-toxic by-products such as ethane, ethene and ethyne.

Manufacture of the supported catalysts involves impregnation of an adsorbent such as activated carbon material with metallic iron. These catalysts can be prepared using a variety of procedures known to those skilled in the art. One method of producing a supported catalyst of this invention comprises mixing the adsorbent with a calculated amount of a hydrated iron salt such as ferric nitrate while warming to melt the hydrated iron salt. The iron can be an iron (II) or an iron (III) salt. The mixture is dried and pyrolyzed to decompose the iron salt to iron oxide, forming an intermediate product comprising the adsorbent impregnated with a form of iron oxide. The intermediate product is then subjected to reduction conditions to reduce the iron oxide to elemental iron, thereby producing an adsorbent impregnated with elemental iron.

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A second method for preparing the supported catalyst involves a slow precipitation of goethite (iron hydrogen oxide) from a solution of an iron salt (e.g., ferrous sulfate) by addition of a dilute sodium bicarbonate solution. The precipitation is carried out with vigorous mixing in a suspension of an adsorbent such as activated carbon. An intermediate product formed comprising the adsorbent impregnated with a form of iron oxide. This intermediate product is then washed, dried, and finally reduced to convert the iron oxides to elemental iron, thereby producing an adsorbent impregnated with elemental iron.

The supported catalysts of this invention may further comprise another reactant in addition to, or in place of, the iron deposited within the pores of the supporting adsorbent matrix. Accordingly, other supported catalysts of this invention include adsorbents impregnated with iron and/or other metals including, but not limited to, aluminum, magnesium, platinum, palladium, nickel, zinc, copper, cobalt, chromium, molybdenum, and manganese.

For example, carbon impregnated with aluminum is highly effective in adsorbing and degrading methylene chloride. In one embodiment, the effectiveness of the aluminum-impregnated carbon can be enhanced by increasing the pH of the supported catalyst to a basic pH, such as by adding a small percentage of magnesium hydroxide to the supported catalyst.

The supported catalysts of this invention can be applied to treatment of water contaminated with a variety of water miscible or soluble halogenated organic compounds. Chlorinated solvents are particularly common contaminants in aquifers and other subsurface water-containing environments. Contaminants that may be effectively treated include halogenated solvents such as, but not limited to, (TCE), dichloroethylene (DCE), tetrachloroethylene, dichloroethane, trichloroethane, perchloroethene (PCE), vinyl chloride (VC), chloroethane, carbon tetrachloride, chloroform, dichloromethane and methyl chloride. Other classes of contaminants that may be effectively treated include brominated methanes, brominated ethanes,

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brominated ethenes, fluorochloromethanes, fluorochloroethanes, fluorochloroethenes, polychlorinated biphenyls (PCBs), and pesticides.

This invention further provides a method of remediating a site contaminated with halogenated hydrocarbons, comprising injecting a supported catalyst of this invention into one or more locations of the contaminated site. Illustrative examples of contaminated environments that can be treated with a supported catalyst of this invention include, but are not limited to, soil, sediment, sand, gravel, groundwater, aquifer material, and landfills. For example, in one embodiment the supported catalyst can be injected into multiple sites within an aquifer, as described in Example 3. In this embodiment, the application method results in a substantially homogeneous distribution of the supported catalyst in the contaminant plume, as opposed to creating a barrier or filled trench as in conventional methods. Thus, the remediation method according to the embodiment described in Example 3 using a supported catalyst does not rely on groundwater diffusion for effective treatment. Rather, the adsorbent component of the supported catalyst concentrates the contaminants within the adsorbent matrix where a high surface area of iron is available, thereby increasing the rate of contaminant degradation. Contaminated ground water in the site subsequently contacts the supported catalyst, whereby reductive dehalogenation of the halogenated hydrocarbon compounds is achieved.

The supported catalyst of this invention provides a number of advantages over conventional remediation products and methods. For example, it rapidly reduces concentrations of contaminants in groundwater so that regulatory standards can be approached or achieved in a short time frame (e.g., within several days or a few weeks, versus several months or years with conventional methods). In addition, the supported catalyst is non-toxic, does not decompose over time, and toxic degradation by-products are not released, so groundwater quality is protected throughout treatment. The supported catalyst has the ability to treat a variety of chlorinated chemicals and is effective in all types of soil and groundwater conditions. It remains active for an extended period of time so that typically only a single treatment

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is required. The material is easy to use and does not require any special safety controls or equipment for installation.

This invention further provides a bioremediation composition for *in situ* bioremediation of environments contaminated with hydrocarbons. The vast majority of sites contaminated with fuel hydrocarbons are naturally in an anaerobic state. The bioremediation composition of this invention takes advantage of this condition and is designed to promote anaerobic oxidation of hydrocarbons through a sulfate-reduction mechanism. In addition, the bioremediation composition of this invention comprises an adsorbent having an affinity for hydrocarbon contaminants, thereby providing a means for concentrating the contaminants and increasing the rate of bioremediation.

Accordingly, a bioremediation composition of this invention for *in situ* bioremediation of an environment contaminated with hydrocarbon comprises an adsorbent capable of adsorbing hydrocarbons, a mixture of two or more species of facultative anaerobes capable of metabolizing said hydrocarbons under sulfate-reduction conditions, a sulfate-containing compound that releases sulfate ions over a period of time, and a nutrient system for metabolism of said facultative anaerobes, wherein said nutrient mixture includes a sulfide scavenging agent.

An illustrative example of a bioremediation composition of this invention comprises a mixture of the ingredients listed in Table 1.

Table 1

Ingredient	Composition (wt%)
Adsorbent	51.3 to 77
Micronutrients	3.8 to 10.2
Sulfate-containing compound	19.2 to 38.5
Mixture of Facultative anaerobes	1×10^8 CFU/gm-carbon

The adsorbent provides a means for concentrating the mixture of facultative anaerobes at the site of contamination. In addition, the adsorbent provides an efficient matrix for adsorbing and thus concentrating the

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hydrocarbon contaminants. As a result, the rate of bioremediation is dramatically increased relative to rates obtained using conventional methods. In one embodiment, the adsorbent is activated carbon, which has a high affinity for hydrocarbons. In addition, activated carbon has an affinity for facultative anaerobes, which is advantageous for *in situ* bioremediation where growth of the anaerobes is desired.

The mixture of facultative anaerobes comprises hydrocarbon degraders that metabolize the hydrocarbon contaminants under sulfate-reduction conditions. A facultative anaerobe is a microbe such as bacteria and fungi that can switch between aerobic and anaerobic types of metabolism. Under anaerobic conditions, they grow by fermentation or anaerobic respiration. Further, since oxygen is not toxic to facultative anaerobes, the facultative anaerobes used in the composition of this invention are not sensitive to the low levels of oxygen frequently found at contaminated sites. In one embodiment, the mixture of facultative anaerobes comprises symbiotic facultative anaerobes that work in concert with each other. That is, one type of facultative anaerobe will break down a hydrocarbon contaminant to a first intermediate, and another type of facultative anaerobe will break down the first intermediate to a second intermediate or final by-product, etc.

In one embodiment, the mixture of facultative anaerobes includes at least one anaerobe that is a sulfate-reducing bacteria. Generally, sulfate-reducing bacteria are distributed widely in nature where anoxic conditions prevail. For example, such bacteria have been found in sewage, polluted water, sediment of lakes, sea and marine muds, oil wells, and the like. In one embodiment, the composition of the present invention is designed to dramatically increase the activity of naturally occurring sulfate-reducing bacteria by introducing cultured bacteria into the contaminated environment. Rather than depending on indigenous bacteria to inhabit the injected adsorbent, an aqueous suspension of the adsorbent is blended with the mixture of facultative anaerobes that includes bacteria specifically cultured for degradation of hydrocarbons. This mixture is stirred for a short period of time prior to injecting into the contaminated site to ensure all micronutrients have

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dissolved to provide a homogeneous mixture. In addition, this pre-mixing provides the cultured bacteria with an advantage over indigenous bacteria, maximizing the opportunity for the cultured bacteria to predominate. By not relying on indigenous bacteria to decompose the hydrocarbon contaminants, the compositions of this invention provide a means for removing hydrocarbon contaminants in a much shorter time period.

Commercial cultured mixtures of facultative anaerobes vary over a considerable range and the amount added will depend on the source and whether it is a dry, mineral-based product, or if it is a liquid concentrate. Regardless of the source, a sufficient amount of the facultative anaerobe mixture is added so that a targeted suspension concentration of 5 to10 million CFU (colony forming units) per milliliter is obtained.

In general, the cultured bacteria will comprise a multiple species or strains of bacteria. The species or strains of bacteria are advantageously derived from *Pseudomonas, Phenylobacterium, Stenotrophomonas, Gluconobacter, Agrobacterium, Vibrio, Acinetobacter*, or *Micrococcus*, yeasts or other genera can also be employed. Exemplary bacterial strains include *Pseudomonas pseudoalkaligenes, Phenylobacterium immobile, Stenotrophomonas maltophilia, Gluconobacter cerinus, Agrobacterium radiobacter* or *Pseudomonas alcaligenes*.

As discussed above, the bioremediation composition of this invention metabolizes hydrocarbon contaminants under sulfate-reduction conditions, wherein some or all of the facultative anaerobes reduce sulfate to hydrogen sulfide and metabolize (oxidize) at least some hydrocarbon contaminants in the process. Thus, decomposition of hydrocarbons under sulfate-reduction conditions requires a source of sulfate ions. Accordingly, the bioremediation composition of this invention includes a sulfate-containing compound. Preferably the sulfate-containing compound has a low water solubility and is non-toxic. An illustrative example of a suitable sulfate-containing compound is gypsum (calcium sulfate), which is a non-toxic, naturally occurring compound found in soil. Since gypsum has a low solubility in water, it breaks

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down over time to provide a slow release of sulfate ions, thus a low but persistent level of sulfate can be maintained during bioremediation using a composition of this invention. In this manner, gypsum acts as a "time released" source of sulfate ions, which is advantageous since the mixture of facultative anaerobes consumes the hydrocarbon contaminants over a period of time. As long as there is an adequate supply of dissolved sulfate, the activity of the facultative anaerobes will be optimized. Accordingly, any non-toxic sulfate-containing compound that releases sulfate ions in a manner similar to gypsum is suitable for purposes of this invention. As used herein, "nontoxic" refers to standards set forth for drinking water standards as regulated by the United States Environmental Protection Agency and defined by the Occupational Health and Safety Administration.

Low levels of micronutrients, which are needed to support growth of the cultured facultative anaerobes, are mixed in with the other components of the bioremediation composition. A suitable nutrient system for the facultative anaerobes includes a nitrogen source such as an ammonium salt, and a phosphorus source such as an alkali metal phosphate compound. Preferably, the micronutrient source does not contain sand, gravel, fillers, or other insoluble products found in commercial fertilizers. One example of a suitable micronutrient source for purposes of this invention contains nitrogen (e.g., 24% by weight as ammonia and ammonium nitrate in a ratio of about 2:1), phosphorus (e.g., 10% by weight as ammonium phosphate), potassium (e.g., 2% by weight as potassium chloride), sulfur (e.g., 5% by weight as ammonium sulfate), and iron (e.g., 2% by weight as ferrous sulfate). The nutrient system also includes a sulfide scavenging agent. In one embodiment, the sulfide scavenging agent is a ferrous iron salt such as iron sulfate.

After injection into the contaminated soil or groundwater, the bioremediation composition rapidly reduces concentrations of the hydrocarbon contaminants in soil and/or groundwater. Hydrocarbon contaminant molecules are adsorbed by the composition and are thus co-located together with the cultured facultative anaerobes in the pores of the adsorbent matrix. The hydrocarbon contaminant concentration within the

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adsorbent matrix thus becomes substantially higher than that which existed in the soil or groundwater. As a result, rates of degradation are significantly faster than rates commonly observed using current technology. As adsorbed contaminants are degraded, active sites become available to adsorb fresh contaminant, and the cycle is repeated until the microcosm runs out of food (i.e., hydrocarbons).

By-products of sulfate reduction include carbon dioxide, water, a variety of fermentation products such as light alcohols (ethanol, propyl alcohol, isopropyl alcohol, butyl alcohol, etc.) and hydrogen sulfide. In a typical installation, elevated concentrations of hydrogen sulfide do not occur because a sulfide scavenging agent (e.g., iron sulfate) is incorporated as one of the micronutrients. For example, an iron salt can scavenge hydrogen sulfide and form insoluble iron sulfide, thus preventing toxic levels of hydrogen sulfide from accumulating. Thus, transient concentrations of hydrogen sulfide are maintained well below regulatory thresholds, protecting groundwater quality.

The mixture of facultative anaerobes included in the composition of this invention is capable of biodegrading various aliphatic, aromatic and polycyclic aromatic hydrocarbons. For example, the compositions can be used to biodegrade aromatic hydrocarbons present in gasoline such as benzene, toluene, ethylbenzene, and xylenes. Examples of polycyclic aromatic hydrocarbons that can be biodegraded using the bioremediation composition of this invention generally include any of the various aromatic compounds containing multiple ring structures. Some of the most toxic (carcinogenic) aromatic hydrocarbons (polycyclic aromatics) are fairly resistant to bioremediation, requiring long periods of time for assimilation, but they are tightly held by activated carbon. Polycyclic aromatic hydrocarbons are generally present in and derived from fossil fuels, especially coal and petroleum. Relatively high concentrations of polycyclic aromatic hydrocarbons are found in coal-tar pitch, petroleum and coal-tar naphtha, and various other high-boiling point petroleum fractions, as well as various products derived therefrom including roofing pitch, sealants, road tars, asphalts, pipe coatings, water-proofing materials, dyes, pesticides, paint

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additives and wood preservatives. A single large spill of such materials containing high concentrations of polycyclic aromatic hydrocarbons can result in serious contamination requiring rapid remedial action. Additionally, various fuels, such as kerosene and gasoline, or other substances containing low concentrations of polycyclic aromatic hydrocarbons can have a cumulative effect. Potential applications of the invention include soil bioremediation at manufactured gas plant sites, coke oven sites, petroleum refineries, fuel depots, gas stations, and other industrial sites.

As described, in the preparation of a bioremediation composition of this invention, the facultative anaerobes and adsorbent are mixed with water for a short period of time prior to application to allow the facultative anaerobes to inhabit the pores of the adsorbent matrix prior to injection into the contaminated environment. As a result, the "adsorbent microcosm" is pre-inhabited by large numbers of facultative anaerobes tailored for rapid assimilation of fuel hydrocarbons, optimizing the opportunity of such anaerobes to dominate the "sulfate-reducing" niche over indigenous microbes.

This invention further provides a method for bioremediation of a site contaminated with hydrocarbons, comprising injecting a bioremediation composition of this invention at or within one or more locations of the contaminated site. Illustrative examples of contaminated environments that can be treated with a bioremediation composition of this invention include, but are not limited to, soil, sediment, sand, gravel, groundwater, aquifer material, and landfills. For example, in one embodiment the bioremediation composition can be injected into multiple sites within an aquifer, as described in Example 3. According to the method described in Example 3, the method of applying numerous injections throughout the contaminant plume provides a substantially homogenous distribution of the bioremediation composition. Thus, the method described in Example 3 does not rely on groundwater movement for effective removal of the contaminants, but rather the bioremediation composition adsorbs and decomposes the contaminant throughout the plume. As a result, the method of this invention is capable of remediating contaminated soil in a matter of weeks or months rather than

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requiring a number of years for substantially complete remediation as with conventional methods that involve the use of reactive sheets.

The bioremediation compositions of this invention provide several advantages over conventional methods and compositions for bioremediation. For example, regulatory cleanup standards can be approached very quickly compared to current techniques. The time required is dependant on soil type with silty/clay soils taking a longer period of time. In high conductivity soils (sandy or gravely soils), a 99% reduction in the concentration of contaminants can be achieved in a matter of days.

Another advantage of the bioremediation composition is that contaminants are fully degraded into non-toxic products such as carbon dioxide, water and methane. Further, the bioremediation product is non-toxic. Accordingly, no toxic by-products are generated, the impact to groundwater as a consequence of composition installation is incidental, and no drinking or groundwater standards are normally exceeded at any time during treatment. Soil and groundwater contamination may be treated simultaneously, and the compositions are easy to install using equipment commonly found throughout the industry.

Example 1

Preparation Of A Supported Catalyst By Low Temperature Decomposition Of Metal Nitrates

A measured amount of activated carbon is mixed with an associated amount of hydrated ferric nitrate calculated to provide the desired weight percentage of elemental iron in the final product. The iron salt is typically moist and on warming easily melts, so that a uniform mixture results. As the mixture is stirred, it is warmed to roughly 50°C to melt the salt. If necessary, a small amount of water may be added to produce a mixture having a creamy consistency. The mixture is then dried at a temperature of from 90 to 110°C so that the mixture can be crushed to a free flowing granular powder. Some decomposition of the nitrate salt occurs during this process.

The dried powder is then loaded into a furnace and heated in accordance with a temperature program while maintaining reducing conditions

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throughout. Initially, the temperature is slowly raised to 150 to 200°C to completely dry the catalyst and continue degradation of the iron nitrate. The temperature continues to increase, and at 300°C, the nitrate salt is completely decomposed into oxide.

Once the nitrate is completely degraded into oxide, a reducing gas such as methane gas or hydrogen gas is introduced into the furnace atmosphere and the temperature is raised to from 550 to 800°C, completely reducing the oxide to elemental iron. Methane gas is safer to use than hydrogen and therefore is preferred. The theoretical amount of water is typically formed upon complete reduction of the oxide as the temperature rises to between 400 and 450°C.

Final properties of the catalyst are influenced by the ultimate reducing temperature. For example, when the catalyst is reduced at temperatures below 700°C and then exposed to the air after cooling, an exothermic reaction may occur, oxidizing a portion of the reduced iron. However, when the final reduction is carried out at a high temperature, for example between about 700 and 800°C, the catalyst is stable and exposure to the air has no effect. If reduction is completed at a temperature of less than 450°C, the material can be pyrophoric. At reduction temperatures between about 450 and 700°C, various catalyst activities can be obtained.

Example 2:

Preparation Of A Supported Catalyst Comprising Activated Carbon Impregnated With Elemental Iron By A Precipitation Procedure

An appropriate amount of hydrated iron sulfate is dissolved in deionized water in a tank with stirring, and a measured amount of activated carbon is added. Stirring is continued after the addition is complete and a vacuum is applied to the tank to de-aerate the carbon. Once the carbon is de-aerated, a sufficient amount of a dilute solution of sodium bicarbonate is slowly added to initiate precipitation of goethite and other iron oxides onto the suspended carbon. Pressurizing the tank during addition of the bicarbonate can enhance the impregnation process. After the addition of bicarbonate is

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completed, mixing is continued for several more hours. The process is complete when testing of an aliquot for ferrous iron is negative. The slurry is then washed with deionized water and filtered several times. Finally, the collected catalyst is dried at 110°C. At this point, the carbon is impregnated with iron oxides and is ready for reduction.

The dried powder is loaded into a furnace and heated in accordance with a temperature program while maintaining reducing conditions throughout. Initially, the temperature is slowly raised to 150 to 200°C to completely dry the catalyst and continue degradation of the iron nitrate. The temperature continues to increase, and at 300°C, the nitrate salt is completely decomposed into oxide.

Once the nitrate is completely degraded into oxide, a reducing gas such as methane gas or hydrogen gas is introduced into the furnace atmosphere and the temperature is raised to from 550 to 800°C, completely reducing the oxide to elemental iron. Methane gas is safer to use than hydrogen and therefore is preferred. The theoretical amount of water is typically formed upon complete reduction of the oxide as the temperature rises to between 400 and 450°C.

Example 3:

Application Of A Composition Of This Invention

Small diameter (e.g., about 0.75 to 2 inches in diameter) injection rods are driven to targeted depths (e.g., 5 – 150 feet). The depth will depend on the power of the drill rig and the hardness of the soil. Hydraulically powered direct-push drill rigs are used to pound/push the injection rod to the desired depths, and then withdraw it about 6 inches to open up a small void below the injection point. A premixed aqueous suspension of a supported catalyst or bioremediation composition of this invention is injected under pressure down the rod. Pressure is allowed to build in the formation, and slurry begins to flow out into the formation. No attempt is made to control the path of fluid flow, but rather the objective is to achieve a substantially homogeneous distribution of the suspension within the formation. The suspension tends to

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emanate outward in all directions from the base of the injection, and the average or effective radius of influence is controlled by the amount of fluid pumped into the rod.

After injection of the first batch of the suspension, a second (fresh) batch of the suspension can be prepared, a new injection rod installed, and the process repeated. Treatment in this fashion is continued throughout the plume, reducing concentrations of contaminants in the groundwater concentrations as treatment progresses. If one could view a cross-section of the formation, the treatment regime is intended to create a three-dimensional network of material, dispersed randomly and fairly uniformly throughout the treated formation.

Many treatment technologies, ZVI for example, only work well when installed in groundwater (saturated soils) and is not effective for treatment of vadose zone (unsaturated) soils. Because activated carbon is very effective at adsorbing organic compounds from vapor streams, the compositions of this invention are able to perform nearly as well when installed in the vadose zone. As a result the products can be used equally well for treatment of contaminated soils and groundwater.

The foregoing description is considered as illustrative only of the principles of the invention. The words "comprise," "comprising," "include," "including," and "includes" when used in this specification and in the following claims are intended to specify the presence of one or more stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, or groups thereof. Furthermore, since a number of modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and process shown described above. Accordingly, all suitable modifications and equivalents may be resorted to falling within the scope of the invention as defined by the claims that follow.

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CLAIMS

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A supported catalyst for *in situ* remediation of soil and/or groundwater contaminated with a halogenated hydrocarbon, comprising an adsorbent impregnated with zero valent iron, wherein the adsorbent is capable of adsorbing the halogenated hydrocarbon.

2. The supported catalyst of claim 1, wherein said adsorbent is activated carbon.

3. The supported catalyst of claim 2, wherein said activated carbon has a surface area between about 800 and 1800 m^2/g.

4. The supported catalyst of claim 1, wherein said halogenated hydrocarbon is selected from the group consisting of halogenated aliphatic hydrocarbons, halogenated aromatic hydrocarbons, and halogenated polycyclic hydrocarbons.

5. The supported catalyst of claim 1, wherein said iron is iron powder, turnings, or chips.

6. The supported catalyst of claim 1, wherein the exposed surface area of said iron is between about 50 and 400 m^2/g.

7. The supported catalyst of claim 1, wherein said supported catalyst comprises between about 1 and 20 % by weight of said iron.

8. The supported catalyst of claim 7, wherein said supported catalyst comprises between about 15 and 20 % by weight of said iron.

9. The supported catalyst of claim 1, further comprising a reactant selected from the group consisting of aluminum, magnesium, platinum, palladium, nickel, zinc, copper, cobalt, chromium, molybdenum, and manganese.

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10. The supported catalyst of claim 1, further comprising a metal hydroxide in an amount sufficient to provide a catalyst having a pH greater than 7.

11. The supported catalyst of claim 1, produced by the method comprising:

(a) mixing an activated carbon with a hydrated iron salt;

(b) warming said mixture to melt said hydrated iron salt, thereby forming a homogeneous mixture;

(c) pyrolyzing said homogeneous mixture at a temperature sufficient to reduce said iron salt to iron oxide, thereby provide said activated carbon impregnated with said iron oxide; and

(d) subjecting said iron oxide-impregnated activated carbon to reducing conditions to reduce said iron to zero-valent iron.

12. The supported catalyst of claim 11, wherein said hydrated iron salt is ferric nitrate.

13. The supported catalyst of claim 11, wherein said pyrolyzing conditions comprise heating said mixture to a temperature between about 150 to 300°C.

14. The supported catalyst of claim 11, wherein said reducing conditions comprise heating said iron-oxide impregnated carbon to a temperature between about 450 and 800°C.

15. The supported catalyst of claim 1, produced by the method comprising:

(a) dissolving a known amount of hydrated iron salt in deionized water;

(b) suspending a known amount of activated carbon in this solution;

(c) de-aerating the suspension by applied vacuum;

(d) adding a dilute solution of sodium bicarbonate to said suspension from step (c) over a period of time to initiate precipitation of iron oxides onto said suspended carbon to provide said carbon impregnated with iron oxides;

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(e) collecting said iron oxide-impregnated carbon; and

(f) subjecting said iron oxide-impregnated activated carbon to reducing conditions to reduce said iron to zero-valent iron.

16. A composition for *in situ* bioremediation of soil and/or groundwater contaminated with hydrocarbons, comprising an adsorbent capable of adsorbing hydrocarbons, a mixture of facultative anaerobes capable of metabolizing said hydrocarbons under sulfate-reduction conditions, a sulfate-containing compound that releases sulfate over a period of time, and a nutrient system for promoting growth of said anaerobes, wherein said nutrient system includes a sulfide scavenging agent.

17. The composition of claim 16, wherein said adsorbent comprises activated carbon.

18. The composition of claim 16, wherein said sulfate-containing compound is calcium sulfate.

19. The composition of claim 16, wherein said facultative anaerobes are symbiotic.

20. The composition of claim 16, wherein said nutrient system includes a nitrogen source and a phosphorous source.

21. The composition of claim 16, wherein said nitrogen source is an ammonium salt and said phosphorus source is a monobasic alkali-metal phosphate.

22. The composition of claim 16, wherein said nitrogen source is ammonia and ammonium nitrate in a molar ratio of about 2.3 to 1.

23. The composition of claim 16, wherein said sulfide scavenging agent is iron sulfate.

24. The composition of claim 16, wherein said hydrocarbons are selected from the group consisting of aliphatic hydrocarbons, aromatic

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hydrocarbons, aliphatic alcohols, esters, ethers, and ketones, and polycyclic hydrocarbons.

25. A method for *in situ* remediation of soil and/or groundwater that has been contaminated with a halogenated hydrocarbon, comprising introducing into the contaminated soil an aqueous suspension of a supported catalyst comprising an adsorbent capable of adsorbing halogenated hydrocarbons and impregnated with zero valent iron.

26. The method of claim 25, wherein said introducing comprises:

(a) driving small diameter injection rods in the contaminated soil to a depth between about 5 and 150 feet;

(b) partially withdrawing said rod to open a void below the injection point;

(c) injecting said aqueous suspension under pressure down said rod until the pressure in said void increases to a point whereby said suspension emanates outward from said void; and

(d) repeating steps (a) through (c) throughout said contaminated soil until a substantially homogeneous distribution of said aqueous suspension throughout said contaminated soil is obtained.

27. A method for *in situ* bioremediation of soil and/or groundwater that has been contaminated with a hydrocarbon, comprising introducing into the contaminated soil an aqueous suspension of composition comprising an adsorbent capable of adsorbing said hydrocarbons, a mixture of facultative anaerobes capable of metabolizing said hydrocarbons under sulfate-reduction conditions, a sulfate-containing compound that releases sulfate over a period of time, and a nutrient system for promoting growth of said anaerobes, wherein said nutrient system includes a sulfide scavenging agent.

28. The method of claim 27, wherein said introducing comprises:

(a) driving small diameter injection rods in the contaminated soil to a depth between about 5 and 150 feet;

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(b) partially withdrawing said rod to open a void below the injection point;

(c) injecting said aqueous suspension under pressure down said rod until the pressure in said void increases to a point whereby said suspension emanates outward from said void; and

(d) repeating steps (a) through (c) throughout said contaminated soil until a substantially homogeneous distribution of said aqueous suspension throughout said contaminated soil is obtained.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/20735

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C02F 3/00; B01J 21/18
US CL : 210/610, 615, 631, 763; 502/185

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 210/611, 616, 617

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
USPTO EAST "activated carbon" and "zero-valent" and anaerobic and bioremediation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,478,954 A (CONNOLLY et al.) 23 October 1984 (23.10.1984), see entire document,	1-15
---	especially column 5 and column 16	---
A		16-28
A	US 5,436,211 A (ERBEL) 25 July 1995 (25.07.1995), column 1 lines 10 - 15	1-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 September 2003 (28.09.2003)	14 OCT 2003
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703)305-3230	Authorized officer Chester T. Barry Telephone No. 703-308-0651

Form PCT/ISA/210 (second sheet) (July 1998)

Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(d) and C.F.R. §1.97(e)(2) / Fee Authorization

This Information Disclosure Statement is being filed under 37 C.F.R. §1.97(d) after the mailing date of a Final Office Action or Notice of Allowance, but before the payment of the issue fee. The undersigned asserts in accordance with 37 CFR 1.97(e)(2), that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement under 37 C.F.R. §1.97(e)(2). Accordingly, the Information Statement Disclosure Fee of $260.00 is submitted herewith under 37 C.F.R. § 1.17(p). However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

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Statement under 37 C.F.R. §1.704(d)(i) / Patent Term Adjustment

The applicant states that each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in § 1.56 (c) more than thirty days prior to the filing of the information disclosure statement. Thus, the applicant holds that the submission of this Statement does not affect any patent term adjustment.

Respectfully submitted,

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Europäisches Patentamt
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KR20120074080A ABSORBENT MATERIALS AND METHOD FOR REMOVING PERCHLORINATED COMPOUNDS IN WASTE WATER

Applicants: RES INST IND SCIENCE & TECH [KR]

Inventors: KIM MIN KYUN [KR]

Classifications:
IPC ***C02F1/28; C02F1/58;***

CPC **B01J20/02 (KR); C02F1/283 (KR);**

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Publication: KR20120074080A·2012-07-05

Published as: KR20120074080A

ABSORBENT MATERIALS AND METHOD FOR REMOVING PERCHLORINATED COMPOUNDS IN WASTE WATER

Abstract

PURPOSE: A method for eliminating perfluoro compounds in wastewater and an absorbent for eliminating the perfluoro compounds in the wastewater are provided to improve the quality of water by eliminating the perfluoro compounds from wastewater and recycling steel-manufacturing slag. CONSTITUTION: A method for eliminating perfluoro compounds in wastewater includes a process which passes wastewater through a filter filled with an absorbent(41). Steel-manufacturing slag fine powder is used as the absorbent. The pH value of the wastewater through the filter is kept in a range between 4.0 and 6.0. The flow rate of the wastewater is kept in a range between 1.0 and 2.0mL/min. The temperature of the filter is kept in a range between 15 and 35 degrees Celsius. The steel-manufacturing slag includes calcium oxide, silicon dioxide, aluminum oxide, magnesium oxide, manganese oxide, iron oxide, carbon, titanium dioxide, and phosphorus pentoxide.

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전체 청구항 수 : 총 4 항

(54) 발명의 명칭 **폐수 중의 과불화화합물 제거용 흡착제 및 제거방법**

(57) 요 약

흡착제가 충진된 필터 내부에 폐수를 통과시켜 과불화화합물을 제거하는 방법이 소개된다. 흡착제로는 제강슬래그 미분말이 사용되며, 필터를 통과하는 폐수는 pH 4.0~6.0, 흐름속도 1.0~2.0 mL/min로 유지되도록 하며, 필터온도는 15~35℃로 유지되도록 한다.

대 표 도 - 도1

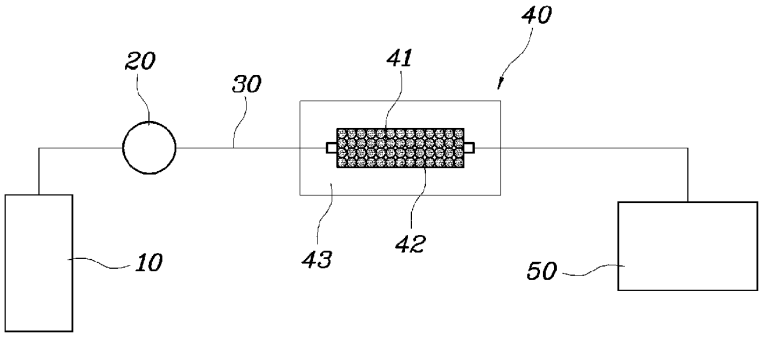


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특허청구의 범위

청구항 1

흡착제가 충진된 필터 내부에 폐수를 통과시켜 과불화화합물을 제거하되,

상기 흡착제로는 제강슬래그 미분말이 사용되며,

상기 필터를 통과하는 폐수는 pH 4.0~6.0, 흐름속도 1.0~2.0 mL/min로 유지되도록 하며, 필터온도는 15~35℃로 유지되도록 함을 특징으로 하는 폐수 중의 과불화화합물 제거방법.

청구항 2

청구항 1에 있어서, 상기 제강슬래그는,

중량%로, 산화칼슘(CaO) 25~35%, 이산화규소(SiO_2) 38~51%, 산화알루미늄(Al_2O_3) 2~3, 산화마그네슘(MgO) 5~6%, 산화망간(MnO) 2~3%, 전철분(T-Fe) 30~40%, 탄소(C) 0.6~0.8%, 이산화티탄(TiO_2) 1~1.5%, 오산화인(P_2O_5) 1~1.5%을 포함하는 조성을 갖는 것을 특징으로 하는 폐수 중의 과불화화합물 제거방법.

청구항 3

청구항 1 또는 청구항 2에 있어서, 상기 제강슬래그는 0.1mm 이하로 분쇄된 미분말임을 특징으로 하는 폐수 중의 과불화화합물 제거방법.

청구항 4

중량%로, 산화칼슘(CaO) 25~35%, 이산화규소(SiO_2) 38~51%, 산화알루미늄(Al_2O_3) 2~3, 산화마그네슘(MgO) 5~6%, 산화망간(MnO) 2~3%, 전철분(T-Fe) 30~40%, 탄소(C) 0.6~0.8%, 이산화티탄(TiO_2) 1~1.5%, 오산화인(P_2O_5) 1~1.5%을 포함하는 조성을 가지며, 0.1mm 이하로 분쇄된 미분말의 제강슬래그임을 특징으로 하는 폐수 중의 과불화화합물 제거용 흡착제.

명 세 서

기 술 분 야

[0001] 본 발명은 제철공정에서 부산하는 슬래그를 이용한 폐수 중의 과불화합물(perfluorinated compounds, PFCs) 제거용 흡착제 및 제거방법에 관한 것이다.

배 경 기 술

[0002] 최근 분석기술의 발달로 인해 정수처리 분야에서 다양한 신종 오염물질들이 정의되고 이의 처리방안에 대한 연구가 진행되고 있다.

[0003] 과불화화합물도 이러한 신종 오염물질로 분류되는 것 중 하나로서 반도체 산업을 비롯한 다양한 산업체로부터 수계를 통해 배출되는데, 매우 안정화되며 난분해성이기 때문에 하천, 호수, 퇴적물 등 우리가 생활하는 환경에 널리 잔존하는 것으로 보고되고 있다.

[0004] 한편, 과불화화합물은 이의 독성으로 인해 태아의 사산, 체중감소 등도 의심되는 물질이다. 특히 이 물질은 친수성과 소수성을 함께 가지고 있으므로 계면활성제로 널리 이용되어 왔으므로 폐수 중에서 과량의 농도로 발견될 수 있다.

[0005] 이와 같은 폐수 중에 함유된 과불화화합물을 저감하기 위한 종래의 기술은 일반적으로 활성탄이나 이온교환수지 등이 많이 사용되고 있다. 그러나, 활성탄이나 이온교환수지는 고가의 가격으로 경제적인 면에서도 부담이 커지고 있는 실정이다.

발명의 내용

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해결하려는 과제

[0006] 본 발명은 상술한 바와 같은 종래기술의 문제점에 대한 인식에 기초하여 제안된 것으로, 폐수에 함유된 과불화화합물의 제거를 위해 고가의 활성탄 대신 저가의 슬래그를 활용하여 운영비를 절감함과 아울러 폐기물로 취급되는 제철부산물을 재활용하는데 그 목적이 있다.

과제의 해결 수단

[0007] 상기의 목적을 달성하기 위한 본 발명에 따른 폐수 중의 과불화화합물 제거방법은, 흡착제가 충진된 필터 내부에 폐수를 통과시켜 과불화화합물을 제거하되, 상기 흡착제로는 제강슬래그 미분말이 사용되며, 상기 필터를 통과하는 폐수는 pH 4.0~6.0, 흐름속도 1.0~2.0 mL/min로 유지되도록 하며, 필터온도는 15~35℃로 유지되도록 한다.

[0008] 한편, 본 발명에 따른 과불화화합물 제거용 흡착제는, 중량%로, 산화칼슘(CaO) 25~35%, 이산화규소(SiO_2) 38~51%, 산화알루미늄(Al_2O_3) 2~3, 산화마그네슘(MgO) 5~6%, 산화망간(MnO) 2~3%, 전철분(T-Fe) 30~40%, 탄소(C) 0.6~0.8%, 이산화티탄(TiO_2) 1~1.5%, 오산화인(P_2O_5) 1~1.5%을 포함하는 조성을 갖는다.

[0009] 상기 흡착제는 0.1mm 이하로 분쇄된 미분말의 제강슬래그일 수 있다.

발명의 효과

[0010] 상술한 바와 같은 본 발명에 의하면, 과불화화합물을 제거하기 위해 제철부산물인 제강슬래그를 사용함으로써 제강슬래그를 재활용함과 동시에 고부가가치화함으로써 자원재활용과 수질 개선을 동시에 이룰 수 있다.

[0011] 또한, 본 발명에 의하면, 폐수 중에 포함된 퍼플루오르옥탄술포네이트(perfluorooctane sulfonate, 이하 PFOS)나 퍼플루오르옥탄산(perfluorooctanoic acid, 이하 PFOA)과 같은 과불화화합물을 효과적으로 제거할 수 있다.

도면의 간단한 설명

[0012] 도 1은 본 발명의 일실시예에 따른 과불화합물 제거 공정의 설명을 위한 개략도이다.

발명을 실시하기 위한 구체적인 내용

[0013] 이하에서는 첨부된 도면을 참조하여 본 발명의 바람직한 실시예에 따른 폐수 중의 과불화화합물 제거용 흡착제 및 제거방법에 대하여 살펴본다.

[0014] 본 발명은 제철과정에서 부산하는 슬래그를 폐수 중의 과불화화합물 제거용 흡착제로 활용하기 위한 방안을 연구하던 중, 특히 제강슬래그가 과불화화합물 흡착제용으로 우수한 성능을 가지고 있음을 알게 된 것에 기초한다.

[0015] 아래의 표 1은 본 발명에서 이용되는 제강슬래그의 화학적 조성을 나타낸 것이다.

표 1

[0016]

성분	CaO	SiO_2	Al_2O_3	MgO	MnO	T-Fe	C	TiO_2	P_2O_5
wt%	25~35	38~51	2~3	5~6	2~3	30~40	0.6~0.8	1~1.5	1~1.5

[0017] 위의 표 1에서 보는 바와 같이 제강슬래그는 칼슘이나 알루미늄 등 알칼리성 금속이 매우 높게 함유되어 있으므로 과불화화합물과 같이 음이온 형태의 유기화합물에 대한 흡착능이 매우 우수한 것으로 판단된다.

[0018] 위와 같은 제강슬래그는 과불화화합물의 흡착 성능을 향상시키기 위해 분쇄된다. 실험 결과 제강슬래그를 직경 0.1mm 이하로 분쇄함에 의해 표면적은 17㎡/g로 향상되었다. 이렇게 분쇄된 제강슬래그는 재질이 단단하여 내구성이 커서 충전제의 수명이 반영구적이다.

[0019] 도 1에는 위와 같은 제강슬래그 미분말의 흡착제를 이용한 과불화화합물 제거 시스템이 도시되어 있다.

[0020] 도 1에서 보듯이, 시스템은 폐수가 폐수탱크(10)로부터 정량펌프(20)를 거쳐 공급라인(30)을 따라 필터(40)로

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공급된 후, 폐수회수탱크(50)로 보내어지도록 구성된다.

[0021] 상기 정량펌프(20)는 폐수의 주입속도 조절을 위한 것이며, 필터(40)는 본 발명에 따라 제조된 제강 슬래그의 흡착제(41)가 칼럼(42) 내에 충진되고 온도제어장치(43)에 의해 칼럼(42)의 온도가 유지되도록 구성된다.

[0022] 위와 같은 시스템을 이용한 본 발명에 따른 흡착제의 과불화화합물 흡착 및 저감 성능에 대한 실험 예를 살펴본다. 아래에는 몇 가지의 대표적인 실험 예들만 기재되어 있다는 점에 유의할 필요가 있다.

[0023] 실시예 1

[0024] 먼저 흡착능 실험에 이용할 제강슬래그를 볼밀로 파쇄하여 직경 0.1mm 이하의 미분말 형태로 제조한 후, 증류수로 세척 후 표면의 유기물 제거를 위해 600℃에서 12시간 이상 열처리 하였다.

[0025] 위와 같이 제조된 미분말 형태의 제강슬래그 100g을 충진재로 이용하여 흐름속도 변화에 따른 과불화화합물의 흡착능을 비교, 평가하였다.

[0026] 실험에 사용한 과불화화합물은 퍼플루오르옥탄산(PFOA)로서, 농도 100㎍/L의 PFOA를 함유하는 폐수를 1분 동안 필터 내부에 주입하였다. 폐수의 주입 흐름속도는 1.0~10.0 mL/min까지 변경하였으며, 칼럼의 온도는 섭씨 25도로 유지하였고, 폐수의 pH는 0.02M NaH_2PO_4를 이용하여 3.0으로 조정하였으며, 그 결과를 표 2에 나타냈다.

표 2

[0027]

흐름속도(mL/min)	배출농도(㎍/L)	제거효율(%)
1.0	44.8	55.2
2.0	48.7	51.3
5.0	67.2	32.8
10.0	91.4	8.6

[0028] 위의 표 2에서 보듯이, 과불화화합물이 포함되어 있는 폐수를 흐름속도를 변화시키면서 제강슬래그를 통과시킨 결과, 흐름속도 1.0~2.0mL/min의 범위에서 제거효율이 우수하며, 특히 100㎍/L의 PFOA중 55.2%가 흡착, 제거된 1.0mL/min의 흐름속도에서 가장 높은 흡착능을 보였다. 흐름속도 1.0mL/min 미만은 공정효율 측면에서 바람직하지 못한 것으로 판단된다.

[0029] 실시예 2

[0030] 위의 실시예 1에서와 동일한 시스템 및 미분말 형태의 제강슬래그 100g이 충진된 필터를 이용하여 칼럼 온도 변화에 따른 제강슬래그의 과불화화합물 흡착능을 비교하였다.

[0031] 칼럼의 온도를 섭씨 15~25도로 변화시키면서, 농도 100 ㎍/L의 PFOA를 함유하는 폐수를 1분 동안 1.0 mL/min의 흐름속도로 필터에 주입하였다. 폐수의 pH는 0.02M NaH_2PO_4를 이용하여 3.0으로 조정하였으며, 그 결과를 표 3에 나타냈다.

표 3

[0032]

칼럼온도(℃)	배출농도(㎍/L)	제거효율(%)
15	51.5	48.9
25	44.8	55.2
35	53.4	46.6
50	68.7	31.3

[0033] 위의 표 3에서 보듯이, 과불화화합물이 포함되어 있는 폐수를 제강슬래그가 포함된 칼럼의 온도를 변화시키면서 제강슬래그를 통과시킨 결과, 칼럼온도 15~35℃에서, 보다 바람직하게는 20~30℃에서 과불화화합물 제거효율이 우수하며, 100 ㎍/L의 PFOA중 55.2%가 흡착, 제거된 25 ℃의 칼럼 온도에서 가장 높은 흡착능을 나타냈다.

[0034] 실시예 3

[0035] 위의 실시예 1에서와 동일한 시스템 및 미분말 형태의 제강슬래그 100g이 충진된 필터를 이용하여 폐수의 pH

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변화에 따른 제강슬래그의 과불화화합물 흡착능을 비교하였다.

[0036] 폐수의 pH를 2.0~12.0으로 변화시키면서, 농도 100 ㎍/L의 PFOA를 1분 동안 1.0 mL/min의 흐름속도로 필터에 주입하였으며 칼럼의 온도는 섭씨 25도로 유지 하였다. 폐수의 pH를 조절하기 위해 각 pH에 적당한 완충용액을 조제하여 사용하였다. 실험 결과는 아래 표 4에 나타내었다.

표 4

[0037]

폐수의 pH	배출농도(㎍/L)	제거효율(%)
2.0	48.3	51.7
3.0	44.8	55.2
4.0	46.9	53.1
5.0	38.2	61.8
6.0	43.9	56.1
7.0	51.4	48.6
8.0	58.7	41.3
9.0	78.1	21.9
10.0	81.4	18.6
11.0	83.5	16.5
12.0	89.6	10.4

[0038] 위 표 4에서 보듯이, 과불화화합물이 포함되어 있는 폐수의 pH를 변화시키면서 제강슬래그를 통과시킨 결과, 폐수의 산도가 pH 3~6인 범위에서 대체로 우수한 흡착능을 보였고, pH 5에서 61.8%의 가장 높은 흡착능을 나타냈다. 과불화화합물의 흡착을 위해 산성화시킨 폐수를 다시 중성화할 필요가 있기에 폐수의 산도는 pH 5를 타겟으로 하여, pH 4~6 정도로 조절되는 것이 바람직한 것으로 판단된다.

[0039] 이상 본 발명의 특정 실시예에 관하여 도시하고 설명하였지만, 하기의 특허청구범위에 기재된 발명의 기술적 사상으로부터 벗어나지 않는 범위 내에서 본 발명은 다양하게 수정 및 변경될 수 있고 또 이것이 본 발명의 기술분야에서 통상의 지식을 가진 자에게 자명하다는 것이 이해될 필요가 있다.

부호의 설명

[0040] 10: 폐수탱크 20: 정량펌프

30: 폐수 공급관 40: 필터

41: 흡착제 42: 칼럼

43: 온도제어장치 50: 폐수회수탱크

도면

도면1

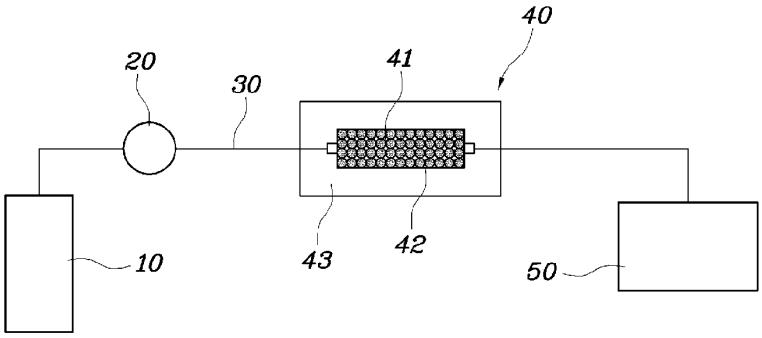


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APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**12/28/2022 09:08:58 AM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	61358286	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Nicholas Kokkinos

Documents

TOTAL DOCUMENTS: 5

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
KR20120074080A_w_Eng_trans.pdf	6	Foreign Reference	446 KB
EP1521723A1.pdf	29	Foreign Reference	1562 KB
123450-013001_Transmittal for SIDS_12-28-2022.pdf	2	Transmittal Letter	109 KB
123450-013001_SafeHarbor_sb0133_12-28-2022.pdf	2	Patent Term Adjustment Statement under 37 CFR 1.704(d) filed with an IDS	227 KB
123450-013001-SB08.pdf	4	Information Disclosure Statement (IDS) Form (SB08)	1020 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
KR20120074080A_w_Eng_trans.pdf	B813CA168093B30A87F1B47B789F1B5894B00BCF5C378F6BA3431EC4AD355478A595A41C0DC8500F4346BC2B7836AA4657CB940DD6F74E53A37BFD35553A1BDE
EP1521723A1.pdf	F37E7B19E8DE68500F36F3C494830158D9CCD89C4AC69C579F657D1FC9AB54F3FC13B1D70154AB75022A418D231CB17591FC7FA13239A76B194CA8BFA09E8B87
123450-013001_Transmittal for SIDS_12-28-2022.pdf	0D6C882652783199E54E8903372194CDB1F5D45A11B0C3AD99A5ED7583ED84179E2197450599DEF619D357A8FD0A19A11DB5FC0E4CB5AC53DB3ABAB9D5ACE2FE
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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. DISTEFANO
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

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Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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X See attached certification statement.

X The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2022-11-23
Name/Print	Nicholas C. Kokkinos	Registration Number	76,979

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4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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UNITED STATES
PATENT AND TRADEMARK OFFICE

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Alexandria, VA 22313 - 1450
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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**11/23/2022 10:52:27 AM ET**	**123450-013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	61213903	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Nicholas Kokkinos

Documents

TOTAL DOCUMENTS: 4

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
123450-013001_SafeHarbor_sb0133_11-23-2022.pdf	2	Patent Term Adjustment Statement under 37 CFR 1.704(d) filed with an IDS	249 KB
123450-013001_Transmittal for SIDS_11-23-2022.pdf	2	Transmittal Letter	109 KB
123450-013001-Supp IDS.pdf	4	Information Disclosure Statement (IDS) Form (SB08)	1017 KB
WO8100399A.pdf	24	Foreign Reference	1866 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
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New International Application Filed with the USPTO as a Receiving Office

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Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(d) and C.F.R. §1.97(e)(2) / Fee Authorization

This Information Disclosure Statement is being filed under 37 C.F.R. §1.97(d) after the mailing date of a Final Office Action or Notice of Allowance, but before the payment of the issue fee. The undersigned asserts in accordance with 37 CFR 1.97(e)(2), that no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in § 1.56(c) more than three months prior to the filing of the information disclosure statement under 37 C.F.R. §1.97(e)(2). Accordingly, the Information Statement Disclosure Fee of $260.00 is submitted herewith under 37 C.F.R. § 1.17(p). However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

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Statement under 37 C.F.R. §1.704(d)(i) / Patent Term Adjustment

The applicant states that each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in § 1.56 (c) more than thirty days prior to the filing of the information disclosure statement. Thus, the applicant holds that the submission of this Statement does not affect any patent term adjustment.

Respectfully submitted,

DLA PIPER LLP (US)

/Nicholas Kokkinos/

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Date: November 23, 2022

UNITED STATES
PATENT AND TRADEMARK OFFICE

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ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	11/23/2022 10:52:27 AM ET	123450-013001

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

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APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	61213903	AUTHORIZED BY	Nicholas Kokkinos
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
DA / 604406	E2022AMA54254798	Paula Watson

PRE-AUTHORIZED ACCOUNT	PRE-AUTHORIZED CATEGORY
604406	37 CFR 1.16 (National application filing, search, and examination fees); 37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.20 (Post Issuance fees); 37 CFR 1.21 (Miscellaneous fees and charges)

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
1806	SUBMISSION OF AN INFORMATION DISCLOSURE STATEMENT	260.00	1	260.00
			TOTAL AMOUNT:	$260.00

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National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: PTA.IDS
Document Description: Patent Term Adjustment Stmt Under 37 CFR 1.704(d)

PTO/SB/133 (10-21)

PATENT TERM ADJUSTMENT STATEMENT UNDER 37 CFR 1.704(d)		
	Application Number	16/839,862
	Filing Date	April 3, 2020
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Practitioner Docket No.	123450-013001

APPLICANT HEREBY STATES THE FOLLOWING (please review 37 CFR 1.704(d) before filing this form):

☑ Each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

AND/OR

☐ Each item of information contained in the information disclosure statement is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

INSTRUCTIONS:

- **This form will not satisfy the requirement of 37 CFR 1.97(e).** The present statement is filed under 37 CFR 1.704(d) and will not substitute for compliance with any of the requirements of 37 CFR 1.97 and 1.98. For an information disclosure statement to comply with 37 CFR 1.97(c) or (d), the information disclosure statement must be accompanied by a statement under 37 CFR 1.97(e) notwithstanding any statement filed under 37 CFR 1.704(d).
- The present form (PTO/SB/133) should be filed concurrently with the information disclosure statement to derive benefit under 37 CFR 1.704(d).

Signature	/Nicholas Kokkinos/	Date	11/23/22
Typed or Printed Name	Nicholas C. Kokkinos	Practitioner Registration Number	76,979

***Note**: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature. If necessary, submit multiple forms for more than one signature, see below*.*

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The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

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3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
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5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(71) Applicant: THE CARBORUNDUM COMPANY [US/US]; 345 Third Street, Post Office Box 156, Niagara Falls, NY 14302 (US).

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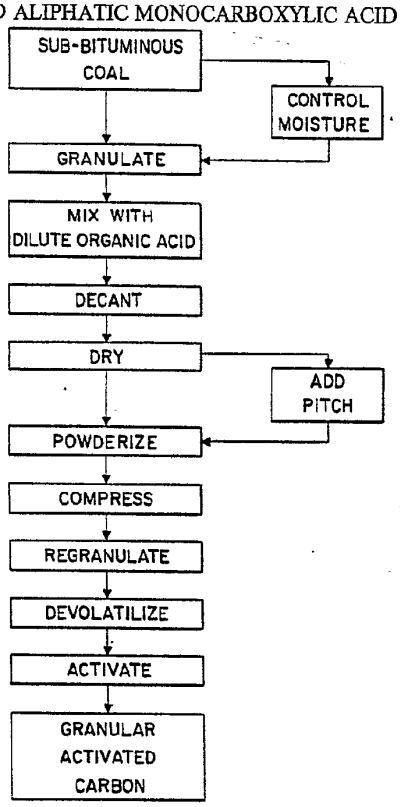
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(54) Title: HARD GRANULAR ACTIVATED CARBON MANUFACTURED FROM SUB-BITUMINOUS COAL TREATED WITH DILUTE SOLUTION OF SATURATED ALIPHATIC MONOCARBOXYLIC ACID

(57) Abstract

Hard granular activated carbon, suitable for liquid phase applications such as water and waste water treatment, is manufactured from sub-bituminous coal by crushing and screening the as received coal containing about 10 to about 25% moisture by weight to produce granules, treating the granules with a dilute aqueous solution of a satured aliphatic monocarboxylic acid such as formic or acetic acid, at a concentration of about 2% to about 30% by weight, the concentration being increased as the acid strength decreases, for a time and at a temperature and solution to coal ratio sufficient for further processing, decanting the acid, and drying the granules at least partially to a moisture, including acid, content below about 25% by weight. The dried granules are mixed with from 0 to about 15% by weight of coal tar pitch, and are milled to form fine powder of not less than about 60% by weight -325 mesh, preferably more than about 65% by weight -325 mesh. The powder is compressed into shapes, such as pellets or thin corrugated sheets under high pressure, and then granulated to form 6/20 mesh granules. The reformed granules are devolatilized, without prior charring, by directly heating to and at a temperature higher than the charring temperature in a substantially oxygen-free atmosphere, and then activated by heating to and at a temperature higher than the devolatilizing temperature in an atmosphere containing a gaseous activating agent.



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HARD GRANULAR ACTIVATED CARBON MANUFACTURED FROM SUB-BITUMINOUS COAL TREATED WITH DILUTE SOLUTION OF SATURATED ALIPHATIC MONOCARBOXYLIC ACID

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to granular activated carbon manufacture, and more particularly to a new and improved process for making hard granular activated carbon from sub-bituminous coal treated with dilute solution of saturated aliphatic monocarboxylic acid, and to a new and improved hard granular activated carbon made by such process and having properties which make it suitable for use in liquid phase applications such as water and waste water treatment.

Glossary of Terms

In order to facilitate a clear understanding of this invention, various terms of art employed herein are defined as follows.

Abrasion number - is a measure of the resistance of the activated carbon granules to degrading on being mechanically abraded. It is measured by contacting a sample with steel balls in a pan on a machine and shaking the contents for a given time and determining the resultant particle size distribution and hence the mean particle diameter. The abrasion number is the ratio of the final average (mean) particle

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diameter to the original average (mean) particle diameter (determined by screen analysis) times 100.

Activated carbon - is a carbon which is "activated" by heating to high temperature preferably with steam or carbon dioxide as the gaseous activating agent in producing an internal porous particle structure.

Activation or activating - means heating coal at high temperatures on the order of about 600°C. to about 1100°C. in the presence of a gaseous activating agent, as is well known in the art. The heating rate during activation from the minimum activation temperature to the maximum activation temperature may vary widely, e.g., from about 100 to about 1000°C. per hour, but usually is nearer 100°C. per hour.

Adsorption isotherm - is a measurement of the adsorptive capacity of an adsorbent (viz. granular activated carbon) as a function of the concentration, or pressure, of the adsorbate (viz. N_2) at a given temperature. It is defined as the constant temperature relationship between the amount adsorbed per unit weight of adsorbent and the equilibrium concentration, or partial pressure.

Apparent density - is the weight per unit volume of homogeneous granular activated carbon. To assure uniform packing of the granules during measurement, a vibrating trough is used to fill the measuring device.

Ash - is a principal mineral constituent of coal, carbon and pitch. It is normally defined as a weight percent basis after a given amount of sample is reduced to ash.

Average (mean) particle diameter - is a weighted average diameter of a granular activated carbon sample. A screen analysis is run and the average particle diameter is calculated by multiplying the weight of each fraction by its

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average diameter, adding the products, and dividing by the total weight of the sample. The average diameter of each fraction is taken as the size midway between the sieve opening through which the fraction has passed and the sieve opening on which the fraction was retained. It usually is expressed in mm.

Carbon tetrachloride activity number - is the steady state percentage increase in the weight of a bed of activated carbon after air which has been saturated with carbon tetrachloride at 0°C. is passed through the carbon at 25°C. It is expressed as a percentage number.

Charring - means heating coal at low temperatures on the order of about 175°C. to about 275°C. in the presence of oxygen.

Coking value - is usually expressed as percent residual carbon obtained when a dry sample of coal, tar or pitch is vaporized or pyrolized for a specific time at a specific temperature that limits the available oxygen supply (ASTM Method D-2416). The coking value, expressed as percent residual carbon, indicates the coke forming properties of the material.

Devolatilizing - means heating coal at intermediate temperatures on the order of about 400°C. to about 600°C. in an oxygen-free atmosphere.

Direct activation or directly activating - means heating a coal, preferably in a granular form, directly (without prior charring and devolatilization) and rapidly (at a heating rate of about 500°C. per hour or more) to an activating temperature higher than the devolatilization temperature (of the order of 600° to 1100°C.) in an atmosphere containing a gaseous activating agent and maintaining the desired activating temperature for the desired period of time.

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Granular activated carbon - is "activated carbon" which has a particle size, i.e., "mesh", which is not less than about 60 and preferably not less than about 40.

Iodine number - is the milligrams of iodine adsorbed by one gram of granular activated carbon at an equilibrium filtrate concentration of 0.02 N iodine. It is measured by contacting a single sample of carbon with an iodine solution and extrapolating to 0.02 N by an assumed isotherm slope. This number can be correlated with the ability of granular activated carbon to adsorb low molecular weight substances.

Mesh - (or mesh size) is the particle size of granules as determined by the U.S. Sieve Series or the Tyler Series. Usually, this term refers to the sizes of the two screens, in either of the above Series, between which the bulk of a sample falls. For example, "8/30 mesh" (or "8 by 30 mesh" or "8 x 30 mesh") means that 90% by weight of the sample will pass through a No. 8 screen but will be retained on a No. 30 screen. Likewise, 6/0 mesh means that 90% by weight will pass through a No. 6 screen, with no lower limit on granular size. Alternatively, this term refers to a maximum particle size, such as in defining the fineness of powder material. For example, "65% by weight -325 mesh powder" means that 65% by weight of a given sample passes through a No. 325 mesh screen.

Molasses number - is calculated from the ratio of the optical densities of the filtrate of a molasses solution treated with a standard activated carbon and the activated carbon in question.

Pitch - is a black or dark viscous substance obtained as a residue in the distillation of organic materials and especially tars.

Powder - means powdered activated carbon which has a particle size, i.e., "mesh", which is smaller than about 40

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and preferably smaller than about 60. The larger the mesh number, the smaller the size.

Sub-bituminous coal - is an intermediate stage coal which ranks above lignite and brown coals, but below bituminous coal. In the as received condition it has, by weight, (1) a proximate analysis of: from about 10% to about 25% moisture, from about 35% to about 45% volatile material, from about 2% to about 5% ash, and from about 25% to about 45% fixed carbon, and (2) an ultimate analysis of: from about 65% to about 75% carbon, from about 4% to about 8% hydrogen, from about 0.5% to about 2.0% nitrogen, and from about 0.5% to about 1.0% sulfur. See ASTM Standard D-388-66.

Surface area - is the amount of surface area per unit weight of granular activated carbon; it is determined from the nitrogen adsorption isotherm by the Brunauer, Emmett and Teller (BET) method, and it is expressed in m^2/gram.

Volumetric Iodine and Molasses Numbers - are determined by multiplying by the apparent density, in order to express these properties independently of such density.

Discussion of the Art

Granular activated carbon is particularly useful in liquid phase applications, such as water and waste water treatment, not only because it is highly effective in purifying the intake, as well as the effluent from municipal and industrial systems but also because it can be regenerated for repeated use. In order to accomplish these objectives, however, it must possess certain properties, namely, a minimum surface area of about 900 m^2/gram for adequate adsorption capacity, a minimum volumetric Iodine number of about 410, preferably about 480, for adequate adsorption, especially of low molecular weight substances, a minimum volumetric Molasses number of about 90, preferably about 100, for adequate decolorizing, a maximum ash content (by weight)

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of not more than about 12%, and preferably not more than about 8%, for purity, a minimum abrasion number of about 70 and preferably not less than about 80, for adequate hardness in maintaining granular integrity in use and in regeneration, and a minimum apparent density of not less than about 0.46 gram/cc, preferably not less than about 0.48 gram/cc, for obtaining the dense, closely packed beds and columns needed in water and waste water treatment.

Hard granular activated carbon can be obtained from bituminous, sub-bituminous and brown coals, such as disclosed in U.S. Patents 4,144,193, 4,032,476, 4,131,566, 4,149,994, 4,149,995, and 4,157,314.

However, in each of these patents, inorganic mineral acids were employed, and until the present invention, it was not known that anyone else had accomplished this objective by a saturated aliphatic monocarboxylic acid treatment of sub-bituminous coal.

In the '193, '566, '994 and '314 patents, a dilute aqueous solution of inorganic mineral acid was employed, requiring removal of the acid prior to further processing, in order to avoid corrosion of the heat treating equipment. In the '476 and '995 patents, a small amount of concentrated mineral acid was mixed with the coal granules, thereby eliminating the acid removal step, but requiring special lining of the heat treating equipment in order to avoid the corrosive action of the acid.

As for the heat treatment itself, each of the aforesaid patents, except the '566 patent, discloses the elimination of the charring or low temperature heat oxidation step found to be necessary in dealing with bituminous coal. In the '566 patent, both the acid treatment and charring steps were found to be necessary for attaining the desired results when treating low rank agglomerating but not good coking bituminous

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the '314 patent, it has been found that both the charring and devolatilization steps could be eliminated prior to the activation step in heat treating the sub-bituminous granules. Likewise, the disclosures of U.S. Patents 3,483,134, 3,876,505, and 4,014,817 are of interest, but each discloses the necessity for the charring or low temperature heat oxidation step, and none discloses a hard granular activated carbon product.

Various organic compositions have been added to coal to facilitate its conversion into activated carbon. Pitch, which is a complex mixture of organic materials, has long been a well-known additive, e.g., see U.S. Patent 3,539,467. U.S. Patent 3,483,134 discloses the addition of a volatizable organic material such as an aldehyde, amino compound, cereal grain, or plant material to bituminous coal to facilitate activated carbon production, but, as noted above, does not produce a hard product. U.S. Patent 3,864,277 discloses the addition of lignosulfonate as a binder to transform soft, woody materials into activated carbon. In addition, Canadian Patent 906,754 teaches the preparation of activated low grade coal (not carbon) by treatment with spent industrial acids including mineral and/or organic acids. However, only aromatic organic compounds are mentioned for admixture with mineral acids.

Therefore, while various organic additives and binders have long been utilized in the art, no one else has utilized saturated aliphatic monocarboxylic acids as treating agents for the production of hard granular activated carbon from sub-bituminous coal according to the process of this invention.

SUMMARY OF THE INVENTION

It is to be understood that coals are composed essentially of organic carbonaceous materials of varying volatiles together with portions of inorganic salts and other compounds. The object of processes for the formation of

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activated carbon is to produce carbon in an active form within a suitable physical environment - that is, with a suitable pore size, density and hardness. It is highly desirable that the ash content be as small a percentage of the total mass of product as is possible, this to improve the physical characteristics of said product. The ash, which arises primarily from the inorganic material present in the starting coal, may be minimized either by removal of the inorganic materials prior to activation or by increasing the overall proportion of carbonaceous materials retained in the product during the course of its production.

It is believed that the inorganic mineral acid treatment taught by certain of the patents referred to above serves to fix relatively volatile carbonaceous materials of the starting material coal in a relatively non-volatile form, thus minimizing loss of carbonaceous material via volatilization during the course of production. The salutary properties and yield resulting from the inorganic treatment are thought to be directly attributable, at least in part, to this fixation effect.

Viewing the inorganic acids used in the aforementioned treatment processes as being inorganic materials from which ash may form, makes it clear that removal thereof prior to further production is essential to a minimization of ash content in the product. The often elaborate washing procedure which is necessary to effect this removal adds measureably to the cost of production. In addition, subsequent drying of the washed coal is hindered by the residual inorganic acid.

The use of saturated aliphatic monocarboxylic organic acids, as taught by this invention, offers salutary benefits to the production of granular activated carbon from subbituminous coal. These organic acids are believed to be as effective in fixing volatile carbonaceous materials of subbituminous coal as are inorganic acids, but such organic acids do not require elaborate washing procedures prior to

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further processing. Furthermore, due to the fact that these organic acids are carbonaceous materials in their own right, and are not inorganic, failure to remove the totality of the treating organic acid will not lead to a significant increase in the ash content of the products. In addition, these organic acids are, in general, volatile and can be recovered upon heating of the treated coal. Thus, simple decantation of the organic acid from the coal or a simple rinsing procedure will generally suffice without further washing.

Accordingly, a general primary objective of the present invention is (1) to provide a new and improved process for making hard granular activated carbon from low cost sub-bituminous coal wherein the charring step necessary for processing bituminous coal is eliminated, while the overall yield of granular activated carbon is increased significantly by appropriate treatment of sub-bituminous coal with a dilute aqueous solution of saturated aliphatic monocarboxylic organic acid, with or without the addition of carbonaceous binder; (2) as well as to provide a new and improved hard granular activated carbon made by such process and having the aforementioned desired properties of adsorption (as measured by volumetric Iodine number), decolorization (as measured by volumetric Molasses number), purity (as measured by ash content), hardness (as measured by abrasion number) and density (as measured by apparent density), which make it suitable for use in liquid phase applications, such as water and waste water treatment.

To this end, the invention includes (1) a process for making hard granular activated carbon, comprising: forming granules from sub-bituminous coal; reducing the granules to form fine powder; compressing the powder to form shapes; reducing the shapes to reform granules, and thereafter subjecting the reformed granules to heat treatment, without charring, until activated, wherein the improvement comprises: treating the initially formed granules with a dilute aqueous solution of saturated aliphatic monocarboxylic acid, at a

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concentration from about 2% to about 30%, for a time and at a temperature and solution to coal ratio sufficient for further processing, decanting excess acid, and drying the granules at least partially to a moisture, including acid, content below about 25% and mixing the granules with 0 to about 15% of a carbonaceous binder; and (2) hard granular activated carbon made by such process and having the physical characteristic of high granular integrity permitting repeated handling, use, regeneration and reuse. All percentages used herein are by weight, unless otherwise specified, and the shapes formed by compressing may be of various configurations larger than the granules such as pellets, briquettes, thin sheets of corrugated cross-section, etc. Likewise, the heat treatment may involve separate sequential devolatilization and activation steps, or direct activation eliminating the separate devolatilization step.

A specific primary objective is to provide (1) such process wherein the preferred saturated aliphatic monocarboxylic acid is formic acid, at a preferred concentration of from about 3% to about 6% by weight, and (2) hard granular activated carbon made by such process and having an abrasion number of not less than about 70.

Another specific primary objective is to provide (1) such process wherein the treated granules are mixed within from 0 to about 15% by weight of a carbonaceous binder, and (2) hard granular activated carbon made by such process and having an abrasion number of not less than about 80.

Additional objectives and advantages of the invention will become apparent upon consideration of the following detailed description and accompanying drawing wherein:

BRIEF DESCRIPTION OF THE DRAWING

The single figure is a block diagram or flow sheet illustrating schematically the various steps of the process,

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as well as the resulting product, both embodying the invention.

EXAMPLE 1

(No Acid + Pitch)

The starting material for this and each of the following examples was a batch of Wyoming sub-bituminous (Elkol) coal, that being used in this Example having the following analysis percent by weight, in the as received and dry conditions respectively:

PROXIMATE ANALYSIS

CONSTITUENTS	AS RECEIVED	DRY
Moisture	15.1	-
Volatile Material	37.1	43.70
Ash	2.92	3.44
Fixed Carbon	44.88	52.86

2000 grams of coal granules having a mesh size of 8/30 and 220 grams of coal tar pitch (10%) were blended by stirring together in a Hobart mixer for approximately 10 minutes. The mixture was pulverized in a hammer mill to produce a fine powder of 81% -325 mesh. This powder was compressed into cylindrical pellets of 0.5 inch diameter by 0.5 inch height at 80,000 psi to an apparent density of 1.2 grams/cc, with the pellets being crushed in a jaw mill and screened to reform and collect granules of 6/20 mesh size. These reformed granules then were devolatilized as follows.

600 grams were placed in a stainless steel screen basket which was rotated within a tube furnace at about 2 rpm. The furnace was constructed such that the gaseous environment of the basket and granules could be controlled. The granules were heated to about 600°C. while in an inert gas atmosphere of nitrogen or argon. This temperature and atmosphere were

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maintained for 1 hour, after which time the material was allowed to cool to room temperature. 336 grams of carbonized (devolatilized) material with an apparent density of .629 gram/cc were obtained, giving a yield on devolatilization of 56%.

300 grams of this material were activated as follows: The granules were placed in a controlled atmosphere rotary kiln and were heated to a temperature of 870°C. under a nitrogen flow, at which time steam carried by the flowing nitrogen was passed through the system at a rate corresponding to about 800 grams of water per hour. This was continued for a period of 30 minutes, after which time the material was allowed to cool to room temperature under flowing nitrogen. 153 grams of granular activated carbon were obtained, with an activation yield of 51.0%, and an overall yield of 28.6% (51.0 x 56/100). The product had the following properties: apparent density .501 gram/cc; Iodine number 722 (722 x .501 = 361 volumetric); Molasses number 249 (249 x .501 = 125 volumetric); abrasion number 83; ash content 6.28%, and mean particle diameter 1.58 mm.

As will be evident, this material was not suitable for liquid phase applications, because of its low Iodine number.

EXAMPLE 2
(5% Formic Acid + Pitch)

The sub-bituminous coal employed in this Example had the following analysis:

PROXIMATE ANALYSIS

CONSTITUENTS	AS RECEIVED	DRY
Moisture	17.40	-
Volatile Material	38.20	46.25
Ash	2.44	2.95
Fixed Carbon	41.95	50.79

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The procedure of Example 1 was repeated, except as follows. 800 grams of 6/20 mesh granules were stirred for 1 hour at 95°C. with an aqueous solution of 150 cc of 90% formic acid in 3020 cc of water (about 5.1% acid and about 4/1 solution to coal ratio). The acid was decanted from the coal, which was quickly rinsed with water and decanted again. The treated coal was dried at 120°C. for 1/2 hour to a moisture content of about 2 or 3%, with 1592 grams of the dried coal being mixed with 102 grams of coal tar pitch (6% pitch), and this mixture was ground in a hammer mill to yield a fine powder of 77% -325 mesh. The powder then was compressed into the aforesaid cylindrical pellets in a hydraulic press operating at 80,000 psi, which pellets were then crushed into granules, those of 6/20 mesh being collected.

600 grams of the reformed granules were devolatilized as in Example 1, and following cooling to room temperature, 296 grams of the devolatilized material having an apparent density of 0.635 gram/cc were produced at a yield of 49.3%.

Next, 300 grams of this material were activated as in Example 1, but the temperature was increased to 1000°C., with the steam rate corresponding to 750 cc of water per hour and the temperature maintained over a period of 1/2 hour.

147 grams (activation yield 49.7%, overall yield 24,5%) of granular activated carbon having the following properties were produced: apparent density 0.495 gram/cc; abrasion number 84; mean particle diameter 1.46 mm; Iodine number 918 (volumetric 454); Molasses number 231 (volumetric) 107; and ash content 6.9%. Thus, the product was well suited in all respects for use in liquid phase applications.

During the course of experimentation, the following were learned. The size of the granules being acid treated, temperature of treatment (which usually is below 100°C because of the use of the dilute aqueous acid solution), time of treatment, concentration of acid and the ratio of dilute

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aqueous acid solution to coal all have important effects on further processability of the coal to form granular activated carbon. Therefore, the specific members cited in this and in the ensuing inventive Examples are merely illustrative and not restrictive. For example, both coarser and finer granules can be employed during treatment with corresponding results, with the time of treatment being longer for coarser particles and shorter for finer particles. Likewise, the lower the temperature the longer the time, and vice versa. In Addition, the lower the concentration of acid, the longer the time, and vice versa, while the solution to coal ratio probably should not be less than about 1/1. Generally speaking then, these parameters should be sufficient for further processing of the coal to form granular activated carbon.

Moreover, this acid treatment is believed to have a beneficial effect on the coal resulting in increased activity, as will be evident from the substantial increase in the Iodine number from 722 in Example 1 to well over 900 in this and in each of the remaining inventive Examples. Expressed in percentages, the Iodine number was increased by at least 25% (this Example) and as much as 45% (Example 4).

EXAMPLE 3

(3.5% Formic Acid + Pitch)

The sub-bituminous coal used herein had the following analysis:

PROXIMATE ANALYSIS

CONSTITUENTS	AS RECEIVED	DRY
Moisture	18.67	-
Volatile Material	35.84	44.07
Ash	2.43	2.99
Fixed Carbon	43.06	52.94

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aqueous acid solution to coal all have important effects on further processability of the coal to form granular activated carbon. Therefore, the specific members cited in this and in the ensuing inventive Examples are merely illustrative and not restrictive. For example, both coarser and finer granules can be employed during treatment with corresponding results, with the time of treatment being longer for coarser particles and shorter for finer particles. Likewise, the lower the temperature the longer the time, and vice versa. In Addition, the lower the concentration of acid, the longer the time, and vice versa, while the solution to coal ratio probably should not be less than about 1/1. Generally speaking then, these parameters should be sufficient for further processing of the coal to form granular activated carbon.

Moreover, this acid treatment is believed to have a beneficial effect on the coal resulting in increased activity, as will be evident from the substantial increase in the Iodine number from 722 in Example 1 to well over 900 in this and in each of the remaining inventive Examples. Expressed in percentages, the Iodine number was increased by at least 25% (this Example) and as much as 45% (Example 4).

EXAMPLE 3

(3.5% Formic Acid + Pitch)

The sub-bituminous coal used herein had the following analysis:

PROXIMATE ANALYSIS

CONSTITUENTS	AS RECEIVED	DRY
Moisture	18.67	-
Volatile Material	35.84	44.07
Ash	2.43	2.99
Fixed Carbon	43.06	52.94

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800 grams of coal sized 6/0 mesh were stirred for 1 hour at 90-100°C. together with an aqueous solution of 152 cc of 88% formic acid in 3000 cc of water (approximately 5% acid by weight and about 4/1 solution to coal ratio). The acid solution was then decanted, and the treated coal dried at about 120°C. until surface dry, i.e., about 10% to about 15% moisture. 1672 grams of the treated coal were milled in a hammer mill to yield a fine powder of 69% -325 mesh. This powder was pressed into cylindrical pellets utilizing a hydraulic press operating at 100,000 psi, which pellets were then crushed into granules, of which 6/20 mesh were collected.

662 grams of the 6/20 mesh granules were placed into a stainless steel mesh basket located within a tube furnace as described in Example 1. The granules were rotated and heated to 450°C. while in an inert atmosphere of nitrogen or argon. This temperature and atmosphere were maintained for 1 hour, at which time the material was cooled to room temperature. 399 grams of devolatized material with an apparent density of .674 gram/cc were obtained, this corresponding to a devolatilization yield of 60.3%. 300 grams of this material were activated as follows:

The granules were placed in a controlled atmosphere rotary kiln as described above. They were then heated to 1020°C. under a nitrogen flow, at which time steam carried by flowing nitrogen was passed through the system at a rate corresponding to 750 cc of water per hour. This was continued for 52 minutes. The material was allowed to cool to room temperature under a nitrogen atmosphere to produce 116 grams of granular activated carbon corresponding to an activation yield of 38.7% and an overall yield of 23.3%. The activated carbon had the following properties: apparent density .503 gram/cc; abrasion number 84; mean particle diameter 1.49 mm; Iodine number 1050 (volumetric 528); Molasses number 253 (volumetric 127); and ash content 9.4%.

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EXAMPLE 5
(Acetic Acid + Pitch)

The sub-bituminous coal in this Example had the following approximate analysis:

PROXIMATE ANALYSIS

CONSTITUENTS	AS RECEIVED	DRY
Moisture	17.40	-
Volatile Material	38.20	46.25
Ash	2.44	2.95
Fixed Carbon	41.95	50.79

A procedure similar to Examples 2 and 3 was followed, with the following exceptions, particularly the substitution of acetic acid for formic acid. 800 grams of granules of 6/0 mesh were stirred for 1 hour at 80-90°C. with an aqueous solution of 455 cc of glacial acetic acid in 2770 cc of water (about 14% acid and about 4/1 solution to coal ratio). The acid solution was decanted and the treated coal dried to a moisture level of about 16%. 1737 grams of the treated coal were mixed together with 111 grams of coal tar pitch (6% pitch), which mixture was ground in a hammer mill to a yield fine powder. Following pelletizing and reforming of granules, 600 grams were placed in a rotating tube furnace and heated to 450°C. while in an inert atmosphere of nitrogen, which was maintained for 1 hour, at which time the material was cooled to room temperature. 300 grams of devolatilized 6/20 granules were produced, having an apparent density of .651 gram/cc, with a devolatilization yield of 50%.

300 grams of the devolatilized granules were activated in a controlled atmosphere rotary kiln, as described above, the granules being heated to 870°C. under a nitrogen flow, at which time steam carried by the flowing nitrogen was passed

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through the system at a rate corresponding to 700 cc of water per hour, and this was continued for 170 minutes. After cooling to room temperature under nitrogen, 131 grams of granular activated carbon of +30 mesh were produced, with an activation yield of 44%, and an overall yield of 22%. The product had the following properties: apparent density .522 gram/cc; abrasion number 82; mean particle diameter 1.46 mm; Iodine number 922 (volumetric 481); Molasses number 247 (volumetric 128.9); and ash content 8.09%.

From the foregoing specific Examples, it is evident that hard granular activated carbon suitable for use in liquid phase applications, such as water and waste water treatment can be obtained by treatment with a dilute aqueous solution of saturated aliphatic monocarboxylic acid, such as formic acid and acetic acid, with formic acid being preferred. In addition, other saturated aliphatic monocarboxylic acids can be utilized in the practice of the invention, such as propanoic, butanoic, pentanoic and hexanoic acids, with the acid concentration required being increased with the decrease in strength of the acid.

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WHAT IS CLAIMED IS:

1. A process for making hard granular activated carbon comprising: forming granules from sub-bituminous coal, reducing the granules to form fine powder, compressing the powder to form shapes, reducing the shapes to reform granules, and thereafter subjecting the reformed granules to heat treatment, without charring, until activated, wherein the improvement comprises: treating the initially formed granules with a dilute aqueous solution of saturated aliphatic monocarboxylic acid, at a concentration from about 2% to about 30%, for a time and at a temperature and solution to coal ratio sufficient for further processing, decanting excess acid, and drying the granules at least partially to a moisture, including acid, content below about 25%, and mixing the treated granules with 0 to about 15% of a carbonaceous binder.

2. Hard granular activated carbon made by the process of claim 1.

3. The process of claim 1 wherein the acid is formic acid.

4. The process of claim 3 wherein the concentration of the formic acid is from about 3% to about 6%.

5. Hard granular activated carbon made by the process of claim 4 and having an abrasion number of not less than about 70.

6. Hard granular activated carbon made by the process of claim 1 and having an abrasion number of not less than about 80.

7. The process of claim 1 wherein the acid is acetic acid.

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8. The process of claim 7 wherein the concentration of the acetic acid is from about 10% to about 20% by weight.

9. The process of claim 8 wherein the treated granules are mixed with about 5% to about 15% by weight of a carbonaceous binder.

10. Hard granular activated carbon made by the process of claim 9 and having an abrasion number of not less than about 80.

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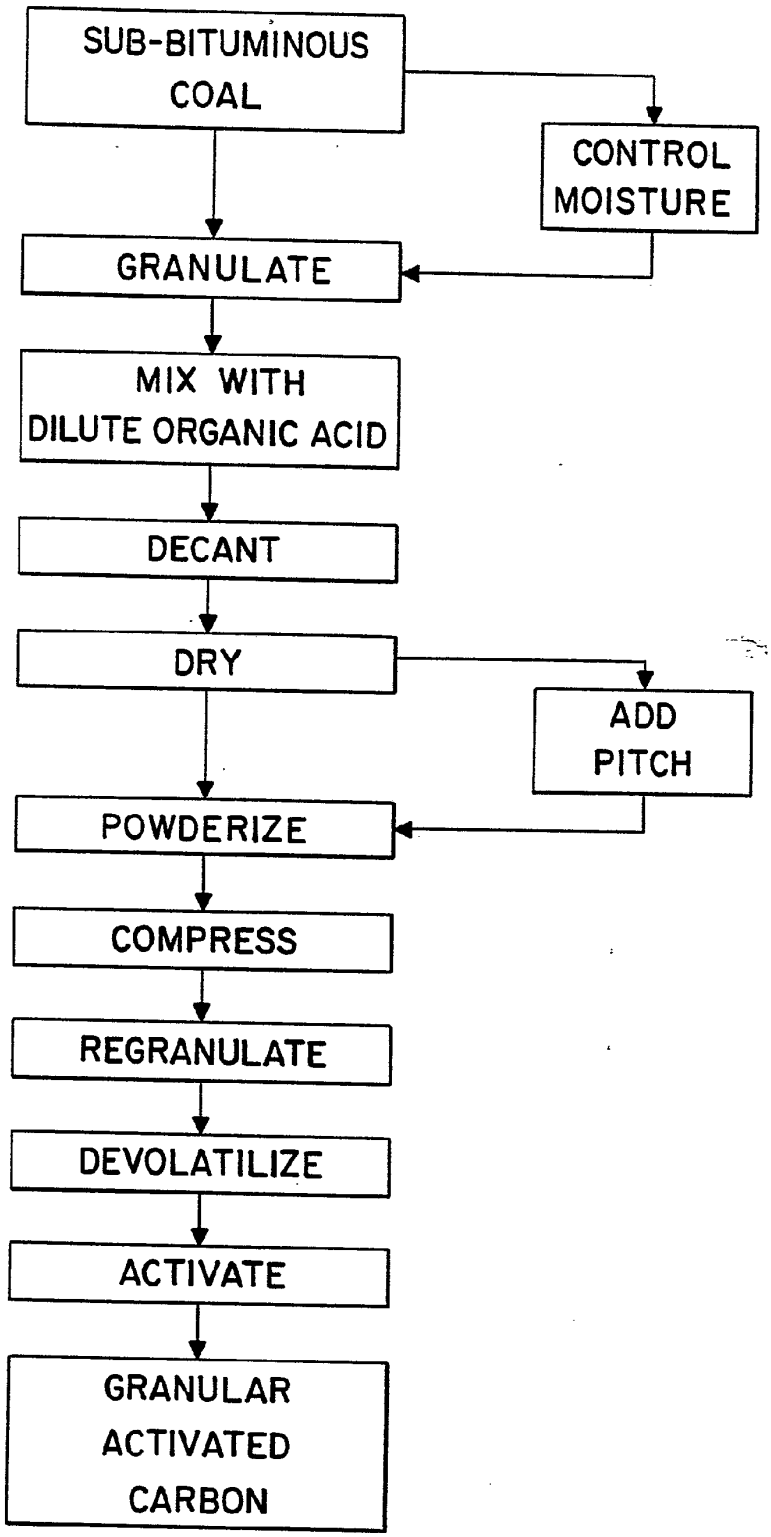


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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/00933

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.3 C01B 31/08; C01B 31/12
US CL. 252/444; 252/422

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	252/421, 422, 444, 445 423/445, 449, 460, 461; 264/29.1

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 4,144,193, Published, 13 March 1979, Murty	1-10
A	US, A, 3,974,227, Published, 10 August 1976, Berthoux et al	1-10
A	GB, A, 13,582, Published, 09 November 1885, Remmers et al	1-10

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
29 OCTOBER 1980	14 NOV 1980
International Searching Authority [1]	**Signature of Authorized Officer** [20]
ISA/US	Paul E. Konopka PAUL E. KONOPKA

Form PCT/ISA/210 (second sheet) (October 1977)

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450-013001	5111

93724 7590 10/28/2022

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EXAMINER	
CHU, YONG LIANG	

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
10/28/2022	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Office Action Summary	Application No. 16/839,862	Applicant(s) DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 09/06/2022.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☑ This action is **FINAL.** 2b) ☐ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-13 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-13 is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Claims 1, 10, and 11 have been amended. Claims 1-13 are pending, and under examination on the merits.

Information Disclosure Statements

Applicants' Information Disclosure Statements, filed on 03/10/2022 and 03/09/2022, have been considered. Please refer to Applicant's copies of the PTO-1449 submitted herewith.

Response to Amendment

The Amendment by Applicants' representative Douglas E. Kayuha on 09/06/2022 has been entered.

Response to Arguments/Amendments

Claim rejection under 35 U.S.C.§112(b)

Applicant's amendment to claim 1 by further defining the first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof **overcomes** the 1st part of the rejection.

However, Applicant fails to respond to the 2nd part of the rejection for including both **narrowly** defined species of carbonate of magnesium ($MgCO_3$) and **broadly** defined species of salts (e.g. magnesium, calcium, strontium, salts) in claim 1. A broad range or limitation together with a narrow range or limitation that falls within the broad range or limitation (in the same claim) may be considered indefinite if the resulting claim does not clearly set forth the metes and bounds of the patent protection desired. See MPEP § 2173.05(c). The claim(s) are considered indefinite because there is a question or doubt as to whether the feature introduced by such

narrower language is (a) merely exemplary of the remainder of the claim, and therefore not required, or (b) a required feature of the claims. The rejection is **maintained**. To overcome the rejection, the narrowly defined range or limitation should be removed from claim 1 and included in a new dependent claim of claim 1.

Claim rejection under 35 U.S.C.§102(a)(1)

Applicant's amendment and argument have been fully considered. They are sufficient to overcome the rejection.

Specifically, amended claim 1 is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas using a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof; and contacting the first sorbent material with a liquid or gas containing the PFAS. Wang *et al*. does not specifically teach a first sorbent material wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof on the first sorbent material, and contacting the first sorbent material with a liquid or gas containing the PFAS. Therefore, the rejection is **withdrawn**.

Claim rejection under 35 U.S.C.§103(a)

Applicants' amendments and arguments have been fully considered. They are not sufficient to overcome the rejection. The 103(a) rejection is revised and cited below necessitated by the amendment filed 09/06/2022.

Claim Rejections - 35 USC § 103 (revised)

In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102 of this title, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103 are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

Claims 1-13 are rejected under 35 U.S.C. 103 as being unpatentable over Wang *et al.*, *Chemosphere*, (**2015)**, v.131, p.178-183 in view of Appleman *et al.*, *Water Research*, (**2014)**, v.51, p.246-255.

Applicant's claim 1 is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas using a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof; and contacting the first sorbent material with a liquid or gas containing the PFAS. Wang *et al.* does not

specifically teach a first sorbent material wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and contacting the first sorbent material with a liquid or gas containing the PFAS.

Determination of the scope and content of the prior art (MPEP §2141.01)

Wang *et al*. discloses the influence of cations on the partition behavior of perfluoro-heptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge (sorbent). For calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, the sorption amount of perfluoroalkyl and polyfluoroalkyl substances (PFAS) increased with calcium and magnesium concentration from 1 to 30 mM and then decreased with those increasing from 30 to 100 mM. A secondary activated sludge activated sludge has higher affinity toward PFAS species than chemically enhanced primary treatment sludge (see Title and Abstract at p.178). Wang *et al*. also discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM comprising a step of mixing 1g of **sludge B1** (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution **containing different cation concentration**, see "2.3 *Aqueous solution composition*" at page 180. The Ca^{2+} ion was prepared from $CaCl_2$, and Mg^{2+} was prepared from $MgCl_2$, see "*2.1 Chemicals*" at page 179. The **sorbent of sludge B1** was prepared through drying at 105 °C overnight and further burned in an oven under 300 °C for 1 h, see the procedure under "2.2 Sorbents" at page 179. The sorbent of **sludge B1** includes carbonaceous char or activated carbon formed by burning in an oven under 300 °C for 1 h, and evidenced by the characteristics of sludge samples in Table 1, Sludge 1B, page 179. In terms of the concentration of Ca^{2+} ion made from $CaCl_2$ (Mw=110.98)

having concentration up to 100 mM, the molar concentration can be converted to weight concentration of 1.1098 wt%. In terms of the concentration of Mg^{2+} ion made from $MgCl_2$ (Mw=95.21) having concentration up to 100 mM, the molar concentration can be converted to weight concentration of 0.9521 wt%.

Appleman *et al.* discloses a method of treatment of poly- and perfluoroalkyl substances in 18 raw drinking water sources and 2 treated wastewater effluents for the attenuation of PFASs. The method applied anion exchange and granular **activated carbon** (GAC) treatment to remove longer-chain PFAS, see Abstract at page 246. The detail analysis of the GAC treatment was disclosed in Figs. 1-2, and "*3.2.5 GAC treatment*" at pages 250-252.

Ascertainment of the difference between the prior art and the claims (MPEP §2141.02)

The difference between the amended claim 1 and Wang *et al.* is that the prior art **does not** teach a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas using a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof; and contacting the first sorbent material with a liquid or gas containing the PFAS. Instead, Wang *et al.* teaches a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from a liquid using ***in-situ*** treated sorbent of sludge B1 with Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM, simultaneously removing PFAS through shaking the mixture at 150 pm for 3 days at room temperature (see "2.3 Aqueous solution composition" at p.180). During this process, Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM were first absorbed on the **sorbent** of sludge B1 to form the first sorbent material for removing PFAS.

Finding of prima facie obviousness--rational and motivation (MPEP §2142-2413)

However, claim 1 would have been obvious over Wang *et al*. because the difference of the **first sorbent material,** wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof, would have been the same or substantially same sorbent material prepared by the method of Wang *et al*. (see "2.3 Aqueous solution composition" at p.180). In addition, Wang *et al*. discloses the importance/criticality of applying cations (e.g. Ca^{2+} and Mg^{2+}) on the partition behavior of perfluoro-heptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge (sorbent). For calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, the sorption amount of perfluoroalkyl and polyfluoroalkyl substances (PFAS) increased with calcium and magnesium concentration from 1 to 30 mM and then decreased with those increasing from 30 to 100 mM. A secondary activated sludge activated sludge has higher affinity toward PFAS species than chemically enhanced primary treatment sludge (see Title and Abstract at p.178). One ordinary skilled in the art would have been motivated to modify a sorbent material with about 0.5 wt.% to about 25 wt.% of an ion, or salts of magnesium, and/or calcium to improve the partition behavior (i.e. absorption) of PFAS species on wastewater. Therefore, Wang *et al*. would have rendered claim 1 obvious.

In terms of claim 2 wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, reactivated carbon, and carbon black, Wang *et al*. discloses that the sorbent of **sludge B1** includes **carbonaceous char** or **activated carbon** formed by burning in an oven under 300 °C for 1 h, and evidenced by the characteristics of sludge samples in Table 1, Sludge 1B, page 179.

In terms of claim 3, Wang *et al*. discloses that the sorbent of sludge B1 includes carbonaceous char or activated carbon formed by burning sludge B (48.5% organic C, see Table 1) in an oven under 300 °C for 1 h.

In terms of claim 4 wherein the first sorbent material is reactivated carbon, Wang *et al.* teach a secondary activated sludge activated sludge has higher affinity toward PFAS species than chemically enhanced primary treatment sludge (see Title and Abstract at p.178). The sorbent of sludge B1 includes carbonaceous char or **activated carbon** formed by burning in an oven under 300 °C for 1 h, and evidenced by the characteristics of sludge samples in Table 1, Sludge 1B, page 179.

In terms of claim 5 wherein the first sorbent material is a reagglomerated activated carbon, Appleman *et al. teaches the sorbent is GAC, and* Wang *et al.* teaches the sorbent was burned at 300 C, which teaches and/or suggests the sorbent of active carbon could be a reagglomerated activated carbon.

In terms of claim 6 wherein further comprising providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, it would not be an inventive optimization, but a repeating step of the known procedure taught by Appleman *et al. and* Wang *et al.*, because one ordinary skilled in the art would have known that a repeating adsorption would cause further removal of the PFAS.

In terms of claims 7-8, using an oxide of Mg or Ca as divalent ions are suggested by Wang *et al.* for improving the sorbents adsorption capability of PFAS.

In terms of claims 9-10, Wang *et al.* discloses the concentration of Ca^{2+} ion made from $CaCl_2$ (Mw=110.98) having concentration up to 100 mM, the molar concentration can be converted to weight concentration of 1.1098 wt%. In terms of the concentration of Mg^{2+} ion made from $MgCl_2$ (Mw=95.21) having concentration up to 100 mM, the molar concentration can be converted to weight concentration of 0.9521 wt%.

In terms of claim 11, wherein the first sorbent material includes about 2 wt.% to about 8

wt.% of an ion, salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof, it would have been obvious over Wang *et al.* for improving the sorbents adsorption capability of PFAS because Wang *et al* teaches the influence of cations on the partition behavior of perfluoro-heptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on wastewater sludge (sorbent). Optimization of the concentration with known mechanism/criticality disclosed by Wang *et al.* would have been an obvious to try.

In terms of claims 12-13, Wang *et al*. teach a secondary activated sludge activated sludge has higher affinity toward PFAS species than chemically enhanced primary treatment sludge (see Title and Abstract at p.178). The sorbent of sludge B1 includes carbonaceous char or **activated carbon** formed by burning in an oven under 300 °C for 1 h, and evidenced by the characteristics of sludge samples in Table 1, Sludge 1B, page 179. Wang *et al*. does not disclose the reactivated carbon has undergone any process to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, potassium and zinc. Therefore, Wang *et al*. would have rendered claims 12-13 obvious.

Conclusions

- Claims 1-13 are rejected.

Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period

will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Telephone Inquiry

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Yong Chu, whose telephone number is (571)272-5759. The examiner can normally be reached on M-F 8:00am-5:00pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Bryan D. Ripa can be reached on 571-270-7875. The fax phone number for the organization where this application or proceeding is assigned is (571) 273-8300.

/YONG L CHU/
Primary Examiner, Art Unit 1731

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	02/25/2022	10/24/2022							
	1	✓	✓							
	2	✓	✓							
	3	✓	✓							
	4	✓	✓							
	5	✓	✓							
	6	✓	✓							
	7	✓	✓							
	8	✓	✓							
	9	✓	✓							
	10	✓	✓							
	11	✓	✓							
	12	✓	✓							
	13	✓	✓							

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00303

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J20/20; 041; 3028	02/25/2022	YC
B01D53/02	02/25/2022	YC
C02F1/283	02/25/2022	YC

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	**Date**	**Examiner**
EAST	02/25/2022	YC
STN	02/25/2022	YC
Patent global Dossier of 16/839,862	02/25/2022	YC
Google scholar search--PFAS removal from wastewater Ca2+ Mg2+--02252022	02/25/2022	YC
The PCT search report "Y" references are not good prior art. Much better prior art references are found and cited by this examiner. A lot of search time spent	02/25/2022	YC
ODP search (PALM inventor name and assignee, EAST and STN search)	02/25/2022	YC
PE2E-search	10/24/2022	YC

/YONG L CHU/ Primary Examiner, Art Unit 1731	

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00304

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/YONG L CHU/ Primary Examiner, Art Unit 1731	

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00305

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20140112856	A1	2014-04-24	Krutka et al.	
	2	20140336568	A1	2014-11-13	Wong	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
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	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
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Norit Americas, Inc. v. Calgon Carbon Corporation
00307

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20200179902	A1	2020-06-11	Huang	
	2	20080283446	A1	2008-11-20	Tatarchuk et al.	
	3	20190270081	A1	2019-09-05	Ilinich et al.	

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Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2013096281	WO	A1	2013-06-27	3M Innovative Properties Co		

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

	2	2013149241	WO	A1	2013-10-03	Fuel Tech, Inc.		
	3	2016185033	WO	A1	2016-11-24	S.A. Lhoist Rech Et Dev		

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Examiner Signature	/YONG L CHU/	Date Considered	10/24/2022

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PE2E SEARCH - Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	British Equivalents	Time Stamp
L1	1	"20140112856".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:57 PM
L2	1	"20140336568".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 12:58 PM
L3	1	"20200179902".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L4	1	"20080283446".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM
L5	1	"20190270081".pn.	(US-PGPUB; USPAT)	OR	ON	ON	2022/10/24 01:02 PM

PE2E SEARCH - Search History (Interference)

There are no Interference searches to show.

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Table 12-1. LIQUID TECHNOLOGIES—REMEDIATION TECHNOLOGIES AND METHODS COMPARISON

This table belongs with the ITRC PFAS Tech Reg Document. The ITRC intends to update this table periodically as new information is gathered. This table has been updated (October 2021) to add a selection of new technologies and new references for some of the technologies presented in the April 2020 table version. The user should note that these additional references have transformed the third column into a selection of representative technologies of likely interest, and not a complete review of all of the references. The expanded body of research has made it too cumbersome to succinctly capture the PFAS and concentrations that were investigated for each reference and what removal efficiency was achieved. Many of these studies were novel at the time of original publication of this table and providing the PFAS and range of concentrations for the body of research was instructive at that time. The user should consult the references directly for additional information on the PFAS and concentrations that were researched.

The user is encouraged to visit the ITRC PFAS web page (https://pfas-1.itrcweb.org) to access the current version of this file. Please see ITRC Disclaimer http://pfas-1.itrcweb.org/about-itrc/#disclaimer.

Users who identify updates to the material in this table are encouraged to send that information to pfas@itrcweb.org

The mechanism of treatment (separation vs. transformation) is listed under each Remediation Technology group.

Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
12.5.2 Flocculation/ Coagulation (Separation)	12.5.2 Alum	PFOA/PFOS ~1,000 µg/L, between 1–20% removal based on coagulant dosage PFOA~8 µg/L, 20% removal PFOS~236 µg/L, 40% removal	Conventional technology. Used commonly for water treatment in other applications. Readily scalable.	Current data show that alum is ***not effective for meeting health advisory*** (low ng/L). May best serve as initial treatment technology. Will likely require polishing.	Requires solids dewatering and disposal.	Permanence of separation is unknown. Data from a wider variety of site conditions/water types. Data as combined approach with other "polishing technologies." Data to understand efficiency at lower initial concentrations (ng/L level).	 D	Bao et al. 2014; CH2M 2017
	Polyaluminum chlorides	PFOA~50–3,000 µg/L; 1 µg/L; 99% removal observed PFOA/PFOS~1,000 µg/L, 1–25% removal based on coagulant dosage	Conventional technology. Used commonly for water treatment in other applications. Readily scalable.	Will likely require polishing.	Requires solids dewatering and disposal.	Permanence of sequestration is unknown. Data from a wider variety of site conditions/water types. Data as combined approach with other "polishing technologies." Data to understand efficiency at lower initial concentrations (ng/L level).	 D	Deng et al. 2011; Bao et al. 2014

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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
	Ferric salts	PFOA/PFOS~1,000 µg/L, 1–50% removal based on coagulant dosage; removal improved to 48–95% at pH 4; PFOA~8 µg/L, 15% removal PFOS~236 µg/L, 30% removal	Conventional technology. Used commonly for water treatment in other applications. Readily scalable.	Current data show that ferric salts are ***not effective for meeting health advisory*** (low ng/L). May be best served as initial treatment technology. Will likely require polishing.	Requires solids dewatering and disposal.	Data from a wider variety of site conditions/water types. Data as combined approach with other "polishing technologies." Data to understand efficiency at lower initial concentrations (ng/L level).	 D	Bao et al. 2014; CH2M 2017
	Covalent bound hybrid coagulants	PFOA ~100 µg/L, 99% removal	99.6% removal of PFOA was observed with test conditions.	***Unproven outside lab in deionized water.*** Commercial availability and scalability of polymer production is unknown.	Requires solids dewatering and disposal of PFOA-containing sludge.	Permanence of separation is unknown. Further R&D needed. Scalability and efficiency at scaled-up level not known.	 D	Zhao et al. 2016
	Specialty coagulants	PFAS~380–480 µg/L, 87–98% removal PFOA~8 µg/L, 20% removal PFOS~236 µg/L, 80% removal	Application of coagulation in conventional water treatment equipment is well known. Readily scalable.	***Limited data on performance of specialty coagulants.***	Requires solids dewatering and disposal.	Scale-up data for larger applications. Permanence of separation is unknown. Data from a wider variety of site conditions/water types. Data as combined approach with other "polishing technologies." Data to understand efficiency at lower initial concentrations (ng/L level).	 D	CH2M 2017; Birk and Alden 2017
	Polymeric coagulant	Polydiallyldimethylammonium chloride (polyDADMAC) increased the sorption coefficient of PFAS by as much as a full order of magnitude. PFOS; PFOA; PFNA; PFHxS; PFHpA; and PFBS.	Application of polymeric coagulants polyDADMAC and in combination with powdered activated carbon (PAC) to increase soil organic content.	In situ treatment of groundwater with injection to create permeable absorptive barrier (PAB) or treatment volume of either polyDADMAC or polyDADMAC+PAC using alginate beads, osmotic pumps, and commercially available floc log and coagulant and PAC.	None, in situ treatment of groundwater.	Field demonstration needs to be done	 D	Aly et al. 2018; Anderson et al. 2019; Simcik 2019

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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
				Data showed as much as 4,100 pore volumes of PFAS for a soil at 100 parts per billion before breakthrough would occur.				
	Electrocoagulation	PFOA~1,000–100,000 µg/L, up to 99% removal; removal depends on cathode and anode chosen, other anions present in solution, etc.	Can be improved by increasing current and decreasing pH. Improved by addition of H_2O_2 to promote advanced oxidation. Research shows zinc hydroxide electrode may have better performance.	Best results have high energy consumption.	Requires solids dewatering and disposal.	Data as combined approach with other "polishing technologies." Permanence of separation is unknown. Scale-up data for larger applications. Data from a wider variety of site conditions/water types. Data to understand efficiency at lower initial concentrations (ng/L level).	 D	Yang et al. 2016; Lin et al. 2015; Wang et al. 2016b
Sorption (Separation)	12.2.1.1 Granular activated carbon (GAC)	Demonstrated for all PFAS tested to date at parts per trillion to parts per billion concentrations for aboveground activated carbon treatment	Treats all tested PFAS to date with high removals prior to breakthrough. Design flexibility to increase removal. Simple to operate. Multiple vendors. Off-site reactivation/regeneration available for PFAS.	Possible faster breakthrough times for shorter chain versus longer chain PFAS under certain influent and other conditions. Becomes less economical at higher influent concentrations (for example, >10–100 ppb). Competitive adsorption w/ other species. Precursors and other PFAS not analyzed for can increase GAC loading and accelerate changeout frequencies. No destruction of PFAS, unless it is reactivated or incinerated at high temperature (>1,100°C). ***Pretreatment may be necessary.***	Spent activated carbon must be removed for offsite disposal, or reactivation/regeneration.	More comprehensive shorter chain adsorption capacity data. Competition with other contaminants and aqueous species. Regulation of individual PFAS in addition to PFOA and PFOS. Impact on PFAS precursors.	 FI	Dickenson and Higgins 2016; Brewer 2017; Cummings et al. 2015; Appleman et al. 2013; Szabo et al. 2017; Burdick et al. 2016; Woodard, Berry, and Newman 2017; Hohenstein 2016; Xiao et al. 2017; AWWA 2016; Mimna 2017; McNamara et al. 2018; Westreich et al. 2018; Liu, Werner, and Bellona 2019; Call 2021

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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
	Carbon nanotubes (CNT)/modified CNT and graphene	PFOA, PFOS	Co-contaminants are remediated. Very high relative surface area (100 times higher than GAC), can be modified with positive charges.	Surface area may become clogged by organic carbon in soil. Expensive to manufacture (currently).	Unknown	Understanding long-term stability of contaminant. Demonstrate adsorption capacity versus cost.	 D	Chen et al. 2011; Li et al. 2011; Kwadijk, Velzeboer, and Koelmans 2013; Lath et al. 2018; Zhao 2020
	12.5.1.1 Colloidal activated carbon (in situ treatment)	Demonstrated full-scale on broad range of PFAS contaminants	Applied to eliminate migration and potential exposure to PFAS. Carbon suspension flows into aquifer coating matrix. PFAS is immobilized onto aquifer matrix. No operation and maintenance. No waste generated. Longevity projected to be multiple decades with single injection. If required, can be reapplied. Highly sustainable with very low carbon footprint.	PFAS contaminants are immobilized, not destroyed. Certain co-contaminants may reduce efficacy.	No waste generated.	Limited number of full-scale applications to date. Need documentation of longevity.	 LA	McGregor 2018; Carey et al. 2019

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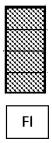
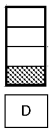
Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
	12.2.1.2 Anionic exchange resins (AEX or IX)	***Demonstrated for all PFAS tested to date at parts per trillion to parts per billion concentrations for aboveground anionic exchange resins.*** Shorter chain PFAS break through faster. Low or high concentration for single use nonregenerable resin; high concentration for regenerable resin.	Higher loading capacity for PFAS versus activated carbon at equivalent influent concentrations and other operating conditions based on a few comparison column and pilot studies. Design flexibility to increase removal. Simple to operate without regeneration. On-site solvent-brine regeneration is currently commercially available from one vendor for its resin designed for PFOA/PFOS removal.	Possible faster breakthrough times for shorter chain versus longer chain PFAS under certain influent and other conditions. Virgin media costs twice as much as activated carbon, but less media replacement is needed. Removal efficiencies are compound specific. Payback for on-site regeneration may be long, but can become more economical versus off-site reactivation of activated carbon at higher influent concentrations of PFAS (for example, >10–100 ppb) because of the higher loading capacity for the anionic resins. Competitive removal with other ions. ***No destruction of PFAS, unless it is incinerated at high temperature (>1,100°C).***	Spent resin must be removed for off-site disposal or on-site regeneration. Solvent-brine, which is flammable, is only demonstrated solution for on-site regeneration. Onsite destruction technologies for concentrated regeneration brine are currently under development.	Full-scale operation experience. Similar future data needs as activated carbon. Improve cost-benefit analysis to compare single use, regenerable, and combined use ion exchange resin approaches to address mixed PFAS.		Deng et al. 2010; Appleman et al. 2014; Du et al. 2014; Dudley, Arevalo, and Knappe 2015; Woodard, Berry, and Newman 2017; McCleaf et al. 2017
	12.5.1.4 Biochar	Treatment appears to be demonstrated for all PFAS tested to date. Most effective for longer chain PFAS.	Possible alternative to GAC. Effectiveness increases with surface area.	***Only proven effective on ultrapure water.*** Natural organic matter reduces effectiveness. Slow reaction kinetics.	Off-site disposal required for spent biochar.	More column/pilot studies. Full-scale operation experience to identify limitations. Similar future data needs as activated carbon.		Xiao et al. 2017; Rahman et al. 2014
	12.5.1.3 Zeolites (natural and modified)	PFOS~2,900–4,000 ng/L with 81– >99% removal	Usually has sorption capacity less than GAC. Would be effective on some organic co-contaminants. Inexpensive mined product.	May react differently with short-chain PFAS or carboxylates (only tested on sulfonates). Is a sequestration technology and not a destructive one. The surface area is relatively low compared to activated carbon and specialized minerals (e.g., aluminum hydroxide has a surface area ~10 m^2/g; pseudoboehmite in RemBind® has a surface area of 250 m^2/g).	Waste adsorbent needs disposal.	Assessment on a broader suite of PFAS of differing chain lengths. Full-scale operation data		Ochoa-Herrera and Sierra-Alvarez 2008; Chiang et al. 2017; Dong 2020

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	Surface-modified clay	86% removal of 65 ug/L total PFAS (13 PFAS) 96% removal 15 ug/L PFOS 90% removal 6 ug/L PFOA Pilot column: Treated influent PFOA (16 ng/L) and PFOS (23 ng/L) to <2 ng/L for 8.7 months. Two studies summarize Rapid Small Scale Column Testing (RSSCT) of surface-modified clay.	High affinity for a variety of PFAS. Resistant to the impacts of dissolved organic carbon (DOC) and co-contaminants. Commercially available media.	Does not remove other soluble co-contaminants.	Spent media must be disposed of through incineration or landfilling.	Media regeneration potential. Engineering parameters for full-scale filtration systems.	 LA	Yan et al. 2020; Yan, Wang, and Liu 2021; Pannu and Plumlee 2021; Hwang and Grieco 2021; Grieco et al. 2021; Najm et al. 2021.
	12.5.1.2 Coated sand	PFOA and PFOS	May remove other co-contaminants at same time.	Field demonstration needed.	Can be regenerated up to 10 times before spent material must be removed for off-site disposal.	Permanence of separation unknown	 D	Badruddoza, Bhattarai, and Suri 2017
	Protein sorbents	PFOS, PFNA, PFOA PFHxS, PFHxA, PFHpA, PFBS, and PFBA	Initial results suggested proteins could be effective filter media with measured k_d values for various protein sorbents.	Research and development to define kinetics of sorption, methods for regeneration of protein sorbents, and design of protein-sorbent filters.	Regeneration testing ongoing. Preliminary results suggest heating for desorption denatures proteins, inactivating them.	Additional studies developing protein-PFAS sorption kinetics, capacity, regeneration and development of filter materials key for filter design and prototyping.	 D	Michalsen et al. 2019

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	Cyclodextrin polymer with ionic liquid coated iron (PILI)	PFOA, PFOS, PFNA, PFBA, PFHxA, PFHxS, PFBAS, FTS 6:2	98-100% removal in the aqueous phase in groundwater.	Research and development to define kinetics of sorption and methods for regeneration of sorbents.	Regeneration testing ongoing.	Additional studies developing protein-PFAS sorption kinetics, capacity, regeneration and development of filter materials key for filter design and prototyping.	 D	Yu 2020
12.5.4 Redox Manipulation (Transformation)	12.5.4.7 UV/Solvated electrons	PFOA=20–24 µM (8,281–9,938 µg/L) PFOS=20 µM (10,000 µg/L)	Compounds almost completely destroyed, with addition of catalysts such as sulfate and persulfate.	Certain methods do not work well under various conditions, such as acidic condition, high temperature, high reductant dosage, and high solution pH. Can be energy intensive.	No secondary waste generated.	Evaluate the impact of background interferences on degradation rates. Improve energy efficiency. Field demonstration.	 D	Park et al. 2009; Park et al. 2011; Qu et al. 2010; Qu et al. 2014; Zhang et al. 2015; Song et al. 2013; Vellanki, Batchelor, and Abdel-Wahab 2013; Zhao, Lv, and Zhou 2012; Ochoa-Herrera et al. 2008; Bentel et al. 2019; Dong 2020; Liu 2020; Zhao 2020
	12.5.4.2 Catalyzed hydrogen peroxide (CHP)-based systems	PFOA=0.24–24 µM (99–9,938 µg/L)	Potentially effective and PFAS are transformed.	Reactions are not contaminant specific. Requires high hydrogen peroxide dosage. Less reactive PFAS species may be produced. Does not treat all PFAS. Only limited number of lab studies have been documented. May not be able to adequately distribute amendment for difficult geology. Possibility of generating PFAAs thru oxidation of precursors.	No waste generated, but incomplete reactions may produce PFAAs.	Mass balance study to better understand extent of mineralization, generation of intermediate PFAS byproducts, and PFAA end products. Impact of co-contaminants on success of PFAS treatment. Technical and cost benefits of achieving cleanup objectives. Optimize oxidant dosing and activation.	 D	Mitchell et al. 2014; da Silva-Rackov 2016; McKenzie et al. 2016

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	12.5.4.1 Ozone-based systems (including ozone with other oxidant combinations)	PFOA and PFOS=50–20,000 µg/L PFAA precursors, PFHxS, PFHxA, PFPeA, PFBA, saturated soils=53,400 µg/kg	Potentially effective and PFAS are transformed.	High ozone and peroxide dosage. High humic acid decreases decomposition. Alkaline adjusted solutions require acidification prior to discharge. Temperature dependent. Dependent on soil permeability in soil/groundwater systems. Undesirable reaction byproducts may be generated (for example, formation of bromate when bromide ions are present).	No waste generated, but incomplete reactions may produce PFAAs.	Mass balance study to better understand extent of mineralization, generation of intermediate PFAS byproducts, and PFAA end products. Impact of co-contaminants on success of PFAS treatment. Technical and cost benefits of achieving cleanup objectives. Optimize oxidant dosing and activation.	 D	Lin et al. 2012; Huang et al. 2016; Kerfoot 2014; Kerfoot 2016; Eberle, Ball, and Boving 2017
	12.5.4.3 Activated persulfate	PFOA=0.24–5.0 µM (99–2,070 µg/L) 6:2 FTSA=0.215 µM (97 µg/L) PFOS demonstrated at 0.1 mg/L with 79.8% reduction when coupled with electron beam	PFOA and 6:2 FTSA degraded (>90%). BTEX had no significant effect on degradation. Can be scaled up. Lower pH enhances defluorination. Energy efficient.	No transformation of PFOS unless coupled with electron beam. Need frequent injection of persulfate. Lower pH enhances scavenging of sulfate radicals at elevated temperature. Elevated temperature difficult to implement in the field at large scale. Inorganic ions hinder decomposition.	No waste generated, but incomplete reactions may produce PFAAs. Unfavorable reaction byproducts or environmental conditions may be generated.	Evaluate the impact of soil. Optimize dosing and activation.	 D	Park et al. 2016; Liu et al. 2012; Yin et al. 2016; Lee et al.2012a; Lee etal. 2012b; Lee et al. 2009; Kim et al. 2019
	Hydrothermal applications using reactive amendments	Sodium hydroxide, sodium borohydride, and potassium ferrate achieved >70–99% defluorination for AFFF and PFOS		High temperature and corrosive conditions required for degradation. Can form HF.	While the alkaline hydrothermal treatment process appears to be more energy-efficient than incineration, the process still requires considerable energy inputs per unit volume of contamination treated.	Improve understanding of degradation reactions and conditions. Demonstrate with different PFAS concentrates and media.	 D	Strathmann 2020

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	12.5.4.5 Photolysis/photochemical oxidation	AFFF, PFOA=0.12–217 µM (50–89,853 µg/L)	PFOA is degraded (87% up to almost 100% in dilute solution) by combined UV wavelengths between 185 and 254 nm over a 4-hour period. Current data suggest no impact on degradation rates with presence of toluene, m-xylene, and p-xylene. PFOS degraded (50% in dilute solution)	***Mostly favored by acidic pH and increased catalyst concentration.*** Organic and inorganic constituents, such as bicarbonate, dissolved organic matter, and dissolved oxygen negatively impact decomposition. VOCs and DOC have negative impact on defluorination. Generates degradation byproducts. Incomplete defluorination at high initial concentrations.	No waste generated.	Improve energy efficiency. Conduct field demonstration.	 D	Tang et al. 2012; Wang et al. 2008; Zhang, Pan, and Zhou 2016; Liang et al. 2016; Cheng et al. 2014; Cao et al. 2010; Giri et al. 2011; Giri et al. 2012; Hori et al. 2004; Hori et al. 2007; Chen, Zhang, and Liu 2006; Chen and Zhang 2006; Sekiguchi, Kudo, and Sankoda 2017 Gomez-Ruiz et al. 2018; Hendren 2019
		PFOS=20–37.2 µM (10,000–18,605 µg/L)	Intermediates can be further decomposed. Can be conducted at room temperature. Can be scaled up	Favored by neutral and weak alkaline conditions. Co-contaminants, such as phenol and ammonia, promote degradation. Temperature dependent. Oxygen atmosphere, low ionic strength, and presence of humic acid decrease degradation.	No waste generated.	Improve energy efficiency. Conduct field demonstration		Jin et al. 2014; Jin and Zhang 2015; Jin, Jiang, and Zhang 2017; Lyu et al. 2015a, b
	Photocatalytic treatment with BOHP/$BiPO_4$	AFFF, PFCAs, GenX, PFOS treated >95% reduction in less than 20 minutes.	Energy-efficient, mineralization rates correlated to chain length.	Chloride and sulfate were shown to slow degradation rates.	No waste generated.	Improve photocatalyst composition, optimize prototypes for scale-up.	 D	Cates 2020

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	UV irradiation (hydrated electron) with electrochemical reduction	PFOS, PFOA, PFNA, PFSA, PFBS, PFHxS	Energy-efficient. Consumes 1/8th energy by UV-only systems.	High reactivity of solvated electrons leads to many competing side reactions and can slow PFAS degradation.	No waste generated.	Evaluating conditions for treating different waters (i.e., degassing of oxygen), optimizing chemical additives (surfactants, sulfites, sulfate) to enhance treatment.	 D	Jassby 2020; Rao et al. 2020; Su et al. 2019
	12.5.4.6 Electrochemical	PFCAs (C2–C8) and PFSAs AFFF GenX 6:2 FTSA=0.12–48 mM (54– 21,607 µg/L)	Degradation is not affected by dissolved organic carbon. Can be combined with other treatment technologies. PFOS and PFOA mineralization has been reported, and the transformation pathways have been proposed and documented.	May consume high energy, but more energy efficient for higher PFAS concentrations. Not all PFAS react similarly. Possibility for formation of byproducts (perchlorate, bromate), depending on the choice of electrolytes (chloride or bromide) for the electrooxidation. ***Electrode cost may be high and not scalable. Not all electrodes have consistent treatment results (fewer electrodes show degradation of PFOS).***	No waste generated.	Assess treatment of wider range of PFAS. Limit formation of perchlorate and bromate. Build long-lasting and inexpensive electrodes. Improve energy efficiency.	 D	Trautmann et al. 2015; Xiao et al. 2011; Lin et al. 2012; Zhou et al. 2012; Zhuo et al. 2011; Niu et al. 2012; Zhao et al. 2013; Zhuo et al. 2012; Zhuo et al. 2014; Chaplin 2014; Carter and Farrell 2008; Liao and Farrell 2009; Schaefer et al. 2015; Schaefer et al. 2017; Schaefer et al. 2019; Gomez-Ruiz et al. 2017; Trautman et al. 2015; Liang et al. 2018; Liu et al. 2019; Urtiaga et al. 2015; Soriano, Gorri and Urtiaga 2017; Pica et al. 2019; Schaefer 2020; Chaplin 2020

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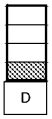
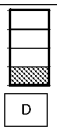
Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
	12.5.4.4 Sonochemical Oxidation/Ultrasound	PFOA=24–117 mM (9,938–48,446 µg/L) APFO=46.4 µM PFOS=20–100 µM (10,003–50,013 µg/L)	PFAS are thermally destroyed and hydroxyl radicals are generated for destruction of co-contaminants. Demonstrated in bench studies. Pilot study is demonstrated for treatment of AFFF.	Rate of reaction decreases above certain power level. Inorganics such as bicarbonate decrease reaction rate. ***High energy requirement. Most reported effective degradation under acidic pH and argon atmosphere with addition of catalysts such as periodate, persulfate, and sulfate.*** Increasing power intensity and frequency increase degradation.	No waste generated	Design and develop effective reactor with optimized operation parameters and conditions. Improve energy efficiency	 D	Moriwaki et al. 2005; Cheng et al. 2008, 2010; Lin et al. 2015; Lin, Hu, and Lo 2016; Rodriguez-Freire et al. 2015; Lee et al. 2016; Hao et al. 2014; Vecitis et al. 2008; Cao et al. 2020
	12.5.4.8 Plasma	In groundwater: PFOA=1.4 µg/L PFOS=0.35 µg/L In prepared solutions: PFOA=1.8 µg/L PFOS=0.14 µg/L	PFOS and PFOA are degraded. Co-contaminants, such as TCE and PCE, were also treated, and did not affect treatment of PFOA and PFAS.	Recirculation of argon. High energy consumption. ***Limited full-scale applications for any contaminant types.*** Reaction byproducts are not well characterized.	No waste generated.	***Further work to confirm treatment of byproducts.*** Cost-benefit evaluation.	 D	Stratton et al. 2017; Jovicic et al. 2018; Singh et al. 2019; Sales 2019
	12.5.4.9 Zero-Valent Iron (ZVI), Doped ZVI, Living diatom/nano-scale ZVI	PFOS=40,000 µg/L, 372 µM (186,048 µg/L) PFOA (95.8%) and PFOS (90.7%) at 10 mg/L	Can be scaled up. Potential to combine with other technologies.	***Not yet proven effective.*** Acidic pH required. Increased ZVI concentrations increase treatment costs. ZVI has tendency to aggregate. Diminished reactivity with aged (days old) ZVI.	PFAS concentrate on ZVI or iron oxide particles.	Further development toward increasing reactivity at higher pH. Reactivity of doped ZVI in natural water.	 D	Arvaniti et al. 2014; Arvaniti et al. 2015; Hori et al. 2006; Albert et al. 2020
	12.5.4.10 Alkaline metal reduction (e.g., vitamin B12 w/ titanium citrate)	PFOS=30,000 µg/L	Can be scaled up. Potential to combine with other technologies (ZVI).	Requires heat increase, along with pH increase (7.5–9) for increased degradation. Primarily attacks branched polymers vs. linear.	No waste generated.	***Conduct demonstration on field samples.*** Perform field testing. Evaluate PFOA.	 D	Ochoa-Herrera et al. 2008

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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
	12.2.2 Reverse osmosis	PFOS=500–1,500,000 µg/L	Established technology. Substantial industry experience designing and operating RO membrane systems. Improvement in PFOS rejection, together with mild flux reduction (<16), was observed at longer filtration time. Flux reduction was also shown to correlate to membrane roughness, with the rougher membranes tending to experience more flux reduction than the smoother ones.	High-flux RO membranes should be avoided when treating high concentrations of PFOS, as any initial high flux exceeding the stable flux would not be sustainable and the rejection of high-flux membranes is less than that achieved using tighter membranes. ***High-flux membranes would perform reasonably well when treating low-strength PFOS solution, providing around 99% rejection efficiency*** while maintaining higher stable fluxes than tighter membranes. Multistage membrane arrays could be designed to further increase removal efficiency. A fraction of PFOS molecules might be entrapped in the polyamide layer of passage of both water and other PFOS molecules. PFOS rejection and fouling were enhanced for greater initial flux and/or applied pressure, where PFOS accumulation was promoted (probably due to increased hydrodynamic permeate drag).	Generates a high volume (~10% of flow) of concentrate (reject water) that must be managed.	***Identify cost effective disposal or treatment technology for high concentration, high volume reject flow***.	 FI	Tang et al. 2006; Tang et al. 2007; Thompson et al. 2011; Dickenson and Higgins 2016; Flores et al. 2013; Appleman et al. 2014

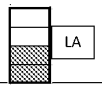
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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
Membrane Filtration (Separation)	12.5.3 Nanofiltration	Various per- and polyfluoroalkyl substances including PFOS, PFPnA, PFBS, PFHxA, PFHpA, PFHxS, PFOA, 6:2 FtS, PFNA, FOSA, PFDA, PFUnA, PFDS, PFDoA, PFTA, PFBA, PFPeA, PFBS; concentrations for various compounds range from lower ng/L to 10,000 µg/L	Established technology. May be functionalized to improve PFAS selectivity.	Salt passage for PFOS was reported to range from < 1% for the tighter NF-90 membrane to about 6% for the looser NF-270 and DK membranes. ***Flux and recovery can be limited by fouling potential of water.***	Generates a concentrate that must be managed.	***Full-scale spiral-wound membrane performance.***	 D	Tang et al. 2007; Steinle-Darling and Reinhard 2008; Loi-Brügger et al. 2008 (address co-contaminants); Dickenson and Higgins 2016; Wang et al. 2018; Soriano, Schaefer, and Urtiaga 2020; Liu 2020
	Ultrafiltration	PFOS: -30 to +43% removal in studies with influent concentrations of 0.0003–0.020 µg/L PFOA: 47– >98% removal in studies PFOA: negligible removal of 0.016 µg/L influent for groundwater with Cl2/UF; 86% removal of 0.086 µg/L for river water using Cl2/coag/floc/sand filtration/ozone/GAC/UF/RO	Low pressure filtration process (e.g., low vacuum to low pressure; 12 psi to + 40 psi). Applicable under wide range of pH (2 to 13 SU).	No sources identified UF as an effective means to remove PFAS from water. May require pretreatment to condition water to minimize UF fouling. Temperature affects water density and viscosity, which directly corresponds to flow rate across filter membranes May be effective on PFOS if combined with powdered activated carbon (PAC). "Low pressure membranes such as MF and UF are not capable of rejecting PFASs since their pore sizes are larger than the effective diameter of the PFAS molecules (~1 nm)." (Tsai et al. 2010; Rahman et al. 2014)	Typical recovery rate of UF systems is 85– >95%. Waste streams include rejectate and possibly backwash water (may be recycled but may be waste if cleaning solutions used).	Insufficient data to demonstrate efficacy.	 D	USEPA 2019b, 2020; Atkinson et al. 2008; Flores et al. 2013; Tsai et al. 2010; Rahman et al. 2014

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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
12.5.5 Biodegradation (Transformation)	Fungal Enzymes	PFOA	Reduction catalyzed by extracellular ligninolytic enzymes. Process would likely be effective on organic co-contaminants.	***Limited evidence of effectiveness.*** Growing and utilizing fungal enzymes is difficult. May be sensitive to environmental changes (e.g., temperature, pH).	No waste generated.	Understanding of mechanisms. Identification of effective strain. Development of implementation approach.		Luo 2015; Mahendra 2016
	Bacterial Enzymes	PFAAs 8:2 and 6:2 fluorotelomer alcohols, 6:2 fluorotelomer sulfonate, fluorotelomer thioether amido sulfonate, PFOA (1,000,000 µg/L)	Green solution (if demonstrated to be effective). Variety of carbon sources could be biostimulants for co-metabolism.	***Limited evidence of effectiveness***. Sensitive to environmental changes (e.g., temperature, pH).	No waste generated.	Understanding of mechanisms. Identification of effective bacterial strains. Evaluating FTOH transformation to a nonterminal PFAA. Development of tools to identify and assess enzymatic effectiveness.		Harding-Marjanovic et al. 2015; Wang et al. 2011; Liu and Mejia Avendaño 2013; Huang 2013; Luo 2015; Merino et al. 2016; Huang and Jaffé 2019
	Phytoremediation	PFOA, PFOS, and 26 other PFAS	Green solution if demonstrated effective.	***Limited evidence of effectiveness.***	Disposal of foliage and harvested materials.	Demonstrated capacity for practical use.		Zhang, Zhang, and Liang 2019

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Remediation Technology Group	Remediation Technology (Includes PFAS-1 document section number for more information)	Chemicals Evaluated and Reported Removal Efficiencies for Select Studies	Strengths (Includes Co-Contaminants, Sustainability, Scalability)	Challenges/Limitations (Includes Co-Contaminants, Sustainability, Scalability)	Waste Management/Life Cycle	Future Data Needs	PFAS Demonstration Maturity (FI – Field Implemented, LA – Limited Application, D – Developing)	References
	12.5.4.11 High-energy electron beam (eBeam)	PFOA and PFOA	Commercialized for food processing	Uncertain scale-up for PFAS and unproven for treatment of other PFAS.	Unknown.	***Demonstration of applicability and suitability for PFAS.***		Wang et al. 2016a; Ma et al. 2017; Pillai 2020
	12.5.7 Foam Fractionation	PFOS~0.093–0.382 mMol/L (46.5–191 mg/L); ~96% removal Lower removal rates for shorter chain compounds	May work for various PFAS compounds chains shorter than C8. Coupling separation with destructive approaches (e.g., ozofractionation) can enhance treatment.	Needs to be tested at various sites; removal depends on foam depth, ionic strength of solution, and aeration rates.	Generates waste stream that still needs disposal	***Understanding the mechanism of removal for the various chain lengths.***		Meng et al. 2018; Dai et al. 2019; Lyu et al. 2020; Buckley et al. 2021; Burns, Stevenson and Murphy 2021
	12.5.8 Deep Well Injection	Could be used for all substances.	Could be a secure disposal method if proper geological formation is identified.	***Cost, regulatory approval,*** and ***community acceptance.***	No residual waste expected.	Demonstration of operational considerations to ensure proper transport and disposal of PFAS.		USEPA 2019a

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Under-reporting Potential of Perfluorooctanesulfonic Acid (PFOS) under High-Ionic Strength Conditions

SD Steffens, EK Cook, DL Sedlak... - ... Science & Technology ..., 2021 - ACS Publications

... , potassium, magnesium, and **calcium** with an initial PFOS ... of shorter and longer chain **PFAS** (eg, perfluorohexanesulfonic ... of enhancing the **removal** of PFOS and other **PFAS** from ...

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Permeability of lime-activated pulverised fuel ash to metal-containing permeants

Y Awe, C Cheeseman... - Waste management & ..., 2001 - journals.sagepub.com

... **PFA** and **PFA**-sand mixtures have been used for lining **wastewater** lagoons and landfills where permeabilities a low as 1.4x10–10 m/s ... A mix of class F **PFA**, lime-kiln dust and **calcium** ...

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E Rathore, P Pal, K Biswas - The Journal of Physical Chemistry C, 2017 - ACS Publications

... evaporation, are unable to selectively and effectively **remove** the heavy metal ions up to the mark ... Samples were introduced using a 100 mL/min **PFA** nebulizer connected to a peristaltic ...

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M Mosaferi, M Mahmoudi, M Pourakbar... - Proceedings of the ..., 2015 - researchgate.net

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... The samples were fixed for 5 min in 2% paraformaldehyde (**PFA**) at 4C and permeabilized for 5 min in ... **Removal** of phosphate, magnesium and **calcium** from swine **wastewater** through ...

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... to **remove** contaminants and finally dried at room temperature. The dried fungal biosorbent was ground in a porcelain mortar to obtain a fine powder. It was then oven-dried at 80 ºC for ...

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... A review of potential applications of different zeolitic products for **waste water** ... **removal** of dry-bottom furnaces. • Boiler slag is a vitreous grained material derived from wet ash **removal** of ...

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DJ Ling, QC Huang, Y Ouyang - Journal of Soils and Sediments, 2010 - Springer

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1731
Confirmation No.	:	5111
Examiner	:	CHU, Yong Liang

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RESPONSE TO NON-FINAL OFFICE ACTION

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This paper is filed in response to the Non-Final Office Action mailed March 3, 2022. The Office Action sets forth a 3-month shortened statutory period for reply. Accordingly, this response is timely filed with the payment of the three-month extension of time fee.

Amendments to the Claims begin on page **2** of this paper.

Remarks begin on page **4** of this paper.

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AMENDMENTS TO THE CLAIMS

The current listing of the claims replaces all prior versions and listings of the claims in the present application.

1. (Currently Amended) A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:
   providing a first sorbent material, wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises ~~including about 0.5 wt.% to about 25 wt.% of~~ an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and
   contacting the first sorbent material with a liquid or gas containing the PFAS.
2. (Original) The method of claim 1, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, reactivated carbon, and carbon black.
3. (Original) The method of claim 2, wherein the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.
4. (Original) The method of claim 2, wherein the first sorbent material is reactivated carbon.
5. (Original) The method of claim 2, wherein the first sorbent material is a reagglomerated activated carbon.
6. (Original) The method of claim 1, further comprising:
   providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and
   contacting the second sorbent material with the liquid or gas containing the PFAS.

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7. (Original) The method of claim 1, wherein the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium, an oxide of strontium, or an oxide of barium.
8. (Original) The method of claim 7, wherein the first sorbent material includes one or more of MgO or CaO.
9. (Original) The method of claim 1, wherein the ion, salt, oxide, hydroxide, or carbonate of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation, chemical vapor deposition, or physical vapor deposition.
10. (Currently Amended) The method of claim 1, wherein about 1 wt.% to about 20 wt.% of the first sorbent material comprises ~~the first sorbent material includes about 1 wt.% to about 20 wt.% of~~ an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
11. (Currently Amended) The method of claim 10, wherein about 2 wt.% to about 8 wt.% of the first sorbent material comprises ~~the first sorbent material includes about 2 wt.% to about 8 wt.% of~~ an ion, salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
12. (Original) The method of claim 1, wherein the first sorbent material is a reactivated carbon comprising ions, oxides or carbonates of calcium, magnesium, sodium, potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, potassium and zinc.
13. (Original) The method of claim 12, wherein the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, and zinc.

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REMARKS

Applicant would like to thank the Examiner for the careful consideration given to the present application. Claims 1-13 are pending. The Office has rejected claims 1-13. Claims 1, 10, and 11 have been amended. Support for the amendments can be found in the specification in paragraph [0040]. Therefore, Applicant submits that no new matter has been added.

Rejection under 35 U.S.C. § 112

In the Office Action dated March 3, 2022, the Office states that claims 1-13 are allegedly indefinite for failing to particularly point out and distinctly claim the subject matter regarded as the invention. Specifically, the Office states that it is not clear to what the phrase "about 0.5 wt. % to about 25 wt. %" is relevant. In response Applicant has amended claims 1, 10, and 11 and submits the following remarks. Support for the amendments to claims 1, 10, and 11 can be found throughout the filed specification, particularly in paragraph [0040] which describes how the ion, oxide, hydroxide, carbonate, or combination is measured.

Citation (Specification)	**Relevant Text**
¶ [0040]	The amount of the above ion, oxide, hydroxide, carbonate, or combination of those materials is measured by weight with respect to the total weight of the treated sorbent material and the ion, oxide, hydroxide, carbonate, or combination of those materials. The amount of the ion, salt, oxide, hydroxide, or carbonate is not limited and in some embodiments is less than about 25% wt. %, less than about 20 wt. %, less than about 15 wt. %, less than about 10 wt. %, less than about 8 wt. %, less than about 6 wt. %, less than about 4 wt. %, less than about 2 wt. %, less than about 1 wt. %, less than about 0.9 wt. %, less than about 0.8 wt. %, less than about 0.7 wt. %, less than about 0.6 wt. %, less than about 0.5 wt. %, less than about 0.4 wt. %, less than about 0.3 wt. %, less than about 0.2 wt. %, or less than about 0.1 wt. %. In some embodiments the amount of the ion, salt, oxide, hydroxide, or carbonate is about 25% wt. %, about 20 wt. %, about 15 wt. %, about 10 wt. %, about 9 wt. %, about 8 wt. %, about 7 wt. %, about 6 wt. %, about 5 wt. %, about 4 wt. %, about 3 wt. %, about 2 wt. %, about 1 wt. %, about 0.9 wt. %, about 0.8 wt. %, about 0.7 wt. %, about 0.6 wt. %, about 0.5 wt. %, about 0.4 wt. %, about 0.3 wt. %, about 0.2 wt. %, about 0.1 wt. %, or any range formed of any of the above two endpoints. In some embodiments, the amount of the ion, salt, oxide, hydroxide, or carbonate is about 1 wt. % to about 10 wt. %, about 2 wt. %

	to about 10 wt. %, about 4 wt. % to about 10 wt. %, about 6 wt. % to about 10 wt. %, about 1 wt. % to about 8 wt. %, about 2 wt. % to about 8 wt. %, about 4 wt. % to about 8 wt. %, about 4 wt. % to about 6 wt. %, or about 6 wt. % to about 8 wt. %.

Claim 1 is provided below for convenience:

> A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material, ***wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate*** of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and contacting the first sorbent material with a liquid or gas containing the PFAS.
> ***(Emphasis added)***

Claim 1 has been amended to claim a method comprising a first sorbent material, ***wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises*** an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof. The phrase "about 0.5 wt.% to about 25 wt.%" refers to the amount of the ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof present in the first sorbent material as a weight percentage of the entire first sorbent material. Claims 10 and 11 have been similarly amended. Therefore, Applicant asserts that claim 1 and claims 2-13, which are dependent on claim 1, are not indefinite and requests the rejections under U.S.C. 112 be removed.

Rejection under 35 U.S.C. § 102

In the Office Action dated March 3, 2022, the Office states that claims 1-3, 7, 13, and 14 are allegedly anticipated by Wang *et al., Chemosphere* ("Wang"). In response, Applicant submits the following remarks.

The Office states that claim 1 lacks novelty in view of Wang. However, Wang fails to teach the method of claim 1 as claimed. Claim 1 claims:

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> A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material, ***wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof*** to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and contacting the first sorbent material with a liquid or gas containing the PFAS.
> ***(Emphasis added)***

The claim clearly claims a method of removing PFAS from liquid or gas comprising providing a first sorbent material, ***wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material comprises an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof.*** Wang fails to disclose a method comprising providing a sorbent material wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material is an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof. In fact, Wang fails to disclose a method comprising a sorbent material comprising any amount of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof. Instead, Wang discloses a method of treating a solution comprising an ion of sodium, potassium, calcium, magnesium, aluminum, or iron with a sludge, wherein the sludge comprises organic matter, sand, silt, and clay. That is, Wang discloses that the solution *to be treated* contains ions of sodium, potassium, calcium, magnesium, aluminum, or iron. In sharp contrast, in the claimed method, it is the treatment itself (*i.e.*, the sorbent material) that may contain such ions. Therefore, Wang fails to disclose all aspects of claim 1 as claimed.

Thus, the method as described in Wang is clearly different than the claimed method. Therefore, Applicant submits that claim 1, and claims 2-13 which are either directly or indirectly dependent on claim 1, contain novelty and are in condition for allowance.

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Rejection under 35 U.S.C. § 103

In the Office Action dated March 3, 2022, the Office states that claims 4-8 and 11-13 are allegedly obvious over Appleman *et al., Water Research* ("Appleman") in view of Wang. In response, Applicant submits the following remarks.

Notably, claims 4-8 and 11-13 are dependent on claim 1. In the Office Action dated March 3, 2022, the Office states that Appleman fails to teach a method comprising providing a first sorbent material wherein about 0.5 wt.% to about 25 wt.% of the first sorbent material is comprised of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof. Therefore, Appleman fails to remedy the deficiencies of Wang. Given the above remarks placing claim 1 in condition for allowance and that Appleman fails to remedy the deficiencies of Wang, Applicant asserts that claims 4-8 and 11-13 are not rendered obvious by Appleman in view of Wang and are in condition for allowance.

AUTHORIZATION

Should the Examiner have any questions or comments, or need any additional information from Applicant's representative, the Examiner is invited to contact the undersigned. The Commissioner is hereby authorized to charge any additional fees which may be required or credit any overpayment to Deposit Account No. 60-4406.

Respectfully submitted,
DLA PIPER LLP

/Douglas Kayuha/

Douglas E. Kayuha
Registration No. 79,855

Date: September 6, 2022
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APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
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Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	60940169	AUTHORIZED BY	Douglas Kayuha
CUSTOMER #	93724	FILING DATE	04/03/2020
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO

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PRE-AUTHORIZED ACCOUNT	PRE-AUTHORIZED CATEGORY
604406	37 CFR 1.17 (Patent application and reexamination processing fees); 37 CFR 1.19 (Document supply fees); 37 CFR 1.21 (Miscellaneous fees and charges)

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Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	60940169	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Douglas Kayuha

Documents

TOTAL DOCUMENTS: 3

DOCUMENT		PAGES	DESCRIPTION	SIZE (KB)
123450-013001_Amendment.pdf		7	-	194 KB
123450-013001_Amendment-A....pdf	(1-1)	1	Amendment/Request for Reconsideration-After Non-Final Rejection	104 KB
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☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A		N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*		x $100 =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*		x $460 =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).				
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))					
* If the difference in column 1 is less than zero, enter "0" in column 2.				TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT	09/06/2022	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 13	Minus	** 20	= 0		x $100 =	0
	Independent (37 CFR 1.16(h))	* 1	Minus	*** 3	= 0		x $480 =	0
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	0

		(Column 1)		(Column 2)	(Column 3)			
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=		x $0 =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=		x $0 =	
	☐ Application Size Fee (37 CFR 1.16(s))							
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							
							TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.	LIE
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".	/ANNIE C SINGLETON/
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".	
The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.	

This collection of information is required by 37 CFR 1.16. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
16/839,862	**03/10/2022 10:08:31 PM ET**	**123450.013001**

Title of Invention

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Application Information

APPLICATION TYPE	Utility - Nonprovisional Application under 35 USC 111(a)	PATENT #	-
CONFIRMATION #	5111	FILED BY	Paula Watson
PATENT CENTER #	60568236	FILING DATE	04/03/2020
CUSTOMER #	93724	FIRST NAMED INVENTOR	Rebecca L. DISTEFANO
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Nicholas Kokkinos

Documents

TOTAL DOCUMENTS: 1

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
123450-013001_SafeHarbor_sb0133.pdf	2	Patent Term Adjustment Stmt Under 37CFR1.704(d)	227 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)
123450-013001_SafeHarbor_sb0133.pdf	273CB81706A8570EAB3F7940F525CB42280BDEDC8DFD0AC4BF20ECF9C5D96BFB640780A8FDCBC1EF2A64A24E5F328E0A9B57A318D1ED5948FDC0C8F86D0A1D99

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Doc Code: PTA.IDS
Document Description: Patent Term Adjustment Stmt Under 37 CFR 1.704(d)

PTO/SB/133 (10-21)

PATENT TERM ADJUSTMENT STATEMENT UNDER 37 CFR 1.704(d)		
	Application Number	16/839,862
	Filing Date	April 3, 2020
	First Named Inventor	Rebecca L. DISTEFANO
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Practitioner Docket No.	123450-013001

APPLICANT HEREBY STATES THE FOLLOWING (please review 37 CFR 1.704(d) before filing this form):

☑ Each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

AND/OR

☐ Each item of information contained in the information disclosure statement is a communication that was issued by a patent office in a counterpart foreign or international application or by the Office, and this communication was not received by any individual designated in 37 CFR 1.56(c) more than thirty days prior to the filing of the information disclosure statement.

INSTRUCTIONS:

- **This form will not satisfy the requirement of 37 CFR 1.97(e).** The present statement is filed under 37 CFR 1.704(d) and will not substitute for compliance with any of the requirements of 37 CFR 1.97 and 1.98. For an information disclosure statement to comply with 37 CFR 1.97(c) or (d), the information disclosure statement must be accompanied by a statement under 37 CFR 1.97(e) notwithstanding any statement filed under 37 CFR 1.704(d).
- The present form (PTO/SB/133) should be filed concurrently with the information disclosure statement to derive benefit under 37 CFR 1.704(d).

Signature	/Nicholas Kokkinos/	Date	03/10/2022
Typed or Printed Name	Nicholas C. Kokkinos	Practitioner Registration Number	76,979

***Note**: Signatures of all the inventors or assignees of record of the entire interest or their representative(s) are required in accordance with 37 CFR 1.33 and 11.18. Please see 37 CFR 1.4(d) for the form of the signature. If necessary, submit multiple forms for more than one signature, see below*.*

☑ *Total of 1 forms are submitted.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1731
Examiner Name	Yong Liang CHU
Attorney Docket Number	123450-013001

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

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U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20140112856	A1	2014-04-24	Krutka et al.	
	2	20140336568	A1	2014-11-13	Wong	

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FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

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NON-PATENT LITERATURE DOCUMENTS Remove

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

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EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00350

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

X That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

X See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2022-03-10
Name/Print	Nicholas C. Kokkinos	Registration Number	76,979

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

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2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00352

Electronic Acknowledgement Receipt

EFS ID:	45200429
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
Filer Authorized By:	Nicholas Charalambos Kokkinos
Attorney Docket Number:	123450.013001
Receipt Date:	10-MAR-2022
Filing Date:	03-APR-2020
Time Stamp:	18:26:28
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	123450-013001_Transmittal-03-10-2022.pdf	107146 1bed3854a66c7178fc64534a4cc625b149e2de74	no	1

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	123450-013001-SB08-03-10-22.pdf	1136167 83c3af3d08826089567ce21a404b8c58f9e1595f	no	4
Warnings:					
Information:					
3	Non Patent Literature	Appleman.PDF	1136762 eb31e971ffffd6dfe28010a271a5eec90143ac60	no	10
Warnings:					
Information:					
		Total Files Size (in bytes):	2380075		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(c)(1) / Fee Authorization

This Information Disclosure Statement is submitted under 37 C.F.R. §1.97(c)(1) after the mailing of a first Office Action on the merits, but before the mailing date of a Final Office Action or a Notice of Allowance. The undersigned asserts in accordance with 37 C.F.R. §1.97(e)(1) that each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. Therefore, applicant holds that no fee is due. However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

Respectfully submitted,
DLA PIPER LLP (US)

/Nicholas Kokkinos/

Nicholas C. Kokkinos
Reg. No. 76,979

DLA PIPER LLP (US)
1650 Market Street, Suite 5000
Philadelphia, PA 19103-7348
Telephone: (215) 656-3300
Date: March 10, 2022

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00355

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (**Not for submission under 37 CFR 1.99)**		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20200179902	A1	2020-06-11	Huang	
	2	20080283446	A1	2008-11-20	Tatarchuk et al.	
	3	20190270081	A1	2019-09-05	Ilinich et al.	

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1	2013096281	WO	A1	2013-06-27	3M Innovative Properties Co		

EFS Web 2.1.18

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

	2	2013149241	WO	A1	2013-10-03	Fuel Tech, Inc.		
	3	2016185033	WO	A1	2016-11-24	S.A. Lhoist Rech Et Dev		

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]
	1		

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
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	First Named Inventor	Rebecca L. Distefano
	Art Unit	1731
	Examiner Name	Yong Liang CHU
	Attorney Docket Number	123450-013001

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Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

X That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

X See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2022-03-09
Name/Print	Nicholas C. Kokkinos	Registration Number	76,979

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FILTRATION MEDIUM COMPRISING A THERMOLYSIS PRODUCT OF A CARBON OXYCHALCOGENIDE AND A METAL SALT, METHOD OF REMOVING CHLORAMINE WITH THIS FILTRATION MEDIUM AND METHOD OF MAKING THIS FILTRATION MEDIUM

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Abstract of WO2013096281 (A1)

Described herein is a filtration medium comprising a substrate, wherein the substrate comprises a thermolysis product of (i) a carbon substrate having a surface of COxEy,

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wherein E is selected from at least one of S, Se, and Te; and wherein x and y are greater than 0; and (ii) a metal salt; and methods of removing chloramine from aqueous solutions.

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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

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(54) Title: FILTRATION MEDIUM COMPRISING A THERMOLYSIS PRODUCT OF A CARBON OXYCHALCOGENIDE AND A METAL SALT, METHOD OF REMOVING CHLORAMINE WITH THIS FILTRATION MEDIUM AND METHOD OF MAKING THIS FILTRATION MEDIUM

(57) Abstract: Described herein is a filtration medium comprising a substrate, wherein the substrate comprises a thermolysis product of (i) a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te; and wherein x and y are greater than 0; and (ii) a metal salt; and methods of removing chloramine from aqueous solutions.

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TECHNICAL FIELD

[0001] A filtration medium comprising a thermolysis product of a carbon oxychalcogenide and a metal salt is described.

BACKGROUND

[0002] Chloramine is commonly used in low concentration as a secondary disinfectant in municipal water distribution systems as an alternative to chlorination with free chlorine. Concerns over taste and odor of chloramine treated water have led to an increase in the demand for water filters with chloramine removal capabilities.

[0003] Carbon particles, such as activated carbon particles, have been used to remove chloramine from aqueous streams. Improvements in removal of chloramine can be achieved by reducing the mean particle diameter of the carbon and by increasing the carbon bed contact time. Although parameters such as contact time and mean particle diameter are known to affect chloramine removal efficiencies, more significant improvements are desired without significantly increasing the pressure drop of filtration media.

[0004] U.S. Pat. No. 5,338,458 (Carrubba et al.) discloses an improved process for the removal of chloramine from gas or liquid media by contacting the media with a catalytically-active carbonaceous char.

[0005] U.S. Pat. No. 6,699,393 (Baker et al.) shows improved chloramine removal from fluid streams, when the fluid stream is contacted with an activated carbon, which has been pyrolyzed in the presence of nitrogen-containing molecules, versus a catalytically-active carbonaceous char.

SUMMARY

[0006] There is a desire to provide a filtration medium, which is less expensive and/or more efficient at the removal of chloramine than currently available filtration media. In some instances, there is also a desire to provide a solid block of carbon to remove chloramine. In other instances, there is a desire to have a granular material that may be used in a packed bed. In still other instances, there is a desire to provide a material that may be used in a web-form.

[0007] In one aspect, a filtration device is described comprising: a vessel for treating fluids containing a substrate, wherein the substrate comprises a thermolysis product of (i) a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te; and wherein x and y are greater than 0; and (ii) a metal salt.

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[0008] In another aspect, a method for removing chloramine from aqueous solutions is disclosed comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a composition comprising a thermolysis product of a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te and wherein x and y are greater than 0; and a metal salt,.

[0009] In yet another aspect, a method of making a substrate comprising: providing a composition comprising (i) a carbon substrate; (ii) a sulfur, selenium, or tellirium source, or combinations thereof; and (iii) a metal salt; and heating the composition.

[0010] The above summary is not intended to describe each embodiment. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages will be apparent from the description and from the claims.

DETAILED DESCRIPTION

[0011] As used herein, the term

"a", "an", and "the" are used interchangeably and mean one or more; and

"and/or" is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B).

Also herein, recitation of ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 10 includes 1.4, 1.9, 2.33, 5.75, 9.98, etc.).

[0012] Also herein, recitation of "at least one" includes all numbers of one and greater (e.g., at least 2, at least 4, at least 6, at least 8, at least 10, at least 25, at least 50, at least 100, etc.).

[0013] The present disclosure is directed to a carbon substrate comprising a thermolysis product of a carbon oxychalcogenide and a metal salt. It has been found that such compositions may be useful for the removal of chloramine from aqueous solutions.

[0014] U.S. Provisional Appl. No. 61/533297 (Attorney Docket No. 67607US002 filed 12 Sep 2011) discloses that a carbon substrate comprising a surface of a carbon oxychalcogenide, which can be used to remove chloramines from aqueous solutions. U.S. Provisional Appl. Nos. _____(Attorney Docket Nos. 67608US002 and 67737US007 filed contemporaneously with the present application) disclose that compositions comprising a thermolysis product of a metal salt may also be used to remove chlormaines from aqueous solutions. All three of these patent applications are herein incorporated by reference in their entirety. It has been discovered that by thermally decomposing metal salts on carbon substrates comprising a surface of a carbon oxychalcogenide, compositions that have improved performance may result.

[0015] In one embodiment, a carbon substrate is provided comprising a surface of an oxychalcogenide. The carbon substrate comprising a surface of an oxychalcogenide is then contacted with a metal salt and heated to thermally decompose the metal salt.

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[0016] In another embodiment, a carbon substrate; a sulfur, selenium, or tellurium source; and a metal salt are provided and then heated to form the substrate.

[0017] Carbon Substrate

[0018] Carbon has several allotropes, including diamond, graphite, and amorphous carbon. In one embodiment, the carbon substrate comprises a substantial amount of sp^2 hybridized carbon. In other words, the carbon substrate has no more than 20%, 15%, 12% or even 10% sp^3 hybridized carbon. As the sp^3 hybridized carbon content increases, the sp^2 hybridized carbon substrate progressively changes into a dense, isotropic network of tetrahedral carbon.

[0019] The morphology of the carbon substrate is not particularly limited and may include a non-particulate, a particulate, or an aggregate. Exemplary morphologies include: a carbon block, a carbon monolith, foams, films, fibers, and nanoparticulates such as nanotubes and nanospheres. A non-particulate is a substrate that is not composed of discernable, distinct particles. A particulate substrate is a substrate that has discernable particles, wherein the particle may be spherical or irregular in shape and has an average diameter of at least 0.1, 1, 5, 10, 20, or even 40 micrometers (μm) to at most 75 μm, 100 μm, 500 μm, 1 millimeter (mm), 2 mm, 4mm, 6.5 mm, or even 7 mm. An aggregate (or a composite) is formed by the joining or conglomeration of smaller particles with one another or with larger carrier particles or surfaces. The aggregates may be free standing (self-supporting against gravity).

[0020] Typically, the morphology the carbon substrate will be selected based on the application. For example, particulate with a large particle size is desirable when the compositions of the present disclosure are used in applications requiring low pressure drops such as in beds through which gases or liquids are passed. Granular activated carbon available under the trade designation "RGC" by Mead Westvaco Corp, Richmond, VA may be preferred in water treatment; Kuraray PGW coconut shell activated carbon, Kuraray Chemical, Osaka, Japan.

[0021] The size of the pores of the carbon substrate can be selected based on the application. The carbon substrate may be microporous carbon, macroporous carbon, mesoporous carbon, or a mixture thereof.

[0022] Particularly useful are carbon substrates that are substantially disordered and have high surface areas (e.g., at least 100, 500, 600 or even 700 m^2/g; and at most 1000, 1200, 1400, 1500, or even 1800 m^2/g based on BET (Brunauer Emmet Teller method) nitrogen adsorption). As used herein, substantially disordered means that the carbon substrate has in-plane domain sizes of about 10-50 Å (Angstrom).

[0023] In one embodiment, the carbon substrate is comprised of activated carbon, in other words carbon that has been processed to make it highly porous (i.e., having a large number of pores per unit volume), which thus, imparts a high surface area.

[0024] Chalcogens

[0025] The chalcogens as used herein to refer to sulfur, selenium, tellurium, or combinations thereof. Sources of such chalcogens are described below.

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[0026] Useful sulfur-containing compounds include, but are not limited to elemental sulfur, SO_2, $SOCl_2$, SO_2Cl_2, CS_2, COS, H_2S, and ethylene sulfide.

[0027] Useful selenium compounds include but are not limited to elemental selenium, SeO_2, and SeS_2.

[0028] Useful tellurium compounds include but are not limited to elemental tellurium, TeO_2, and $(HO)_6Te$.

[0029] Metal Salts

[0030] The metal salts of the present disclosure may include metal salts or metal complexes. Such salts and complexes may comprise a carboxylate, a nitrogen-containing oxyanion, a sulfur-containing anion, a chloride, a phosphate, and combinations thereof.

[0031] Exemplary carboxylates include: oxalates, formates, propionates, acetates, tartrates, benzoates, lactates, and/or citrates.

[0032] The nitrogen-containing oxyanion salt may comprise a nitrate and/or a nitrite ion.

[0033] The sulfur-containing anions may comprise a sulfate, sulfamate, sulfite, bisulfate, bisulfite, and/or thiosulfate ion.

[0034] A chloride salt is a salt comprising a chloride anion, and a phosphate salt is a salt comprising a phosphate ion.

[0035] The metal portion of the metal salt may include any metal, however, metals that are acceptable for presence in drinking water are preferred. Exemplary metals include: copper, iron, silver, and manganese.

[0036] Exemplary metal salts include: cupric oxalate, ferrous oxalate, cupric acetate, ferric citrate, and copper formate, ferric nitrate, manganous sulfate, copper sulfate, and combinations thereof.

[0037] Preparing a carbon substrate comprising a carbon oxychalogenide surface

[0038] In one embodiment, the surface of the carbon substrate comprises CO_xE_y, wherein E is sulfur, selenium, tellurium, or combinations thereof. In one embodiment, x and y are greater than 0. In one embodiment, x is 0. In another embodiment, x is at least 0.005, 0.01, 0.02, 0.03, 0.04, or even 0.05; and is at most 0.07, 0.08, 0.09, 0.1, 0.12, 0.15, or even 0.2. In one embodiment, y is at least 0.001, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, or even 0.06; and at most 0.12, 0.14, 0.15, 0.16, 0.18, 0.2, 0.22, 0.25, 0.3, 0.35, or even 0.4.

[0039] In one embodiment, the carbon substrate has a surface consisting essentially of CO_xE_y, meaning that the surface necessarily includes carbon, oxygen, and E and may also include other atoms so long as the other atoms do not materially affect the basic and novel properties of the invention. In other words, besides carbon, oxygen, and the chalcogen, the surface of the substrate comprises less than 10% or even less than 5 % total of other atoms. These other atoms may originate in the starting materials. For example, a carbon substrate, prior to reactions as described in this disclosure, may contain potassium or minor amounts of other elements, which are not removed during manufacturing and thus, are present in the final product.

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[0040] The surface of the carbon substrate comprising an oxychalcogenide is made by exposing a carbon substrate to a chalogen or chalogen-containing compound, and optionally oxygen. The chalcogen is reacted onto the carbon substrate, by exposing a solid, liquid, or gas form of the chalogen or chalcogen-containing compound to the carbon substrate under heating conditions.

[0041] In one embodiment, the sulfur, selenium, and tellurium compounds may be used in combination with one another to generate a carbon oxychalcogenide containing more than one chalcogenide element, for example, sulfur and selenium.

[0042] In addition to a chalcogen, the surface of the carbon substrate may also comprise oxygen. The carbon substrate, as received, may contain chemically significant amounts of oxygen attached to surface carbon atoms. For example, according to X-ray photoelectron spectroscopic (XPS) analysis, RGC contains about 2.9 atomic percent of oxygen. This amount of oxygen may be sufficient for the present disclosure but, when higher amounts of surface oxygen are desired, additional oxygen may be incorporated into the carbon.

[0043] In one embodiment, additional oxygen may be added to the carbon substrate before exposure to the chalcogen-containing compound. For example, the carbon substrate can be heated in air or treated with aqueous nitric acid, ammonium persulfate, ozone, hydrogen peroxide, potassium permanganate, Fenton's Reagent, or other well known oxidizing agents.

[0044] In another embodiment, additional oxygen can be incorporated into the carbon substrate having a surface comprising a oxychalcogenide by carrying out the reaction between the carbon substrate and the chalcogen-containing compound in the presence of air or water. The amount of air used can be limited to prevent combustion of the carbon. Additional oxygen may also be supplied by addition of water or steam, which can be added during the heating reaction or may be present on the surface of the carbon substrates, such as in the case of high surface area carbonaceous materials, particularly hydrophilic oxidized carbons, which chemisorb water. Oxygen may be added during the heating reaction in the form of dioxygen, sulfur dioxide, carbon dioxide, or combinations thereof.

[0045] In addition to adding an oxygen source during heating of the carbon and the chalcogen, in an alternative embodiment, the heating is conducted in the absence of added oxygen.

[0046] Reactions of elemental carbon typically exhibit large activation energies and so are conducted at high temperature. Reactions used to introduce chalcogens and optionally oxygen into the carbon substrate surface may be conducted at a temperature of at least 200, 250, 300, 400, or even 500°C; and at most 650, 700, 800, 900, 1000, 1200, or even 1400 °C. In one embodiment, as the reaction temperature increases the composition of the present disclosure becomes more efficient at the removal of chloramine.

[0047] The thermal reaction may occur in air. However, to control combustion, it is possible to carry out the thermal reaction under vacuum; with a purge, such as a nitrogen purge; or in an inert atmosphere where the air is pulled from the reaction vessel using a vacuum and then dry nitrogen is used to back-fill the reaction vessel.

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[0048] The chalcogen-containing compound may be used in the solid, liquid or gas form. Reaction temperatures, which are above the boiling point of the chalcogen-containing compounds are used, resulting in solid-gas reaction chemistry.

[0049] In one embodiment, the carbon substrate is wetted with a liquid chalcogen-containing compound and then exposed to the reaction temperature and optional oxygen to form the carbon oxychalcogenide surface. These reactions occur at the surface of the carbon substrate. In the case of a porous carbon substrate, the carbon oxychalcogenide may coat (or cover) the surface of the pores of the porous carbon substrate.

[0050] The carbon substrate having a surface comprising a cabon oxychalcogenide is obtained via solid-gas (or solid-vapor) chemistry. In reactions of this class, only the outer portions of the carbon substrate are exposed to the reactive gas. Such reactions can become self-limiting in that an overlayer of product inhibits inward diffusion of the gas. In such a case, the new compounds that form are confined to regions near the surface and comprise a surface compound. Generally, this means that reactions occur at depths of 10 nanometers (nm) or less on the carbon substrate to form the CO_xE_y coating.

[0051] When the carbon substrate is a large particle, a core-shell structure results, where the core is the carbon substrate, which is covered by a shell or second layer comprising the carbon oxychalcogenide.

[0052] Because the reaction is a surface reaction, when the carbon material is in the form of small particles with high surface area (e.g., RGC powder nominally -325 mesh, having a nominal surface area of 1400-1800 m^2/g), then the surface and interior of the particle may become coextensive. In one instance there may be no apparent chemical distinction between the outer surface and the interior of the particle. In another instance, the chalcogen content on the bulk can approach or even exceed that on the surface.

[0053] The solid-vapor process of this disclosure permits penetration of small molecule reactants into micropores and niches formed by highly irregular surfaces. This results in an advantageous, even distribution of chalcogen.

[0054] Because not all of the chalcogenide from the chalcogen-containing compound is incorporated into the carbon substrate surface (e.g., some may be converted to COE or H_2E), it may be important to analyze the resulting composition to determine the atom fraction of carbon, oxygen, and chalcogen on the carbon substrate surface.

[0055] In the present disclosure, the atom fraction of carbon (C), oxygen (O), and chalcogen (E) on the carbon substrate surface is shown as CO_xE_y, where in one embodiment, x is 0 or is at least 0.005, 0.01, 0.02, 0.03, 0.04, or even 0.05; and at most 0.07, 0.08, 0.09, 0.1, 0.12, 0.15, or even 0.2; and y is at least 0.001, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, or even 0.06; and is at most 0.12, 0.14, 0.15, 0.16, 0.18, 0.2, 0.22, 0.25, 0.3, 0.35, or even 0.4.

[0056] In one embodiment of the carbon substrate having a surface comprising a carbon oxychalcogenide, the carbon, oxygen, and chalcogen chemically interact with one another, meaning, that these elements may be combined chemically (i.e., covalent chemical bonding between contiguous

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elements) or there may be weaker interactions between non-contiguous elements, such as hydrogen bonding.

[0057] Based on the analysis of the carbon substrate having a surface comprising an oxychalcogenide, in at least one embodiment, the oxygen and chalcogen are combined chemically on the surface of the carbon substrate. The oxygen and carbon are an integral part of the surface of the carbon substrate and are not easily removed by heating to 400°C. The nature of the structure and bonding of the carbon oxychalcogenides is complex. Carefully deconvoluted XPS (X-ray photoelectron spectroscopy) spectra of the resulting compositions of the present disclosure reveal that sulfur is in four different chemical environments with $S2p_{3/2}$ binding energies of about 162.0, 164.3, 165.8 and 168.9 eV [C(1s)= 285.0 eV]. They therefore contain chemically combined sulfur in three formal valence states [S(VI), S(IV) and S(II)] and four different chemical environments. These chemical environments are: (1) S(VI) as in SO_4^{2-} or organic sulfones, C-SO_2-C; (2) S(IV) as in organic sulfoxides, C-SO-C; (3) S(II) as in thiophene; and (4) S(II) as in organic sulfides, C-S-C or disulfides, C-S-S-C.

[0058] In one embodiment, the carbon substrate having a surface comprising an oxychalcogenide has a high thermal stability. For example, with carbon oxysulfides, significant weight loss under nitrogen does not begin until about 200°C, well above the boiling point of sulfur, indicating that the carbon substrate having a surface comprising an oxychalcogenide are not mere physical mixtures of starting materials.

[0059] By using a solid-vapor process to incorporate the carbon oxychalcogenide surface onto the carbon substrate, several advantages may be realized. Because the reaction may be solventless or at least free of organic solvent, no drying operation is needed to isolate the product. Further, there are generally no non-volatile by-products that remain to clog small pores in the solid. If no solvent is used, the process as described herein can be envisioned to run as a continuous process, which can reduce cost and/or increase throughput.

[0060] Thermolysis Product of Metal Salts

[0061] Thermolysis involves heating a metal salt at or above the temperature at which the metal salt begins to lose metal-bound water, if present, and at which the salt portion of the compound begins to decompose. As used herein a "thermolysis product" refers to a product that results from the dissociation or decomposition of a compound by heat. This thermolysis process is believed to change the nature of the metal salt to a material having a different stoichiometry and composition and different chemical properties, wherein at least a portion of the salt is thermally decomposed and is removed by volatilization as a gas.

[0062] In one embodiment, upon thermolysis, the oxidation state of the metal changes. For example, in one embodiment of the present disclosure, the metal in the thermoylsis product comprises at least a portion of the metal with an oxidation state of, for example, Cu^0, Cu^{+1}, or Fe^{+2}.

[0063] Although not wanting to be bound by theory, in another embodiment, the thermolysis of the metal salt is thought to produce a material having active surface sites that exhibit enhanced activity for

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catalyzing the decomposition of chloramines. The production of these surface sites by thermolysis of the metal salt results in materials with chloramines removal properties superior to those that result from utilizing similar metal compounds (such as are observed by X-ray diffraction analysis of the thermolysis product) produced by non-thermolysis methods, e.g., metal oxides derived from more traditional methods or finely divided metals.

[0064] The metal salt may be thermally treated in the presence carbon substrates or carbon substrates having a surface comprising an oxychalcogenide. The metal salt may be impregnated into the support prior to thermolysis. For example, a metal salt may be dissolved in a solvent and the resulting solution contacted with the support. The impregnated support then may be heated to form a thermolysis product disposed on the surface of the support.

[0065] In another embodiment, metal salts, which are not sufficiently soluble to dissolve in the solvent (i.e., do not completely dissolve in the volume of solvent used in the experiment) may be impregnated into the support by adding the metal salt and the support to the solvent. In time, the metal salt that is dissolved in the solvent can diffuse into the support and deposit thereon, so that the metal salt is incorporated into or onto the support over time.

[0066] The metal salt is thermally treated in the presence of carbon. The thermal treatment may be conducted in an air environment or in an inert environment, such as in a nitrogen or argon environment.

[0067] The thermolysis temperature, the temperature at which the thermolysis reaction is conducted, may be conducted at a temperature of at least 200, 250, 300, 400, or even 500°C; and at most 650, 700, 800, 900, 1000, 1200, or even 1400 °C. Generally the temperature at which thermolysis is conducted may be determined, by first analyzing the material (e.g., the metal salt or the metal salt impregnated support) to be treated by differential thermal analysis/thermal gravimetric analysis (DTA/TGA) performed under controlled conditions (atmosphere and heating rate) to determine its thermal decomposition behavior. Then trials may then be performed by thermolyzing the material at various temperatures beginning with the onset temperature of decomposition to determine at what point and under what conditions (temperature, time and atmosphere) the most active material is formed.

[0068] In one embodiment, as the reaction temperature changes the thermolysis product of the metal salt changes and there may be a select temperature based on the metal salt and support used, which offers a more efficient removal of chloramine. For example, excessive heating of the metal salt can result in "over-firing" of the reaction product, and the activity of the material can diminish. In one embodiment, the presence of a carbon support during the thermolysis treatment can alter the decomposition temperature.

[0069] Methods of preparing

[0070] In one embodiment, a carbon substrate is provided comprising a surface of an oxychalcogenide following the preparation described herein. The carbon substrate comprising a surface of an

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oxychalcogenide is then contacted with a metal salt (for example by impregnation) and heated to thermally decompose the metal salt described herein.

[0071] In another embodiment, a carbon substrate is heated in the presence of a sulfur, selenium, or tellurium source and a metal salt to form the composition of the present disclosure.

[0072] Composition

[0073] The compositions of the present disclosure comprise a thermolysis product of a carbon support, a chalcogen selected from at least one of S, Se, and Te; and a metal salt. Small amounts of other elements may be present, due to impurities present in the metal salt, the carbon support, the chalcogen source, and/or in atmosphere used during the thermal treatment. Impurities are typically less than 5%, 2%, 1%, 0.1%, 0.05%, or even 0.01% of particular impurity atom based on the weight of the composition.

[0074] In one embodiment, the composition comprises more than 1.2, 1.3, 1.5, 1.8, 2.0, 4.0, 6.0, 8.0 or even 10.0 mass % sulfur based on the total mass of the composition.

[0075] In one embodiment, the composition of the present disclosure comprises less than 0.50, 0.30, 0.10, 0.05, 0.01, or even 0.005 mass % sulfur based on the total mass of the composition.

[0076] In one embodiment, the composition of the present disclosure comprises less than 0.90, 0.80, 0.70, 0.50, 0.30, 0.10, 0.05, 0.01, or even 0.005 mass % nitrogen based on the total mass of the composition.

[0077] In one embodiment, the composition of the present disclosure is substantially free of hydrogen, comprising less than 0.40, 0.30, 0.20, 0.10, 0.05, or even 0.01 mass % hydrogen based on the total mass of the composition.

[0078]

[0079] Use

[0080] In one embodiment, the composition of the present disclosure may be used as a filtration medium. Because of the ability of the substrates of the present disclosure to remove chloramine, in one embodiment, the substrates may be used as a filtration media. Filtration methods as known in the art can be used.

[0081] The substrates may be used either alone, or mixed with inert diluents or functionally active materials such as adsorbents. For example the substrate may be mixed intimately or layered in beds with carbon that has higher capacity for adsorption of volatile organic compounds. In this way, an adsorbent system with more than one functionality can be produced.

[0082] The substrate of the present disclosure may be used in a powdered form, a granular form, or shaped into a desired form. For example, the substrate of the present disclosure may be a compressed blend of the carbon substrates comprising the substrate and a binder material, such as a polyethylene, e.g., an ultra high molecular weight PE, or a high-density polyethylene (HDPE). In another embodiment, the substrate of the present disclosure may be loaded into web, such as a blown microfiber, which may or

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may not be compacted such as described in U.S. Publ. No. 2009/0039028 (Eaton et al.) herein incorporated in its entirety.

[0083] Because the substrate may comprise a ferromagnetic material, in one embodiment, the substrate may be part of a carbon support such as carbon particles, which can be heated by induction heating to form composite blocks. Typically in making a carbon block monolith, carbon particles are heated in an oven to fuse the carbon particles together. When using ferromagnetic material, a high frequency magnetic field may be used to heat the substrate, causing the carbon support to become fused and form a carbon block monolith. In one embodiment, the magnetic field may oscillate at a frequency in a range from about 10^3 Hz to about 10^{15} Hz.

[0084] The use of induction heating to prepare a composite block, may allow more uniform heating and better heat penetration to the core of the composite carbon block and/or increase manufacturing throughput of the carbon block composites. The levels of iron salts versus other metal salts may be varied to optimized the ferromagnetic properties and the chloramine removal properties of the material.

[0085]

[0086] In one embodiment, the substrate is disposed in a fluid conduit, wherein the fluid conduit is fluidly connected to a fluid inlet and a fluid outlet. Such systems may include packed beds. Vessels comprising the substrate may be pressure or gravity to move fluid through the vessel.

[0087] In one embodiment, the substrate may be used to remove chloramines from a fluid stream, particularly a liquid fluid stream, more specifically, an aqueous fluid stream. Chloramines are formed from the aqueous reaction between ammonia and chlorine (hypochlorite). Thus, adding ammonia (NH_3) to a chlorination system converts chlorine to chloramines. Specifically, monochloramine, hereafter referred to as "chloramine," in low concentrations arise from the disinfection of potable water sources. In one embodiment, after contacting the aqueous solution with a composition, as disclosed herein, the resulting aqueous solution comprises a reduced amount of chloramines, for example, at least a 10, 20, 25, 30, or even 50 % chloramine reduction as measured by the Chloramine Removal Test, at 180 seconds described in the Example Section below.

[0088] Previous publications, such as Vikesland, et al. in Environmental Science and Technologies, 200, 34, 83-90 have suggested that the water soluble forms of the ferrous ion are responsible for the removal of chloramines. In one embodiment of the present disclosure, it has been discovered that the metal of the decomposed metal salt responsible for the chloramines removal has limited solubility in water (in other words, a solubility producing metal ion concentrations of less than 2 ppm, 1 ppm, 0.5 ppm, or even 0.1 ppm). When the substrate is washed with water, little to no metal is present in the wash water and the washed substrate retains its activity for chloramine removal. Having an insoluble or limited solubility thermolysis product may be advantageous, because the metal would be immobilized, preventing leaching into the treated water, enable the substrate to be conditioned prior to use, and/or generate longer lifetimes of the filtration media.

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[0089] In one embodiment, the substrate may be disposed in a fluid conduit, wherein the fluid conduit has a fluid inlet and a fluid outlet, with the filtration media (e.g., carbon substrate) disposed therebetween. A chloramine-containing solution may then be passed from the fluid inlet into the fluid conduit to contact the filtration media. The filtrate (solution passing out of the fluid out) should contain less than 1, 0.5, 0.1, or even less than 0.05 ppm (parts per million) chloramines.

[0090] A non-limiting list of exemplary embodiments and combinations of xemplary embodiments of the present disclosure are disclosed below.

[0091] Embodiment 1. A filtration device comprising:

a vessel for treating fluids containing a substrate, wherein the substrate comprises a thermolysis product of (i) a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te; and wherein x and y are greater than 0; and (ii) a metal salt.

[0092] Embodiment 2. The filtration device of embodiment 1, wherein the metal salt comprises (i) a metal carboxylate; (ii) nitrogen-containing oxyanion; (iii) a sulfur-containing anion; (iv) a metal chloride; (v) a metal phosphate; and (vi) combinations thereof.

[0093] Embodiment 3. The filtration device of embodiment 2, wherein the nitrogen-containing oxyanion metal salt comprises a nitrate, a nitrite, and combinations thereof.

[0094] Embodiment 4. The filtration device of embodiment 2, wherein the sulfur-containing anions metal salt comprises a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

[0095] Embodiment 5. The filtration device of embodiment 2, wherein the metal carboxylate comprises an oxalate, an acetate, a citrate and combinations thereof.

[0096] Embodiment 6. The filtration device of any one of the previous embodiments, wherein the metal of the metal salt is copper, iron, manganese, silver, and combinations thereof.

[0097] Embodiment 7. The filtration device of any one of the previous embodiments, wherein x is no more than 0.1, and y is 0.005 to 0.3.

[0098] Embodiment 8. The filtration device of any one of the previous embodiments, wherein x is 0.01 to 0.1.

[0099] Embodiment 9. The filtration device of any one of the previous embodiments, wherein E is sulfur and the sulfur is chemically combined with carbon.

[00100] Embodiment 10. The filtration device of any one of the previous embodiments, wherein the filtration device is a water filtration device.

[00101] Embodiment 11. The filtration device of any one of the previous embodiments, wherein the substrate comprises less than 0.90, mass % nitrogen based on the total mass of the substrate.

[00102] Embodiment 12. The filtration device of any one of the previous embodiments, wherein the substrate comprises greater than 2.0 mass % sulfur based on the total mass of the substrate.

[00103] Embodiment 13. A method for removing chloramine from aqueous solutions comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a

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composition comprising a thermolysis product of a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te and a metal salt wherein x and y are greater than 0.

[00104] Embodiment 14. The method of embodiment 13, wherein the metal salt comprises (i) a metal carboxylate; (ii) nitrogen-containing oxyanion metal salt; (iii) a sulfur-containing anion metal salt; (iv) a metal chloride; (v) a metal phosphate; and (vi) combinations thereof.

[00105] Embodiment 15. The method of embodiment 14, wherein the nitrogen-containing oxyanion metal salt comprises a nitrate, a nitrite, and combinations thereof.

[00106] Embodiment 16. The method of embodiment 14, wherein the sulfur-containing anions metal salt comprises a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

[00107] Embodiment 17. The method of embodiment 14, wherein the metal carboxylate comprises an oxalate, an acetate, a citrate, and combinations thereof.

[00108] Embodiment 18. The method of any one embodiments 14-17, wherein the metal of the metal salt is copper, iron, manganese, silver, and combinations thereof.

[00109] Embodiment 19. The method of any one of embodiments 14-18, wherein x is no more than 0.1, and y is 0.005 to 0.3.

[00110] Embodiment 20. The method any one of embodiments 14-18, wherein x is 0.01 to 0.1.

[00111] Embodiment 21. The method any one of embodiments 14-20, wherein the composition comprises less than 0.90, mass % nitrogen based on the total mass of the composition.

[00112] Embodiment 22. The method any one of embodiments 14-20, wherein the composition comprises greater than 2.0 mass % sulfur based on the total mass of the composition.

[00113] Embodiment 23. A method of making a substrate comprising:

providing a composition comprising (i) a carbon substrate; (ii) a sulfur, selenium, or tellurium source, or combinations thereof; and (iii) a metal salt; and

heating the composition.

[00114] Embodiment 24. The method of embodiment 23, further comprising reacting the carbon substrate and the sulfur, selenium, or tellurium source, or combinations thereof to form a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te and wherein x and y are greater than 0; contacting the carbon substrate having a surface of CO_xE_y with the metal salt; and then heating the composition.

[00115] Embodiment 25. The method of any one of embodiments 23-24, wherein the metal salt comprises (i) a metal carboxylate; (ii) nitrogen-containing oxyanion metal salt; (iii) a sulfur-containing oxyanion metal salt; (iv) a metal chloride; (v) a metal phosphate, and (vi) combinations thereof.

[00116] Embodiment 26. The method of embodiment 25, wherein the nitrogen-containing oxyanion metal salt comprises a nitrate, a nitrite, and combinations thereof.

[00117] Embodiment 27. The method of embodiment 25, wherein the sulfur-containing oxyanions metal salt comprises a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

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[00118] Embodiment 28. The method of embodiment 25, wherein the metal carboxylate comprises an oxalate, an acetate, a citrate, and combinations thereof.

[00119] Embodiment 29. The method of any one embodiments 24-28, wherein the metal of the metal salt is copper, iron, manganese, silver, and combinations thereof.

[00120] Embodiment 30. The method of any one of embodiments 24-29, wherein x is no more than 0.1, and y is 0.005 to 0.3.

[00121] Embodiment 31. The method of any one of embodiments 24-29, wherein x is 0.01 to 0.1.

EXAMPLES

[00122] Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

[00123] All materials are commercially available, for example from Sigma-Aldrich Chemical Company; Milwaukee, WI, or known to those skilled in the art unless otherwise stated or apparent.

[00124] These abbreviations are used in the following examples: g = gram, hr = hour, in = inch, kg = kilograms, min = minutes, mol = mole; M = molar, cm= centimeter, mm = millimeter, ml = milliliter, L = liter, N = normal, psi=pressure per square inch, MPa = megaPascals, and wt = weight.

[00125] **Testing Methods**

[00126] **Apparent Density Determination**

[00127] The apparent density of a sample (prepared according to Comparative Examples or the Examples according to the disclosure) was determined by tapping a weighed sample in a graduated cylinder until closest packing was achieved. The closest packing was deemed to occur when tapping did not produce a further decrease in volume of the carbon substrate sample.

[00128] **Chloramine Test**

[00129] The chloramine content of water samples was determined from the total chlorine content in the samples. Total chlorine (OCl^- and chloramines) concentration was measured by the DPD Total Chlorine Method, Hach Method 8167, which Hach Company claims to be equivalent to USEPA Method 330.5. The free chlorine (OCl-) concentration was periodically measured by the DPD Free Chloramine Analysis, Hach Method 8021, which Hach company claims is equivalent to EPA Method 330.5. Free chlorine was maintained at a negligible concentration (< 0.2 ppm), thus, the total chlorine analysis was considered a good approximation of the concentration of chloramines in the water. All reagents and the instruments were those described in the standard Hach Method and can be obtained from Hach Company, Loveland, CO.

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[00130] **Chloramine Preparation**

[00131] 3 ppm +/- 0.3 ppm choramine was prepared by adding the appropriate amount of commercial bleach (5.25% NaOCl) to deionized water. While stirring, 1.5 equivalents of a solution of ammonium chloride in water was added to the bleach solution and stirred for 1 hour. The pH was adjusted to 7.6 +/- 0.2 by the addition of NaOH or HCl and tested using a pH meter (obtained from Thermo Fisher Scientific, Inc., Waltham, MA, under the trade designation "ORION 3-STAR").

[00132] **Chloramine Removal Test**

[00133] An aqueous chloramine test solution was prepared comprising 3 ppm NH_2Cl (prepared as described above) at a pH 7.6 at 27°C. Immediately prior to the test, the initial total chlorine content of the aqueous chloramine test solution was measured as described in the Chloramine Test above. With continuous stirring, a 0.46g aliquot of a carbon substrate sample (i.e. a sample prepared according to Comparative Examples or the Examples according to the disclosure). Immediately after mixing, a timer was started. After 30 sec, a 5 mL-aliquot of mixture was removed and within 5 sec of removal, the mixture was passed through a 1-micrometer syringe filter to remove suspended solids. The chloramine content of the filtered aliquot was measured within 30 sec of taking the 5-mL aliquot as described above. Aliquots from the mixture were taken periodically over the course of 5 minutes and analyzed using the Chloramine Test as described above. The efficiency of the chloramine removal is reported as the % chloramine reduction determined by the equation:

$$\left(1-\frac{[NH2Cl]filteredaliquot}{[NH2Cl]initial}\right)\times 100$$

Materials

Material	Description
Carbon Substrate B	Activated carbon powder obtained from MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation "AQUAGUARD Powder". This carbon is sold specifically for chloramine reduction.
Carbon Substrate A (RGC)	Wood-based activated carbon powder MeadWestvaco Specialty Chemicals, North Charleston, SC, under the trade designation "RGC Powder".
Cupric oxalate hemihydrate	Obtained from GFS Chemicals, Inc., Columbus, OH, used as received
Sulfur Powder	99.5% Alfa Aesar, Ward Hill, MA
$MnSO_4 \cdot H_2O$	Manganous Sulfate Monohydrate Powder, ACS Reagent grade obtained from J.T. Baker.

[00134] Comparative Example A

[00135] Carbon Substrate A was tested, without further treatment, using the Chloramine Removal Test. The results are shown in Table 1.

[00136] Comparative Example B

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[00137] Comparative Example B was prepared by combining cupric oxalate hemihydrate (0.63 g,) with Carbon Substrate A (5 g) as a slurry in 75 mL water (target 4.7% loading). The mixture was stirred for 5 days at room temperature. Due to the slight solubility of cupric oxalate hemihydrate, disappearance of the blue colored particulates from solution was indicative of the completion of impregnation (after 5 days in this case). The powder was isolated by filtration and dried at room temperature overnight. The sample was heated in a furnace at 300°C for 1 hr under nitrogen. The furnace was purged with nitrogen prior to heating. The sample was then cooled to room temperature and tested using the Chloramine Removal Test. The result is shown in Table 1.

[00138] Comparative Example C

[00139] 10 g of Carbon Substrate A was thoroughly mixed with 1 g finely powdered sulfur (nominally 10 wt %) and transferred to a reactor consisting of a 15 x 1.5 inch (381 mm x 38.1 mm) glass tube connected via a 20 mm Solv-Seal joint (Andrews Glass Co., Vineland, NJ) to a 10 mm greaseless high vacuum stopcock and vacuum line interface. A plug of glass wool was inserted ahead of the stopcock to prevent loss of entrained solids. After outgassing for 30 min, the reactor and contents were heated in a vertical furnace at 400°C for 1 hr. After cooling to room temperature, the reactor was again evacuated through a liquid nitrogen-cooled trap for 15 min, and then opened to isolate the product. The product was analyzed by X-ray photoelectron spectroscopy (XPS) and the C(1s), O(1s) and S($2p_{3/2}$) peaks were integrated to determine the surface composition of the product which contained 92.6 atomic % of C, 3.4 atomic % of O, and 3.4 atomic % of S. Bulk chalcogen content of the product determined by combustion analysis was $8 \pm 1\%$ of S.

[00140] Example 1

[00141] Cupric oxalate hemihydrate (0.63 g) was combined with a portion of the sulfided carbon of Comparative Example C (5 g) as a slurry in 75 mL water (target 4.7% loading). The mixture was stirred for 5 days at room temperature. Due to the slight solubility of cupric oxalate hemihydrate, disappearance of the blue colored particulates from solution was indicative of the completion of impregnation (after 5 days in this case). The powder was isolated by filtration and dried at room temperature overnight. The sample was then heated in the same tube reactor used to prepare the sulfided carbon described above while sealed under N_2 at 300° C for 1 hour the sample was then cooled to room temperature and tested using the Chlroamine Removal Test. Table 1 summarizes the % chloramine removed from water samples after indicated time (in seconds) elapsed.

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Table 1

Time (seconds)	Example			
	Comp. A	Comp. B	Comp. C	Ex.1
10	6.90	42.86	33.33	68.97
30	17.24	71.43	56.67	89.66
60	24.14	82.14	70.00	96.55
120	34.48	92.86	86.67	96.55
180	41.38	96.55	86.67	96.55
240	48.78	96.55	93.34	96.55
300	55.17	96.55	96.55	96.55

[00142] Comparative Example D

[00143] Carbon Substrate B was tested, without further treatment, using the Chlroamine Removal Test. The results are shown in Table 2.

[00144] Comparative Example E

[00145] $MnSO_4 \cdot H_2O$ was added to deionized water with vigorous stirring. The aqueous manganese sulfate solution then was added to Carbon Substrate A. The impregnated carbon was then heated in a nitrogen-purged muffle furnace at 875 °C for 15 minutes. The crucible was then removed to cool under a nitrogen purge. The impregnation resulted in approximately 6.3% manganese (as Mn) on the carbon. The sample was tested using the Chloramine Removal Test. The results are shown in Table 2.

[00146] Example 2

[00147] Carbon substrate A was heated to 180°C. The sulfur powder was added to the heated carbon and the mixture stirred until the sulfur melted into the carbon. The sulfur containing carbon was then heated to 550°C for 15 minutes in a muffle furnace under a purge of nitrogen. The sample was cooled under nitrogen purge.

[00148] $MnSO_4 \cdot H_2O$ was added to deionized water with vigorous stirring. The aqueous manganese sulfate solution was added to the carbon treated with sulfur above. The impregnated carbon was then heated in a nitrogen-purged muffle furnace at 875°C for 15 minutes. The crucible was then removed to cool under a nitrogen purge. The impregnation resulted in approximately 6.3 wt% manganese (as Mn) on the carbon.

[00149] The sample of Example 2 was tested using the Chloramine Removal Test. The results are shown in Table 2.

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Table 2

Example	Carbon Substrate	Sulfur treated	% Mn in thermolysis precursor	% Chloramine reduction at 150 sec
Comp. Example D	B	No	0	82*
Comp. Example A	A	No	0	42*
Comparative Example E	A	No	6.3	69*
Example 2	A	Yes	6.3	96*

* Denotes samples, where 1.5 cc of carbon substrate sample was used, instead of the 0.46 g in the Chloramine Removal Test. The 1.5 cc aliquot was measured by mass, knowing the apparent density of the sample.

[00150] Foreseeable modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to the embodiments that are set forth in this application for illustrative purposes. To the extent that there is a conflict or discrepancy between this specification and the disclosure in any document incorporated by reference herein, this specification will control.

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What is claimed is:

1. A filtration device comprising:

a vessel for treating fluids containing a substrate, wherein the substrate comprises a thermolysis product of (i) a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te; and wherein x and y are greater than 0; and (ii) a metal salt.

2. The filtration device of claim 1, wherein the metal salt comprises (i) a metal carboxylate; (ii) nitrogen-containing oxyanion; (iii) a sulfur-containing anion; (iv) a metal chloride; (v) a metal phosphate; and (vi) combinations thereof.

3. The filtration device of claim 2, wherein the nitrogen-containing oxyanion metal salt comprises a nitrate, a nitrite, and combinations thereof.

4. The filtration device of claim 2, wherein the sulfur-containing anions metal salt comprises a sulfate, sulfamate, sulfite, bisulfate, bisulfite, thiosulfate, and combinations thereof.

5. The filtration device of claim 2, wherein the metal carboxylate comprises an oxalate, an acetate, a citrate and combinations thereof.

6. The filtration device of any one of the previous claims, wherein x is no more than 0.1, and y is 0.005 to 0.3.

7. The filtration device of any one of the previous claims, wherein x is 0.01 to 0.1.

8. The filtration device of any one of the previous claims, wherein E is sulfur and the sulfur is chemically combined with carbon.

9. A filtration device of any one of the previous claims, wherein the filtration device is a water filtration device.

10. A method for removing chloramine from aqueous solutions comprising: providing an aqueous solution comprising chloramine and contacting the aqueous solution with a composition comprising a thermolysis product of a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te and a metal salt wherein x and y are greater than 0.

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11. The method of claim 10, wherein the metal salt comprises (i) a metal carboxylate; (ii) nitrogen-containing oxyanion metal salt; (iii) a sulfur-containing anion metal salt; (iv) a metal chloride; (v) a metal phosphate; and (vi) combinations thereof.

12. A method of making a substrate comprising:

providing a composition comprising (i) a carbon substrate; (ii) a sulfur, selenium, or tellurium source, or combinations thereof; and (iii) a metal salt; and

heating the composition.

13. The method of claim 12, further comprising reacting the carbon substrate and the sulfur, selenium, or tellurium source, or combinations thereof to form a carbon substrate having a surface of CO_xE_y, wherein E is selected from at least one of S, Se, and Te and wherein x and y are greater than 0; contacting the carbon substrate having a surface of CO_xE_y with the metal salt; and then heating the composition.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/070297

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/72 B01J37/08 B01J20/30 B01J21/18 B01J20/02
ADD. C02F101/12 C02F101/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F B01J B01D C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/296991 A1 (HUGHES MARK A [US] ET AL) 8 December 2011 (2011-12-08) paragraph [0019] - paragraph [0021] -----	1-9,12, 13
X	WO 2011/125504 A1 (KURARAY CHEMICAL KK [JP]; HITOMI MITSUNORI [JP]; YOSHIKAWA TAKAYUKI [J) 13 October 2011 (2011-10-13) paragraph [0019] - paragraph [0021] paragraph [0062] - paragraph [0068] -----	10,11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/070297

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011296991 A1	08-12-2011	AU 2011264921 A1	06-12-2012
		US 2011296991 A1	08-12-2011
		WO 2011156483 A1	15-12-2011
WO 2011125504 A1	13-10-2011	CN 102822093 A	12-12-2012
		TW 201202136 A	16-01-2012
		US 2013023405 A1	24-01-2013
		WO 2011125504 A1	13-10-2011

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Bibliographic data: WO2013149241 (A1) — 2013-10-03

DRY PROCESSES, APPARATUS, COMPOSITIONS AND SYSTEMS FOR REDUCING SULFUR OXIDES AND HCI

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Classification: **- international:** ***B01D53/00***
- cooperative: **B01D53/10 (EP, US)**; **B01D53/14 (KR)**; **B01D53/40 (KR)**; **B01D53/50 (KR)**; **B01D53/508 (EP, US)**; **B01D53/685 (EP, US)**; **B01D53/80 (EP, US)**; **B01J20/043 (EP, US)**; **B01J20/223 (EP, US)**; **F23J15/003 (EP, US)**; B01D2251/402 (EP, US); B01D2251/404 (EP, US); B01D2253/112 (EP, US); B01D2253/304 (EP, US); B01D2253/306 (EP, US); B01D2255/20738 (EP, US); B01D2255/20761 (EP, US); B01D2257/2045 (EP, US); B01D2257/302 (EP, US); B01D2258/0283 (EP, US); F23J2215/20 (EP, US); F23J2219/50 (EP, US); Y02C20/40 (KR)

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Abstract of WO2013149241 (A1)

Dry processes, apparatus, compositions and systems are provided for reducing emissions of sulfur oxides, and sulfur dioxide in particular, and/or HCI in a process

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employing a combination of a dolomite hydrate sorbent and a sorbent doping agent administered to achieve coverage of a three-dimensional cross section of a passage carrying SOx and/or HCl - containing gases with a short but effective residence time at a temperature effective to provide significant sulfur dioxide and/or HCl reductions with high rates of reaction and sorbent utilization. The once-through, dry process can advantageously introduce the sorbent and sorbent doping agent dry or preferably as a slurry to enable uniform treatment. Preferred sorbent doping agents include water-soluble or water-dispersible copper and/or iron compositions which can be heated to an active form in situ by the flue gases being treated.

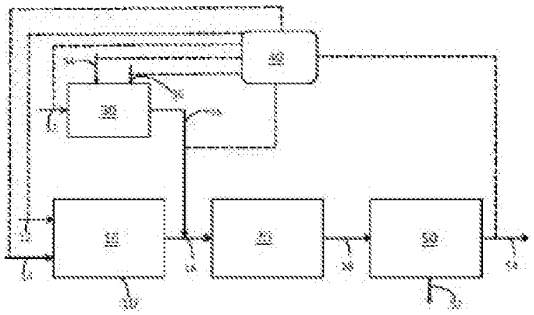


Fig. 1

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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(54) **Title**: DRY PROCESSES, APPARATUS, COMPOSITIONS AND SYSTEMS FOR REDUCING SULFUR OXIDES AND HCI

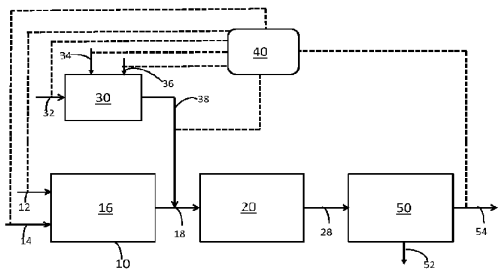


Fig. 1

(57) **Abstract**: Dry processes, apparatus, compositions and systems are provided for reducing emissions of sulfur oxides, and sulfur dioxide in particular, and/or HCI in a process employing a combination of a dolomite hydrate sorbent and a sorbent doping agent administered to achieve coverage of a three-dimensional cross section of a passage carrying SO_x and/or HCI - containing gases with a short but effective residence time at a temperature effective to provide significant sulfur dioxide and/or HCI reductions with high rates of reaction and sorbent utilization. The once-through, dry process can advantageously introduce the sorbent and sorbent doping agent dry or preferably as a slurry to enable uniform treatment. Preferred sorbent doping agents include water-soluble or water-dispersible copper and/or iron compositions which can be heated to an active form *in situ* by the flue gases being treated.

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DRY PROCESSES, APPARATUS, COMPOSITIONS AND SYSTEMS FOR REDUCING SULFUR OXIDES AND HCI

Cross Reference and Priority Claim

[001] This application is claims priority to U. S. Provisional Patent Application No. 61/618233, filed March 30, 2012, the disclosure of which is incorporated herein by reference in its entirety.

Field of the Invention

[002] The invention relates to dry processes, apparatus, compositions and systems for reducing emissions of sulfur oxides, and sulfur dioxide in particular, and HCI in a process employing a highly-effective combination of a sorbent and a sorbent doping agent administered to achieve coverage of the entire cross section of a passage carrying SO_x and/or HCI -containing gases with a short but effective residence time at a temperature effective to provide significant sulfur dioxide and/or HCl reductions with high rates of reaction and sorbent utilization. The invention provides a once-through, dry process and can advantageously introduce the sorbent and sorbent doping agent as a slurry to enable uniform treatment.

Background of the Invention

[003] The problem of sulfur oxides has challenged combustion plant operators and regulators since there became an awareness of the harmful effects of acid rain. Sulfur oxides are formed during the combustion of sulfur-containing carbonaceous fuels and are referred to generally as SO_x while comprising sulfur dioxide (SO_2) and sulfur trioxide (SO_3). The vast majority of SO_x is present as SO_2. The SO_3 (as H_2SO_4) can, however, add to particulates emitted and can cause cold end corrosion. Accordingly, an effective system must address both SO_2 and SO_3. Ideally, the process should also address the problem of hydrochloric acid (HCl).

[004] The art has provided a wide range of technologies. As a group, they can be called flue gas desulfurization technologies, FGD. See, for example, *Srivastava, Ravi K.; Controlling SO_2 Emissions: A Review of Technologies; EPA/600/R-00/093, November 2000*. These include both

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wet and dry technologies and can employ existing equipment, such as duct work, or provide separate reactors.

[005] According to Srivastava, FGD technologies fall into two main categories: (1) once-through and (2) regenerable. In the former, the sorbent is discarded after use; and in the latter, the sorbent is regenerated after it has sorbed SO_2.

[006] In once-through processes, sorbed SO_2 is bound by the sorbent and the sorbent is considered spent. The spent sorbents can be disposed of or recovered as a useful by-product, like gypsum, depending on quality and market factors.

[007] Technologies considered regenerable can treat the sorbents to release the SO_2 and obtain useful products. After regeneration, the sorbent can be recycled for additional SO_2 scrubbing.

[008] Each of the once-through and regenerable technologies can be further broken down as wet or dry. Wet processes produce a wet slurry waste or by-product, and scrubbed flue gas is saturated with water. The dry processes produce dry waste material, and scrubbed flue gas is not saturated.

[009] The reader is referred to Srivastava, *supra*, for a closer view of the various technologies, where the authors group major FGD technologies into three major categories: (1) Wet FGD (composed of once-through wet FGD), (2) Dry FGD (composed of once-through dry FGD) and (3) Regenerable FGD (composed of wet and dry regenerable FGD)

[010] The wet FGD processes can employ wet scrubbers, which typically employ large towers that cause contact between combustion flue gases and a slurry of calcium carbonate or the like that is sprayed countercurrently to the flue gas flow. Suitable chemical slurries can include calcium carbonate (limestone), lime (CaO in slurry as Ca $(OH)_2$), trona (sodium sesquicarbonate), sodium bicarbonate, dolomite, and the like, or blends of these materials. In limestone-based scrubbers, the SO_x is captured to form $CaSO_3$, which is naturally oxidized in part or overtly oxidized to form gypsum ($CaSO_4$), which can be used commercially. Reaction between the SO_x and the sorbent occurs in the liquid phase in a stirred tank over considerable time periods. Fuels high in chlorides will alter the chemical equilibrium in the liquid and can adversely affect scrubber efficiency. Quality and market conditions will dictate the value and

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fate of the spent sorbent. These wet scrubbers are expensive to install and operate and cannot be easily adapted to all plants.

[011] The dry processes can introduce these same type of chemicals, either dry or as slurries that rapidly dry, into a flue gas stream in the furnace, a separate reactor or a duct or other passage carrying the flue gas, wherein the SO_x is captured to some extent and can be disposed of in dry particulate form.

[012] In one group of dry processes, a slurry is sprayed into a separate reactor – adapted from industrial spray driers – to cause intimate contact with the flue gases for moderate reaction times, *e.g.*, ten seconds or more. These processes are quite effective, while not as effective as the wet scrubbers. They, however, are also capital intensive but cannot provide the high quality gypsum achievable by wet scrubbers.

[013] In in-furnace sorbent injection, a dry sorbent is injected directly into the furnace in the optimum temperature region above the flame. As a result of the high temperature (*e.g.,* on the order of 2000°F), sorbent particles (*e.g.*, often calcium hydroxide or calcium carbonate) decompose and become porous solids with high surface systems. Residence time is very short, on the order of a few seconds, and the sorbent particles are easily fouled before the chemical is fully utilized.

[014] In-duct sorbent injection, like in-furnace sorbent injection, involves direct injection of sorbent into SO_x-containing gases. In these processes, the sorbent is introduced into a flue gas duct, but in contrast to spray drying, contact is made without the advantage of a large reaction vessel as used in spray dryers, and suffers from greatly diminished contact times, *e.g.*, often only a few seconds. In-duct injection, typically uses an alkali metal or alkaline earth oxide or hydroxide, like trona, sodium carbonate, calcium hydroxide, magnesium hydroxide, dolomite, or the like, as outlined by Srivastava, *supra*, and U. S. Patent No. 5,658,547 to Michalak, *et al*. U. S. Patent No. 5,492,685 to Moran describes a hydrated lime having high surface area and small particle size prepared by hydrating lime with an aqueous hydration solution of an organic solvent, and preferably washing the resulting hydrate with an aqueous solution of an organic solvent prior to drying. The high surface area hydrates (*e.g.*, up to 85 m^2/g) are sorbents for SO_2 removal from gas streams.

[015] U. S. Patent No. 5,658,547 to Michalak, *et al*., describes removing SO_x and particulates from the combustion gases of a large boiler. In a primary treatment zone, a slurry comprising

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an alkaline SO_x-reducing composition and preferably a nitrogen-containing composition effective to reduce NO_x, is introduced into combustion gases at a temperature of from about 900° to about 1300°C (about 165° to about 2375°F). The gases are cooled by initial contact with steam-generating means, and then by contact with a gas-to-gas heat exchanger. Cooled gases are then subjected to a secondary treatment in which they are first humidified and further cooled by introduction of a water spray or aerosol to reduce the temperature to 100°C (212°F) or below. Contact between the SO_x-reducing composition and the humidified gas is maintained for a reaction period of at least two seconds. Particulate solids are then separated from the gases with a fabric filter. The cleaned gases are reheated by the gas-to-gas heat exchanger prior to discharge to the atmosphere.

[016] These processes require feeding large quantities of these SO_x-reducing reagents, whether to the furnace or to back end duct work, and add significant solids to ash capture equipment and in some cases can degrade performance and cause operating and handling problems under certain conditions. There remains a need for a dry scrubbing process that can increase the sorbent utilization and removal efficiencies.

[017] Other dry processes can include fluidized beds that provide longer reaction times. These processes are typically engineered to recirulate the sorbent for multiple passes with the combustion gases to enhance economy by increasing utilization of the sorbent. The sorbents for these processes are intended for recycling and are, therefore, more expensive to make and handle.

[018] An example of these latter types of processes is seen from U. S. Patent No. 4,755,499 to Neal, *et al*., which describes sorbents that are intended to be resistant to normal physical degradation which results from recurring adsorption and regeneration for use in a fluidized bed absorber. The sorbent is constructed of (a) an alumina substrate having a specified pore volume and (b) an alkali or alkaline earth component in defined amount relative to the substrate. Minor amounts of other metallic oxides can also be employed. The sorbents are manufactured to be regenerable and attrition resistant. They can be regenerated by heating in an inert atmosphere at temperatures up to about 350°C and then reused.

[019] In a related disclosure, U. S. Patent No. 6,281,164, Demmel, *et al*., teach that the useful life of SO_x additives having a SO_2 to SO_3 oxidation catalyst component and a SO_3 absorption component can be extended by employing each of these components as separate

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and distinct physical particles or pellets. The particles are prepared by spray drying or desiccation followed by calcination to produce microspheroidal particles having a range of sizes such that essentially all such particles will be retained by a Standard U.S. 200 mesh screen and essentially all particles will be passed by a Standard U.S. 60 mesh screen. Processing to reduce SO_x entails capturing the SO_x on the particles and then regenerating the particles for reuse. These particles are too expensive for once-through processes and are, in fact, too large to achieve good utilization in those processes.

[020] Another example of regenerable sorbents is found in U. S. Patent No. 5,114,898 to Pinnavaia, *et al*., which describes processes for removing noxious sulfur oxides from gas streams, particularly from flue gases of coal-burning power plants, using heated layered double hydroxide (LDH) sorbents. The sorbent compositions contain metal components, incorporated into the sorbents either by isomorphous replacement of all or part of M^{11} and/or M^{111} ions (the patent defining M^{11} as a divalent metal and M^{111} as a trivalent metal) in layers of LDH structures or by impregnation as a metal salt, to promote the oxidation of sulfur dioxide.

[021] In another related teaching, U. S. Patent No. 5,520,898 to Pinnavaia, *et al*., describes the use of base/clay composite materials as sorbents for the removal of SO_x from flue gas streams. The composite contains a smectite clay and a sorbent component, such as alkaline earth metal hydroxides and carbonates, and a metal oxide or metal oxide precursor, preferably selected from transition metal ions. The smectite-type clays are said to serve as supports for the reactive base and as a dispersing agent for improved reactivities. The swelling properties of smectite clays are said to be responsible for higher reactivity of the sorbents. The injection of the sorbents into these, particularly to the boiler (700°-1000°C), along with coal was considered.

[022] There is a present need for technology that can improve on the capture of SO_2 and/or HCl in high percentages and in an economical manner in terms of material, equipment and disposal.

Summary of the Invention

[023] The present invention provides processes, apparatus, compositions and systems that will have a very positive effect on air quality by enabling reduction of SO_x and HCl emissions

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at a very reasonable cost. The invention can be employed as a retrofit solution to existing plants and can be used in design of new plants.

[024] In one aspect, the invention provides a process for reducing emissions of SO_x and/or HCl from a combustor, comprising: identifying locations within a combustor for feeding a dolomite hydrate sorbent and a sorbent doping agent; determining the physical form and injection parameters for the sorbent and the sorbent doping agent; injecting both the dolomite hydrate sorbent and the sorbent doping agent into combustion gases containing SO_x and/or HCl, the introduction being under conditions effective to capture sulfur oxides and/or HCl with the sorbent at a greater rate than achievable by the same sorbent without the sorbent doping agent; and collecting the spent sorbent.

[025] In some embodiments the sorbent doping agents will comprise at least one member selected from the group of compositions comprising the sorbent doping agent comprises a copper composition selected from the group consisting of copper ammonium acetate, copper diammonium diacetate, copper ammonium triacetate, copper triammonium acetate, copper tetra ammonium sulfate, copper gluconate (and hydrates thereof), and mixtures of any of these. From another perspective, the doping agent can be a member selected from the group consisting of compositions defined by the formula $Cu(NH_3)_x$(lower carboxylate)$_y$, wherein the lower carboxylate is selected from the group consisting of formate, acetate and propionate, x is an integer from 0 to 4, y is an integer from 0 to 2, and x+y is equal to or greater than 1.

[026] In embodiments of the invention, the doping agents will comprise the sorbent doping agent comprises an aqueous cuprammonium lower carboxylate complex of copper lower carboxylate and ammonium lower carboxylate.

[027] In embodiments the doping agents will comprise an aqueous cuprammonium lower carboxylate complex of copper lower carboxylate and ammonium lower carboxylate containing weight proportions of about 13 parts of copper lower carboxylate as measured as the dihydrate to about 2 parts of ammonium lower carboxylate, and about 10 parts of 29 percent aqueous ammonia, said solution being at a pH in the range of about 7.1 to 7.4.

[028] In embodiments the dolomite sorbent hydrate and the sorbent doping agent are injected by injection means comprising a plurality of nozzles within an introduction zone, and the nozzles are positioned to achieve at least 90% coverage within the introduction zone.

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[029] In another aspect, the invention provides an apparatus for reducing SO_x and/or HCl in a gas stream, comprising: injection means positioned at locations on a passage for flue gases generated by the combustion of fuel, said injection means capable of feeding a dolomite hydrate sorbent and a sorbent doping agent at predetermined rates relative to a concentration of SO_x and/or HCl in said flue gases, and said injection means further capable of introducing the dolomite hydrate sorbent and a sorbent doping agent in a predetermined physical form and with predetermined injection parameters for the sorbent and the sorbent doping agent including droplet size, momentum and concentration; whereby the dolomite hydrate sorbent with the sorbent doping agent captures sulfur oxides with high efficiency.

[030] In another aspect, the invention provides system for reducing SO_x and/or HCl in a gas stream, comprising: computer modeling means for identifying locations within a combustor and its duct work for feeding a dolomite hydrate sorbent and a sorbent doping agent and determining the physical form and injection parameters for the dolomite hydrate sorbent and the sorbent doping agent injection means positioned at locations on a passage for flue gases, said injection means capable of feeding a dolomite hydrate sorbent and a sorbent doping agent at predetermined rates relative to a measured concentration of SO_x and/or HCl in said passage, and said injection means further capable of introducing the dolomite hydrate sorbent and a sorbent doping agent in a predetermined physical form and with predetermined injection parameters for the sorbent and the sorbent doping agent including droplet size, momentum and concentration; whereby the dolomite hydrate sorbent with the sorbent doping agent can have the characteristics specified below to capture sulfur oxides and/or HCl with high efficiency.

[031] In yet another aspect, the invention provides compositions for reducing SO_x and/or HCl in a gas stream, comprising: dolomite hydrate sorbent and a sorbent doping agent comprising copper and/or iron which will dehydrate and be caused to shatter into fine particles within the size range of from about 0.01 to about 0.2 microns upon introduction into a hot gas stream containing SO_x and/or HCl, wherein the weight ratio (dry basis) of dolomite hydrate to sorbent doping agent is within the range of from about 100:1 to about 1:1 and the sorbent doping agent is selected from water-soluble or water-dispersible copper and/or iron compositions that release active copper or iron species when heated *in situ* by the flue gases being treated.

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[032] The invention provides several advantages compared with competitive processes, prominent among which are: treating flue gases to reduce SO_x can also reduce HCl; sorbent material usage can be reduced due to sorbent utilization being more efficient; very high sulfur removal rates are enabled; simple equipment can be employed for retrofit.

[033] Other preferred aspects and their advantages are set out in the description which follows.

Brief Description of the Drawings

[034] The invention will be better understood and its advantages will become more apparent when the following detailed description is read in conjunction with the accompanying drawings, in which:

[035] **Fig. 1** is a flow diagram of one embodiment of the invention.

[036] **Fig. 2** is a flow diagram of another embodiment of the invention.

Detailed Description of the Invention

[037] Reference will first be made to **Fig. 1**, which is a flow diagram of one embodiment of the invention. A combustor **10** can be of the type used for producing steam for electrical power generation, process steam, heating or incineration. It will be understood that other types of combustors can be employed to utilize the advantages of the invention. Unless otherwise indicated, all parts and percentages in this description are based on the weight of the materials at the particular point in processing or dry where that is indicated.

[038] Coal is fed to the combustor **10** via line **12** and burned with air from line **14** in a combustion zone **16**. It is an advantage of the invention that coal that is high in sulfur can be combusted with the resulting sulfur dioxides reduced. Advantageously, HCl can be reduced also. It will be understood that the principles of the invention can be applied to other carbonaceous fuels and fuel mixtures (any other fuel of choice, typically a carbonaceous thermal fuel or refuse).

[039] Air for combustion, supplied by line **14**, is preferably preheated by gas-to-gas heat exchangers (not shown) which transfer heat from ductwork (not shown) at the exit end of the combustion equipment, *e.g.*, downstream of heat exchange section **20**, where useful thermal energy is recovered from the combustor. Hot combustion gases flow through the combustor

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as indicated by arrow **18** and flow through heat exchanger section **20**, which transfers heat from the combustion gases to water or steam for the generation of steam or super-heated steam. Other heat exchangers, including an economizer (downstream and not shown) may also be provided according to the design of the particular boiler.

[040] Based on an extensive test program, it has been determined that many of the sorbent materials identified above and long associated in the art as effective for SO_x reduction are far surpassed by a narrow group of combinations of sorbent and sorbent doping agents. The invention identifies dolomite hydrate (also called hydrated dolomite and dolomitic hydrated lime) of fine particle size and high surface area as a highly-effective sorbent when employed with a sorbent doping agent comprising a copper and/or iron composition.

[041] The sorbent doping agent is employed as a water-soluble or water-dispersible composition of copper and/or iron (*e.g.*, as a salt of copper and/or iron that can form the copper or iron oxide by heating *in situ*) that can be added to the dolomite hydrate sorbent for introduction into the flue gas to be treated. These sorbent doping agents release an active form, *i.e.*, species, believed to be the oxides of copper and/or iron, *in situ* when heated by the flue gases being treated. The sorbent doping agent is typically employed (dry basis) at a rate of from about 1 to about 10 pounds per ton of fuel, with a narrower range being from about 2 to about 6 pounds per ton.

[042] The sorbent doping agent will typically be employed with the dolomite hydrate sorbent at a weight ratio (dry basis) of dolomite hydrate to sorbent doping agent within the range of from about 100:1 to about 1:1. More preferred ratios will be within the range of from about 50:1 to about 5:2. Among the sorbent doping agents are iron salts such as iron nitrate and copper salts such as copper nitrate, those listed below, and especially those compositions described in U. S. Patents No. 3,900,504 and No. 4,020,180 to Woerner, the disclosures of which are specifically incorporated herein by reference in their entireties.

[043] In embodiments, sorbent doping agents can be water-soluble or water-dispersible copper and/or iron compositions which are believed to form copper and/or iron oxides when heated *in situ* by the flue gases being treated. Specifically referenced compositions are those described in U. S. Patent No. 4,020,180 as comprising an aqueous cuprammonium lower carboxylate complex of copper lower carboxylate and ammonium lower carboxylate. Desirably in accord with U. S. Patent No. 4,020,180, the complex will contain weight

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proportions of about 13 parts of copper lower carboxylate as measured as the dihydrate to about 2 parts of ammonium lower carboxylate, and about 10 parts of 29 percent aqueous ammonia, said solution being at a pH in the range of about 7.1 to 7.4.

[044] In embodiments, doping agents according to the invention are highly soluble or dispersible in water and react with the hot combustion gases to result in compositions chemically different from when contacted with the combustion gases. Desirably, doping agent compositions include copper compositions that have copper that can be released in an active form at the temperatures involved to form a reactive copper entity. While it is theorized that the copper is oxidized to copper oxide, CuO, applicants do not want to be bound by a particular theoretical reaction.

[045] Among the doping agents of interest to the invention are compositions that comprise copper and an ammonia moiety. Among these are ammonium copper compositions, including those having one or more copper atoms with one or more ammonium moieties. Water solubility or dispersibility is important because introducing them with water has been shown to be a highly-effective manner of achieving the necessary distribution followed by dissociation. Chemical dispersants and agitation can be employed as necessary.

[046] In embodiments of the invention, the sorbent doping agents will comprise a copper composition selected from the group consisting of copper ammonium acetate, copper diammonium diacetate, copper ammonium triacetate, copper triammonium acetate, copper tetra ammonium sulfate, copper gluconate (and hydrates thereof), and mixtures of any of these. From another perspective, the doping agent can be a member selected from the group consisting of compositions defined by the formula $Cu(NH_3)_x$(lower carboxylate)$_y$, wherein the lower carboxylate is selected from the group consisting of formate, acetate and propionate, x is an integer from 0 to 4, y is an integer from 0 to 2, and x+y is equal to or greater than 1.

[047] Closely related compositions and their hydrates as well other copper sources that exhibit similar efficacies in reacting with SO_2 and/or HCl can be employed. Copper compositions that contain no ammonium moiety, can be employed, but it is believed that these compositions will be facilitated in effectiveness by the presence of ammonia, such as a result of processing (*e.g.*, for NO_x reduction) or by supplementation as needed with ammonia or urea or other material effective to produce ammonia at the temperatures involved, as well as compounds equivalent in effect, e.g., ammines and their salts, urea breakdown products,

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ammonium salts of organic and inorganic acids, ammonium carbamate, biuret, ammelide, ammeline, ammonium cyanate, ammonium carbonate, ammonium bicarbonate; ammonium carbamate; triuret, cyanuric acid; isocyanic acid; urea formaldehyde; melamine; tricyanourea and mixtures and equivalents of any number of these.

[048] Among copper containing doping agents not containing an ammonium moiety are copper acetylacetonate (and hydrates thereof), copper citrate (and hydrates thereof, *e.g.*, hemipentahydrate), copper formate (and hydrates thereof), copper acetate monohydrate, copper nitrate (and hydrates thereof), copper 2,4-pentandionate (and hydrates thereof), copper sulfate (and hydrates thereof), copper gluconate (and hydrates thereof), copper soaps of fatty acids, and mixtures of any of these.

[049] The dolomite hydrate sorbent will dehydrate and be caused to shatter *in situ* by the flue gases being treated and comprised of a hot gas stream containing SO_x, into fine particles within the size range of from about 0.01 to about 0.2 microns and containing the copper and/or iron oxides well dispersed therein.

[050] Typically, the dolomite hydrate sorbent will be contacted with the hot flue gases containing SO_x as a slurry with the sorbent doping agent, and the composition will dehydrate and be caused to shatter into fine particles (*e.g.*, within the size range of from about 0.01 to about 0.2 microns) which based on modeling and proper placement of injectors and adjustment of droplet size, momentum and concentration prior to introduction, are dispersed over the cross section of the furnace section, duct or other apparatus where the flue gas is flowing. The dolomite hydrate can also be employed dry where this permits uniform distribution across the flow path of the flue gases being treated.

[051] Preferred conditions will call for introducing the sorbent and doping agent using modeling techniques, such as computational fluid dynamics, which can be employed to initially determine the optimum locations (zones) to direct treatment chemicals within the boiler and/or ducts. Desirably, best sorbent and doping agent introduction will achieve essentially full coverage of the sorbent and doping agent across a three-dimensional section of a passage for the gases to be treated. Preferably, a number of nozzles will be spaced within the zones to achieve at least 90% coverage at the temperature necessary for reaction. This section can have a depth in the direction of flow as necessary to assure complete coverage from the sorbent and doping agent injectors used. In other words, the zone will preferably be

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of a depth in the direction of flow sufficient that each of the conical or like spray patterns from nozzles used to introduce the sorbent and doping agent will overlap with at least one other spray pattern, thereby providing sorbent and doping agent across the entire cross section of the zone. This three-dimensional section for treatment can be referred to as a defined introduction zone, and the aqueous sorbent and doping agent will be introduced into this zone under conditions effective for HCl and/or SO_x emissions control. Following this zone (*i.e.*, downstream of it) the combustion gases now having been treated with the sorbent and doping agent are discharged following sufficient reaction time to reduce the HCl and/or SO_x concentration in the gases.

[052] Dolomite hydrate sorbent, which has been found effective according to the invention for capturing SO_x and/or HCl, is employed as dolomite hydrate and is preferably mixed with water to form a slurry with or without chemical stabilizers, to concentrations suitable for storage and handling, *e.g.*, at least about 25%, and preferably at least about 40%, solids by weight. Preferred concentrations are within the range of from about 30 to about 50 weight %, *e.g.*, from about 35 to about 45 weight %, based on the dry weight of the dolomite hydrate. The sorbent doping agent can be blended with the dolomite hydrate sorbent at any practical point prior to introduction into the hot combustion gases. In some cases it is introduced into the slurry tank or injection equipment directly before introduction into the flue gas being treated.

[053] Reference is made to **Fig. 1**, which depicts a mixing stage **30** provided to prepare dolomite hydrate sorbent slurry, preferably in a form having high surface area, *e.g.*, above about 100 m^2/gram (BET). For example, dolomite hydrate sorbent can be supplied via line **32**, water can be supplied via line **34** and sorbent doping agent can be supplied via line **36**. The sorbent slurry is typically characterized as containing from about 25 to about 45% dolomite hydrate solids by weight in water. Suitable stabilizers can be used to avoid the need for constantly stirring the tanks, but stirring is preferably provided. The material is further characterized by having a mass average particle size of from about 1 to about 5 microns (μ), *e.g.*, nominally about 2 to 4 microns. An alternative scheme is shown in **Fig. 2** wherein the sorbent doping agent can be added through 36' to a slurry of dolomite hydrate sorbent in line **38** and mixed by suitable means in the line. In all cases, the relative amounts of the materials and water can be controlled by a suitable controller **40**; or batching and feed can be adjusted

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manually. Dotted lines in the drawings schematically designate control lines for proper communication between the various controlled lines and valves and the controller **40**.

[054] Preferred conditions will call for introducing the dolomite hydrate sorbent as a slurry incorporating the sorbent doping agent into a flue gas being treated. The flue gas will typically be at a temperature below about 2200°F where treated, and will typically be within the range of from about 2100° to about 1500°F, preferably from about 1900°F to about 1600°F. For HCl reduction, these temperatures are effective as are temperatures below 1600°F, *e.g.*, typically lower than 900°F, say of from about 350°F to about 700°F that will also be effective. The slurry will typically be introduced as fine droplets having a mean diameter of from about 10 to about 350 microns, *e.g.*, from about 50 to about 200 microns, so that the sorbent will be present for contact with the gas as fine particles of dolomite hydrate intimately mixed with the sorbent doping agent. Upon contact with the flue gas, the slurry will dry and, it is believed, will shatter to form ultra fine particles having a particle size of from about 0.01 to about 0.2 microns, *e.g.*, about 0.02 to about 0.1 microns.

[055] The feed rate of the dolomite hydrate sorbent can be established at any rate calculated to effectively reduce the concentration of SO_x in the flue gas and will depend on the amount of fuel and its sulfur content. For coal having about 0.2 to about 3% sulfur, a feed rate of about 50 pounds of sorbent per ton of fuel will be an adequate starting point, with the exact feed rate to be determined based on experimentation. Typical feed rates will be within the range of from about 10 to about 100 pounds of dolomite hydrate (dry) per ton of fuel, and preferred rates will be within the range of from about 20 to about 90 pounds, e.g., 30 to about 70 pounds, of dolomite hydrate per ton of fuel. The dolomite hydrate will typically be employed at a weight ratio of dolomite hydrate to SO_2 in the flue gases of from about 0.15:1 to about 1.4:1. Preferred rates will be within the range of from about 0.45:1 to about 1.2:1.

[056] It is an advantage of the present invention that essentially complete coverage of the sorbent and doping agent is achieved in the combustion gases in an introduction zone at the temperature necessary for reaction. This section can have a depth in the direction of flow as necessary to assure complete coverage from the sorbent injectors used and will depend on the spray pattern of the injectors and the velocity of the gases. In one variation of the invention, the dolomite hydrate sorbent and the sorbent doping agent are introduced through separate injectors in proximity or in tandem such that the spray patterns of each pair

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of injectors (and there may be many across the section) overlap to at least some extent. Desirably, the invention will achieve full effect by modeling, *e.g.*, by mechanical modeling or computational fluid dynamics using computer and data input means to identify locations within a combustor for feeding a dolomite hydrate sorbent and a sorbent doping agent and determine the physical form and injection parameters for the dolomite hydrate sorbent and the sorbent doping agent injection means positioned at locations, *e.g.*, into line **18** in **Figs 1** and **2**, on a passage for flue gases from a combustor. Note that **Fig. 2** shows additional or alternative introduction of slurry into line **28** via line **38'** following heat exchange section **20**, where the temperature will be lower, *e.g.*, less than 900°F, *e.g.*, within the range of from about 700° to about 200°F.

[057] The invention will employ suitable injection means, such as nozzles (not shown) of the internal mix or external mix type, which can be (but don't have to be) air atomized and are capable of feeding a dolomite hydrate sorbent and a sorbent doping agent at a predetermined rate relative to a measured concentration of SO_x in said passage. Internal mix nozzles capable of extremely fine droplet production are preferred. The injection means should be further capable of introducing the dolomite hydrate sorbent and a sorbent doping agent in a predetermined physical form and with predetermined injection parameters for the sorbent and the sorbent doping agent including droplet size, momentum and concentration.

[058] Preferably, air-assisted atomizing nozzles are provided for introducing dolomite hydrate sorbent and sorbent doping agent into combustion gases prior to or flowing through heat exchanger section **20**. The locations for the nozzles are preferably determined by computational fluid dynamics, by methodologies taught for example in U. S. Patent No. 5,740,745 and U. S. Patent No. 5,894,806, which are hereby incorporated by reference. The concentration and flow rates will be initially determined by modeling to assure that the proper amount of chemical is supplied to the correct location in the combustor in the correct physical form to achieve the desired results of reduced SO_2 and/or HCl.

[059] Following introduction of the sorbent and sorbent doping agent, the gases are passed through particulate recovery means **50**, which can include one or more of fabric filters and/or electrostatic precipitators. It is an advantage of the invention that because the combination of and sorbent doping agent is so effective at removing SO_x, after contact times of less than 3 seconds, that the added reaction time provided by a fabric filter is not essential as it is to

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lesser active sorbent treatments of the prior art. Solids can be recovered via line **52**, and flue gas can be exhausted via line **54**.

[060] The following examples are presented to further explain and illustrate the invention and are not to be taken as limiting in any regard. Unless otherwise indicated, all parts and percentages are by weight.

[061] **Example 1**

[062] This example describes the introduction of an array of SO_x-reducing sorbents that the prior art has identified as having utility along with compositions according to the invention.

[063] A laboratory pilot plant scale combustor is employed for a series of tests. The combustor was a vertical, up-fired, 28-foot high cylinder, with an inner diameter of 3.5 feet, which allowed gas velocities of 10 to 20 feet per second and residence times of 1.3 to 2.5 seconds, depending upon the firing rate. The design furnace exit gas temperature was 2200°F.

[064] The body of the furnace was built of seven four-foot tall sections, each being a water-cooled jacket with four inches of cast refractory lining the fireside. The refractory lining limited the heat extraction to ensure the proper simulation of the radiation environment found inside full-scale furnaces.

[065] The burner was mounted coaxially on the bottom of the furnace and is up-fired using natural gas for preheating and pulverized coal for the tests. It was equipped with a flow control system for secondary air flow and a set of registers, which impart swirl to the secondary air, separate from the flow control. The secondary air and the primary air-coal mixture enter the furnace through a refractory quarl with a 25° half angle. Two clean-out ports are provided in this section, to allow bottom ash to be periodically removed from the furnace.

[066] The combustion gases exited the vertical furnace through a horizontal convection pass, which is designed to remove a substantial part of the heat from the flue gas. The extraction of heat was designed to simulate the time-temperature profile found in a utility boiler. A series of three air-cooled tube banks was installed in the convective pass, and the air cooling was used to control either the temperature profile of the flue gas or the tube metal surface temperatures for fouling/ash deposition studies. A crossflow tubular air preheater

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followed the convective tube banks and is used to preheat the primary and secondary air. Finally, four tube-in-shell recuperators were used to cool the flue gas down to a nominal 300°F.

[067] The convective section is 1.5 feet x 1.5 feet x 22 feet, providing gas velocities of 30 to 60 feet per second and residence times of 0.4 to 0.8 seconds, again depending upon the firing rate. The design temperature range for the convective section is 2200 to 1200°F.

[068] A complete-extractive, continuous, emissions-monitoring (CEM) system was interfaced with a computer control system. The combustor was operated at about 3.4 MMBTU/hr, with a typical combustor excess O_2 level of 3%. The combustor has excess O_2 measured at the exit for control, and a flue gas measurement just prior to exiting to the stack for monitoring of other off-gasses, including O_2, CO, CO_2, NO, and SO_2. Additionally, a Fourier Transform Infrared Spectroscopy (FTIR) analyzer was utilized to monitor other gases, including CH_4, CO, CO_2, H_1O, H_2S, H_2SO_4, HCl, HF, HBr, N_2O, NH_3, NO, NO_2, SO_2 and SO_3.

[069] The combustor had several ports capable of injecting wet or dry material. The locations include below and above the fireball, middle, and near exit. Injection was capable of upward (co-current) and downward (counter-current) flow. This example utilized dry injection directed downwardly, counter to the up-flowing combustion gases.

[070] Compositions prepared for the present evaluation included ten sorbent base materials, all available commercially, plus a series of formulations in which the base materials were reacted, mixed or impregnated with various doping agents. The listing of formulations used is shown in **Table 1** for sorbents and **Table 2** for sorbent doping agents, below. The nomenclature used in the reporting includes the base material designation, a hyphen, and then the doping agent. For example, Dolomitic hydrated lime (dolomite hydrate sorbent) has a designation of “DL”. When treated with copper diammonium diacetate sorbent doping agent, designation “3”, the formulation carries a sample ID of “DL-3”. Also included are the as-received particle size (D_{50} weight average) and surface area (BET) properties of each material.

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[071] **Table 1** -- sorbents

Compound	Chemical Formula	Designation	PSD d50	Surface area, m^2/g
Dolomitic Hydrated Lime	$Ca(OH)_2 \cdot Mg(OH)_2$	DL	8, 9 , 14	109, 113, 113
Calcium Carbonate	$CaCO_3$	CC	10, 13, 14	1, 1, 2
Sorbacal H* (Calcium Hydroxide)	$Ca(OH)_2$	CHHP	2.67	20 -23
Calcium Hydroxide	$Ca(OH)_2$	CHN	19	33
Bonite	$Al_{12}CaO_{19}$	CAB	5, 5, 6	46 - 47
CA-47071 Cement Aggregate	$CaO \cdot Al_2O_3$	CAC	9, 11, 12	46, 47, 49
Utilimag 40 (Magnesium Oxide)	MgO	MO		45
Manganese Dioxide HAS	MnO_2	MDH	3.0 to 5.5	200 - 270
Manganese Dioxide HPX	MnO2	MDX	3 - 8	TBD
CAT-AID	Mg-Ca Mixed Oxide	CA	38	61

[072] **Table 2** for sorbent doping agents

Metal (Doping Agents)		Designation
Iron Nitrate	$Fe(NO_3)_3$	1
Iron Oxide	Fe_2O_3	2
Ammonium Copper Acetate	C2H7CuNO2	3
Copper Nitrate	CuNO3	4

[073] The doped materials were impregnated with an aqueous based solution containing the dopant, or physically mixed with the base sorbent. Details on composition of most of the mixtures are shown in the following **Tables 3-1** and **3-2**:

Table 3-1. Fe_2O_3 Dosing

Name	Final Fe wt%
CHHP2	1.5
MDX2	1.5

Table 3-2. $Fe(NO_3)_3$ Dosing

Name	Fe wt%	Added Moist%	$Fe(NO_3)_3$ Solution wt%	$Fe(NO_3)_3$ Solution Added (kg)
MDH1	1.50	11.27	43.48	2.831
DL1 Clumpy	0.72	4.25	55.16	1.076
DL1	0.14	0.82	55.16	0.207
CHHP1	0.81	4.73	55.16	1.200
CC1 Clumpy	0.28	1.62	55.16	0.410

[074] A rotary mixer was typically utilized to prepare the compositions, while liquid solutions were applied with a spraying system in a slow, controlled manner as to minimize agglomeration.

[075] Addition of the sorbents to the combustor (with or without doping agent) was accomplished via dry injection. The combined sorbent and sorbent doping agents were introduced into the combustion gases as-is in that no additional drying was performed on the mixture materials.

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[076] The samples were added to a rotary screw feeder which had been previously calibrated for addition rate of each material. The screw feeder exited into the entry of an eductor system which injected directly into the desired entry point of the combustor or downstream flue. In the present study, dry injection was performed into a port above the fire ball in the combustor (Port 3 in **Table 4**) where the temperature was about 2000° ±100° F, with injector facing upward.

[077] Additionally, candidate materials were injected into the flue, near the heat exchangers, where the typical temperature is 385° F. This is denoted as "Recap 4" in **Table 4**. Injection rates were selected from 3, 6, 9, 18 pounds per hour (lbs/hr), and maximum flow rate for each material. Depending on the density of the material, the maximum rate varied, from 9 to 10 up to 20 lbs/hr. During select time periods, a flue gas isokinetic particulate sample was obtained. The procedure uses "Method 17" (40 CFR 60. Appendix A to Part 60) as the basis for collection, but the process is modified to ideally collect the particulate sample only. Typically, 30-60 minutes was required to collect sufficient sample for further analysis.

[078] **Table 4** –Analytical Results **(Next Page)**

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Condition No	Product	Base Sorbent	Additive	Rate, lbs/hr	Location	CO2 (CEMS)	NO (CEMS)	SO2 (CEMS)	CO (CEMS)	O2 (1) (CEMS)	O2 (2) (CEMS)	CO ppm (FTIR)	CO2 % (FTIR)	HCL (FTIR)	HF (FTIR)	NH3 (FTIR)	NO (FTIR)	NO2 (FTIR)	SO2 (FTIR)	SO3 (FTIR)	dSO2, from base	dHCl, from base	% SO2 Reduction	% HCL Reduction
1	BASELINE	0		0	Port 3	13.2	268	885	32	3.2	4.6	19	10.6	79	3.7	0.01	214	-0.18	730	-2.4	0	0	0%	0%
2	DL	Dolomitic Lime (Ca,Mg Hydroxide)	-	3	Port 3	13.6	252	776	45	3.0	4.7	35	10.5	77	2.9	0.06	212	-0.15	611	-0.8	-119	-2	13%	3%
3	DL	Dolomitic Lime (Ca,Mg Hydroxide)	-	6	Port 3	13.6	267	782	55	2.8	4.8	41	10.7	78	2.5	0.00	196	-0.17	568	-0.4	-163	-1	18%	1%
4	DL	Dolomitic Lime (Ca,Mg Hydroxide)	-	9	Port 3	13.2	266	664	59	2.7	4.6	46	10.8	78	2.0	0.10	194	-0.15	535	-1.0	-231	-1	26%	1%
5	DL-1	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	3	Port 3	13.3	303	650	57	2.7	4.6	38	10.6	79	1.9	0.07	229	0.20	571	-0.1	-245	0	27%	0%
6	DL-1	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	6	Port 3	13.5	284	578	63	2.9	4.5	46	10.6	76	1.5	0.16	247	0.07	455	-0.3	-317	-3	35%	4%
7	DL-1	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	9	Port 3	13.7	312	434	73	2.9	4.5	35	10.7	83	0.9	0.12	201	-0.11	613	0.3	-461	4	52%	-5%
8	DL-3 (R1)	Dolomitic Lime (Ca,Mg Hydroxide)	C2H7CuNO2	3	Port 3	13.5	255	679	49	2.9	4.4	49	10.5	76	1.3	0.16	208	-0.11	361	-0.3	-216	-3	24%	4%
9	DL-3 (R1)	Dolomitic Lime (Ca,Mg Hydroxide)	C2H7CuNO2	6	Port 3	13.6	260	475	67	3.2	4.5	45	10.6	79	1.2	0.11	217	-0.12	411	0.2	-420	0	47%	0%
10	DL-3 (R1)	Dolomitic Lime (Ca,Mg Hydroxide)	C2H7CuNO2	9	Port 3	13.6	259	410	79	3.1	4.3	44	10.7	80	1.0	0.21	190	-0.15	409	0.0	-485	1	54%	-1%
11	CC	Calcium Carbonate	-	3	Port 3	13.9	263	861	37	2.8	4.5	25	10.7	82	2.2	0.05	201	-0.14	649	-0.6	-84	3	4%	-4%
12	CC	Calcium Carbonate	-	6	Port 3	13.8	272	779	86	3.4	4.5	24	10.7	82	2.1	0.17	202	-0.19	600	-0.6	-116	3	13%	-3%
13	CC	Calcium Carbonate	-	9	Port 3	13.8	258	709	97	2.8	4.4	25	10.8	82	2.1	0.14	202	-0.22	601	0.3	-186	3	21%	-4%
14	CC-1	Calcium Carbonate	Iron Nitrate	3	Port 3	13.7	260	868	56	2.9	4.5	28	10.5	84	2.2	0.01	207	-0.15	737	-0.3	-27	5	3%	-6%
15	CC-1	Calcium Carbonate	Iron Nitrate	9	Port 3	13.7	275	842	34	3.2	4.6	23	10.6	83	2.7	0.06	215	-0.16	696	-0.5	-53	4	6%	-5%
16	CC-3	Calcium Carbonate	C2H7CuNO2	3	Port 3	13.8	267	877	34	2.8	4.5	22	10.6	83	3.0	0.04	207	-0.18	717	-0.4	-18	4	2%	-5%
17	CC-3	Calcium Carbonate	C2H7CuNO2	9	Port 3	13.9	261	767	35	3.1	4.5	26	10.8	84	3.0	0.02	193	-0.14	659	-0.3	-120	5	14%	-6%
18	CAB	Calcium Aluminate (Bonite)	-	3	Port 3	13.8	248	952	35	3.3	4.6	23	10.7	85	3.2	0.18	194	-0.11	785	-1.3	57	6	-6%	-8%
19	CAB	Calcium Aluminate (Bonite)	-	9	Port 3	13.7	256	909	35	2.6	4.5	29	10.8	85	3.3	0.03	190	-0.17	788	-1.2	44	6	-5%	-6%
20	CAC	Calcium Aluminate (Cement Aggregate)	-	3	Port 3	13.8	263	961	34	3.0	4.5	21	10.7	84	3.2	0.05	200	-0.19	780	-1.7	68	5	-7%	-7%
21	CAC	Calcium Aluminate (Cement Aggregate)	-	9	Port 3	13.8	241	973	34	3.0	4.5	21	10.7	85	3.1	0.04	203	-0.14	780	-1.9	76	6	-9%	-7%
22	BASELINE			0	Port 3	13.8	250	968	33	3.0	4.8	18	9.5	77	3.1	0.10	252	-0.11	685	-1.2	73	-2	-8%	3%
23	BASELINE			0	Port 3		237	926	30	3.1		24	10.6	83	3.1	-0.02	203	-0.21	790	-2.6	31	4	-3%	-5%
24	MDH	Manganese Oxide (HAS Grade)	-	3	Port 3		247	924	42	3.2		26	10.8	84	3.2	0.04	199	-0.03	819	-2.3	29	5	-3%	-6%
25	MDH	Manganese Oxide (HAS Grade)	-	9	Port 3		252	921	49	3.0		28	10.6	82	3.2	0.01	214	-0.22	794	-2.3	26	4	-3%	-4%
26	MDH-1	Manganese Oxide (HAS Grade)	Iron Nitrate	9	Port 3		284	921	48	3.0		30	10.6	83	3.3	0.08	224	-0.12	812	-2.9	26	4	-3%	-5%
27	MDH-3	Manganese Oxide (HAS Grade)	C2H7CuNO2	9	Port 3		262	914	51	2.9		38	10.9	84	3.3	0.00	209	-0.27	826	-2.5	19	5	-2%	-6%
28	MDX	Manganese Oxide (HPX Grade)	-	9	Port 3		230	927	54	2.9		37	10.7	83	3.5	-0.05	201	-0.17	803	-2.3	32	4	-4%	-5%
29	MDX-2	Manganese Oxide (HPX Grade)	Iron Oxide	9	Port 3	14.1	235	923	49	2.9	4.5	34	10.8	84	3.6	0.01	201	-0.05	805	-2.4	28	5	-3%	-6%
30	MDX-3	Manganese Oxide (HPX Grade)	C2H7CuNO2	9	Port 3	13.7	255	900	49	2.7	4.9	32	10.6	82	3.6	0.02	210	-0.16	774	-2.5	5	3	-1%	-4%
31	CHHP	Calcium Hydroxide (Sorbacal H)	-	3	Port 3	14.1	219	759	34	3.2	4.5	25	10.8	81	3.6	0.03	189	-0.12	563	-2.1	-136	3	15%	-3%
32	CHHP	Calcium Hydroxide (Sorbacal H)	-	6	Port 3		232	632	44			38	10.8	80	3.2	-0.04	192	-0.07	489	-0.5	-263	1	29%	-2%
33	CHHP	Calcium Hydroxide (Sorbacal H)	-	9	Port 3	14.2	227	511	51	3.1	4.5	27	10.7	82	2.7	0.06	185	-0.23	682	-0.7	-384	3	43%	-4%
34	CHHP-1	Calcium Hydroxide (Sorbacal H)	Iron Nitrate	3	Port 3	14.0	226	814	55	3.0	4.5	23	10.7	84	3.6	-0.01	198	-0.29	628	-0.8	-81	5	9%	-6%
35	CHHP-1	Calcium Hydroxide (Sorbacal H)	Iron Nitrate	6	Port 3	14.7	253	719	38	2.9	4.4	23	10.7	83	3.5	0.14	193	-0.17	630	-0.6	-176	4	20%	-5%
36	CHHP-1	Calcium Hydroxide (Sorbacal H)	Iron Nitrate	9	Port 3	14.1	243	671	39	3.1	4.6	25	10.6	82	3.4	-0.03	207	-0.27	572	0.3	-224	3	25%	-4%
37	BASELINE			0	Port 3	13.8	218	832	30	3.1	4.6	21	10.7	84	4.1	0.00	179	0.00	792	-2.1	-63	6	7%	-7%
38	CHHP-2	Calcium Hydroxide (Sorbacal H)	Iron Oxide	3	Port 3	14.0	210	693	51	2.9	4.5	21	10.8	85	4.0	-0.03	183	-0.13	696	-1.4	-202	6	23%	-7%
39	CHHP-2	Calcium Hydroxide (Sorbacal H)	Iron Oxide	6	Port 3	14.2	211	565	34	3.3	4.5	23	10.8	82	3.6	0.11	183	-0.16	599	-1.3	-330	3	37%	-4%
40	CHHP-2	Calcium Hydroxide (Sorbacal H)	Iron Oxide	9	Port 3	13.6	253	426	58	2.7	4.4	27	10.7	82	3.0	0.04	200	-0.20	405	-0.2	-469	3	52%	-4%
41	CHHP-3	Calcium Hydroxide (Sorbacal H)	C2H7CuNO2	3	Port 3	13.9	226	709	28	3.3	4.5	19	10.8	86	3.7	0.13	194	-0.26	692	-0.6	-136	7	21%	-9%
42	CHHP-3	Calcium Hydroxide (Sorbacal H)	C2H7CuNO2	6	Port 3	14.1	229	670	28	3.1	4.5	18	10.7	84	3.7	-0.02	206	-0.07	638	-0.3	-225	5	25%	-7%

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43	CHHP-3	Calcium Hydroxide (Sorbacal H)	$C_2H_2CuN_2O_2$	9	Port 3	14.1	226	562	32	3.2	4.5	22	10.8	84	3.7	0.08	196	-0.31	556	-1.0	-333	5	37%	-6%
44	CHN	Calcium Hydroxide (Lhoist)	-	3	Port 3	14.2	215	698	24	3.0	4.5	16	10.6	84	3.9	0.08	194	-0.05	669	-1.4	197	5	22%	-6%
45	CHN	Calcium Hydroxide (Lhoist)	-	6	Port 3	13.8	223	602	24	2.9	4.5	17	10.7	82	3.6	0.13	195	-0.27	507	-0.6	293	3	33%	-4%
46	CHN	Calcium Hydroxide (Lhoist)	-	9	Port 3	14.0	224	516	27	3.0	4.5	16	10.5	84	3.2	0.08	204	-0.22	722	0.1	385	5	43%	-7%
47	MO	Magnesium Oxide	-	3	Port 3	13.7	243	779	24	3.0	4.8	17	10.5	85	2.3	0.07	215	0.08	735	-0.7	125	6	14%	-8%
48	MO	Magnesium Oxide	-	9	Port 3	13.8	232	792	27	3.1	4.5	18	10.6	86	1.2	0.11	199	-0.17	756	0.1	-103	7	12%	-9%
49	DL-1 NC	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	3	Port 3	14.1	229	649	30	3.1	4.5	19	10.6	85	1.4	0.11	206	-0.18	619	-0.3	252	6	28%	-7%
50	DL-1 NC	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	6	Port 3	14.5	220	584	30			20	10.7	83	1.6	0.08	201	-0.21	570	0.2	311	4	35%	-5%
51	DL-1 NC	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	9	Port 3	13.9	238	553	30	3.0	4.5	21	10.6	88	1.7	0.06	203	-0.14	536	-0.2	342	4	38%	-5%
53	CA	CAT-AID	-	3	Port 3	13.8	233	775	24	3.2	4.4	15	10.6	83	2.9	-0.02	199	-0.11	731	-0.9	120	4	13%	-6%
54	CA	CAT-AID	-	6	Port 3	14.1	225	776	23	3.0	4.3	14	10.8	82	2.5	0.11	189	-0.19	735	-0.4	119	3	13%	-3%
55	CA	CAT-AID	-	9	Port 3	14.1	225	764	22	3.1	4.5	13	10.6	74	2.4	0.09	202	-0.10	669	-0.6	131	-5	15%	6%
56	CA	CAT-AID	-	18	Port 3	14.2	225	718	22	2.8	4.2	13	10.9	76	2.2	0.04	188	-0.14	695	-0.5	177	-3	20%	4%
57	CA	CAT-AID	-	MAX	Port 3	14.2	235	527	21	3.0	4.4	12	10.6	46	1.4	0.15	212	-0.13	451	-1.1	368	-35	41%	42%
58	BASELINE			0	Port 3	13.7	235	869	34	2.8	4.5	24	10.5	83	2.2	0.05	216	-0.17	787	-2.2	26	4	3%	-5%
59	DL-2	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Oxide	3	Port 3	13.8	247	676	39	3.0	4.4	29	10.7	82	2.1	0.20	206	-0.11	636	-1.8	219	3	24%	-4%
60	DL-2	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Oxide	9	Port 3	13.5	254	527	47	2.9	4.8	39	10.5	81	1.3	0.15	210	-0.04	491	-0.2	368	2	41%	-2%
61	CHN-2	Calcium Hydroxide (Lhoist)	Iron Oxide	3	Port 3	13.7	248	708	33	3.4	4.5	23	10.5	81	1.8	0.01	212	-0.22	661	-0.5	187	2	21%	-3%
62	CHN-2	Calcium Hydroxide (Lhoist)	Iron Oxide	9	Port 3	13.7	238	565	34	3.2	4.5	23	10.7	81	2.0	0.13	200	-0.11	522	-0.2	330	2	37%	-3%
63	CHN-2	Calcium Hydroxide (Lhoist)	Iron Oxide	18	Port 3	13.7	240	400	39	2.9	4.5	29	10.5	78	1.7	0.26	214	-0.12	357	-0.7	495	-1	55%	2%
64	CA-1	CAT-AID	Iron Nitrate	3	Port 3	13.6	273	774	31	3.0	4.6	22	10.5	80	2.1	0.09	230	0.18	710	-0.9	121	1	14%	-2%
65	CA-1	CAT-AID	Iron Nitrate	9	Port 3	13.6	339	749	29	3.2	4.7	20	10.5	76	2.0	0.08	281	-0.12	689	-0.7	146	-8	16%	3%
66	CA-1	CAT-AID	Iron Nitrate	18	Port 3	13.9	415	693	28	3.1	4.5	19	10.3	70	1.7	0.08	366	-0.02	624	-0.6	202	-9	23%	12%
67	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	3	Port 3	13.3	264	605	36	3.1	4.9	27	9.8	75	1.5	0.11	220	-0.05	522	0.0	286	-4	32%	6%
68	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	9	Port 3	13.3	276	415	49	3.1	5.1	36	9.8	71	1.4	0.16	223	-0.09	353	0.0	482	-8	54%	10%
69	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	10.6	Port 3	13.2	265	393	46	3.3	5.1	37	9.9	72	1.0	0.05	220	-0.09	336	0.1	502	-7	56%	9%
70	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	9	Port 3	13.4	265	415	44	3.1	3.9	36	10.0	73	1.2	0.20	224	-0.18	346	-0.1	480	-6	54%	7%
71	BASELINE			0	Port 3		263	844	50	2.9		35	10.2	75	2.0	0.14	174	-0.13	720	-1.3	-51	-4	6%	5%
72	CHHP-4	Calcium Hydroxide (Sorbacal H)	Copper Nitrate	3	Port 3	13.1	284	726	46	3.2	4.7	32	10.0	74	2.2	0.15	192	-0.07	604	-0.2	169	-5	19%	7%
73	CHHP-4	Calcium Hydroxide (Sorbacal H)	Copper Nitrate	9	Port 3	13.1	281	598	57	2.6	4.8	40	10.1	72	2.1	0.13	198	-0.08	511	-0.2	297	-7	33%	9%
74	CHHP-4	Calcium Hydroxide (Sorbacal H)	Copper Nitrate	18	Port 3	13.2	309	426	81	3.1	4.9	42	10.3	72	1.9	0.12	198	0.02	463	0.3	469	-7	52%	9%
75	CHHP-4	Calcium Hydroxide (Sorbacal H)	Copper Nitrate	9	Port 3	12.9	301	605	47	3.3	4.9	32	10.3	74	2.2	0.07	194	-0.03	522	0.1	292	-5	33%	6%
76	CHHP-2	Calcium Hydroxide (Sorbacal H)	Iron Oxide	3	Port 3	13.6	268	737	37	3.0	4.3	25	10.7	78	2.6	0.12	193	-0.21	626	-0.8	158	-1	18%	2%
77	CHHP-2	Calcium Hydroxide (Sorbacal H)	Iron Oxide	9	Port 3	13.5	280	551	46	3.0	4.4	32	10.5	74	2.7	0.14	201	-0.09	447	-0.9	364	-5	41%	6%
78	CHHP	Calcium Hydroxide (Sorbacal H)	-	3	Port 3	13.8	265	733	36	3.0	4.4	23	10.6	77	2.7	0.10	197	-0.25	624	-0.8	162	2	18%	3%
79	CHHP	Calcium Hydroxide (Sorbacal H)	-	9	Port 3	3.5	287	488	49	3.1	4.4	35	10.7	79	2.3	0.14	199	-0.11	427	-0.4	407	4	45%	5%
80	DL-3 (R2)	Dolomitic Lime (Ca,Mg Hydroxide)	$C_2H_2CuNO_2$	3	Port 3	13.8	289	483	46	2.8	4.3	33	10.5	74	2.0	0.16	214	-0.20	404	-0.7	412	-5	46%	6%
81	DL-3 (R2)	Dolomitic Lime (Ca,Mg Hydroxide)	$C_2H_2CuNO_2$	9	Port 3	13.7	279	125	72			55	10.6	65	1.3	0.15	202	-0.25	88	-1.3	770	-19	86%	17%
82	DL-3 (R2)	Dolomitic Lime (Ca,Mg Hydroxide)	$C_2H_2CuNO_2$	10	Port 3	13.7	288	83	67			50	10.6	61	1.0	0.13	194	-0.22	59	-0.7	812	-18	91%	22%
83	BASELINE			0	Port 3	13.4	280	818	29	3.1	4.4	19	10.5	78	2.2	0.08	212	-0.14	895	-0.7	77	-1	9%	1%
84	CHHP-3	Calcium Hydroxide (Sorbacal H)	$C_2H_2CuN_2O_2$	3	Port 3	13.9	268	759	30	3.3	4.1	22	9.9	74	2.2	0.15	236	-0.12	520	0.3	136	-5	15%	7%
85	CHHP-3	Calcium Hydroxide (Sorbacal H)	$C_2H_2CuN_2O_2$	9	Port 3	13.7	275	631	33	2.9	4.2	20	10.8	77	2.3	0.21	194	-0.15	541	-1.0	264	-2	29%	3%
86	HL	Hydrated Lime (SRI Stock Lhoist)	-	3	Port 3	13.7	272	716	27	2.9	4.2	18	10.7	78	2.6	0.06	193	-0.15	624	-1.1	179	-1	20%	1%
87	HL	Hydrated Lime (SRI Stock Lhoist)	-	9	Port 3	13.7	286	553	35	2.8	4.3	24	10.5	75	2.6	0.22	208	-0.06	461	-0.9	342	-4	38%	5%
88	HL	Hydrated Lime (SRI Stock Lhoist)	-	18	Port 3	13.7	211	354	42	3.0	4.3	28	10.9	74	2.0	0.18	146	-0.27	298	-0.1	541	-5	60%	6%
89	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	3	Port 3	13.6	232	586	34	2.7	4.2	23	10.6	79	2.4	0.08	162	-0.18	495	0.0	309	0	35%	0%
90	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	9	Port 3	13.6	327	345	49	3.1	4.2	38	10.5	75	1.8	0.22	242	-0.12	281	-0.5	546	-4	61%	5%

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91	BASELINE			0	Recap 4		234	794	30	3.1		20	10.4	80	2.6	0.05	212	-0.14	796	-1.6	0	0	0%	0%
92	CA	CAT-AID	-	3	Recap 4		236	706	31	2.9		19	10.3	77	2.5	0.07	218	-0.06	775	-1.7	-9	-3	1%	4%
93	CA	CAT-AID	-	9	Recap 4		247	769	30	2.9		21	10.7	76	2.3	0.10	198	-0.02	802	-1.6	-25	-4	3%	4%
94	CA	CAT-AID	-	18	Recap 4		233	795	31	3.1		18	10.5	69	1.6	0.09	215	-0.15	775	-1.7	-9	-11	1%	14%
95	CAB	Calcium Aluminate (Bonite)	-	9	Recap 4		244	804	32	3.0		19	10.5	80	2.6	0.04	210	-0.09	794	-1.8	10	0	-1%	0%
96	CAC	Calcium Aluminate (Cement Aggregate	-	9	Recap 4		239	800	31	3.3		18	10.2	78	2.7	0.07	226	-0.03	773	-1.9	6	-1	-1%	2%
97	MO	Magnesium Oxide	-	9	Recap 4	13.2	255	786	28	2.9	5.0	16	10.2	64	0.9	0.04	233	-0.05	759	-0.7	-8	-15	1%	19%
98	MO	Magnesium Oxide	-	18	Recap 4	13.2	260	780	29	3.0	5.0	16	10.3	55	0.7	0.04	222	-0.10	762	-0.6	-14	-25	2%	32%
99	CHHP	Calcium Hydroxide (Sorbacal H)	-	9	Recap 4	13.4	244	801	30	2.9	5.0	16	10.4	54	0.6	0.00	229	-0.22	782	-1.3	7	-26	-1%	32%
100	DL-3	Dolomitic Lime (Ca,Mg Hydroxide)	$C_5H_7CuNO_2$	9	Recap 4	13.5	248	771	29	3.1	4.8	17	10.6	28	0.5	0.11	225	-0.15	771	-1.3	-23	-52	3%	65%
101	DL-4	Dolomitic Lime (Ca,Mg Hydroxide)	Copper Nitrate	9	Recap 4	12.9	277	751	27	2.7	5.0	15	10.1	33	0.3	0.10	244	-0.03	730	-0.9	-43	-47	5%	58%
102	MDH	Manganese Oxide (HAS Grade)	-	9	Recap 4	13.0	272	665	25	2.6	5.0	14	10.0	52	0.3	0.16	240	4	666	-0.9	-129	-20	16%	35%
103	MDH	Manganese Oxide (HAS Grade)	-	3	Recap 4	13.3	248	752	27	2.8	4.9	14	10.5	65	0.4	0.03	210	11	747	-0.6	-42	-15	5%	19%
104	MDH	Manganese Oxide (HAS Grade)	-	18	Recap 4	13.5	220	612	20	2.9	4.6	15	10.3	44	0.6	0.05	158	58	619	-1.3	-182	-36	23%	45%
105	CC	Calcium Carbonate	-	9	Recap 4	13.3	251	789	25	3.0	5.0	13	10.4	79	0.7	0.07	211	6	774	-0.6	-5	-1	1%	1%
106	CHHP 3	Calcium Hydroxide (Sorbacal H)	$C_5H_7CuNO_2$	9	Recap 4	13.3	241	618	26	3.3	4.9	14	10.1	57	0.9	0.09	224	3	750	-1.6	24	-22	-3%	28%
107	DL-1	Dolomitic Lime (Ca,Mg Hydroxide)	Iron Nitrate	9	Recap 4	13.4	252	805	26	3.0	5.0	13	10.3	44	0.5	-0.11	226	0.34	771	-1.7	11	-36	-1%	45%
108	CHN	Calcium Hydroxide (Lhoist)	-	9	Recap 4	13.3	249	809	25	3.0	5.0	13	10.4	36	0.4	0.07	219	0.20	762	-1.7	15	-43	-2%	54%

[079] **Example 2**

[080] This example reports tests made with slurries of materials that showed the best results for dry injection in Example 1.

[081] During wet injection, about 257lbs/hr coal was added to the combustor. At this rate, suction pyrometry determined a temperature at Port 2 of 1850-2019 ° F.

[082] In wet injection, the previously prepared slurry samples of the sorbent “DL” and the additives (1, 2, 3 or 4) were separately added to the same horizontal plane of the combustor. While the previous trial was evaluated at Port 3, the current trial was performed at Port 2 in order to better match the temperatures attained previously. This change of ports was necessitated because an air preheater was inoperable.

[083] **Table 5** relates gallons per hour (gph) sorbent feed rate to lbs per ton fuel rate.

Feed Rate Conversion (Liquid Injection)
1lb/hr sorbent=8.56lbs/ton fuel

Gph	lbs/ton fuel (dry)	Lbs/ton fuel (as is)
1	44	88
2	87.5	175
3	131.5	263

[084] During select time periods, a flue gas isokinetic particulate sample was obtained. The procedure uses “Method 17” as the basis for collection, but the process is modified to

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ideally collect the particulate sample only. Typically, 20-60 minutes is required to collect sufficient sample for further analysis.

[085] **Table 6** -- Wet Feed Data

Condition No.	Wet/Dry Injection	Product Designation	Base Sorbent Rate, gph	Additive (liquid as separate stream, solid mixed in)	Additive Rate, gp	CO2, % (CEM)	NO ppm (CEM)	SO2 ppm (CEMS)	CO ppm (CEM)	O2 % (1) (CEMS)	CO ppm (FTIR)	CO2 % (FTIR)	HCl ppm (FTIR)	HF ppm (FTIR)	NH3 % (FTIR)	NO ppm (FTIR)	NO2 % (FTIR)	SO2 ppm (FTIR)	SO3 ppm (FTIR)	dSO2, from base run	dHCl, from base run	% SO2 Reduction	% HCl Reduction
0	BASELINE	BASELINE-Wet Injection				14.0	313	1167	46	2.6	35	11.6	72	4.5	0.00	271	-0.21	1118	2.0	0	0	0%	0%
1	Slurry	DL (1gph)- No Add	1	-		13.9	303	865	60	2.7	44	10.4	64	5.7	-0.16	245	-0.26	739	4.1	378	-9	34%	12%
2	Slurry	DL (2gph)- No Add	2	-		14.0	299	722	64	2.6	47	10.6	63	2.3	-0.02	240	-0.32	637	6.6	480	-10	43%	14%
3	Slurry	DL (2gph)- Add 3 (0.1 gph)	2	3	0.1	13.2	220	469	69	2.4	48	9.6	58	2.0	-0.04	166	-0.31	398	8.2	719	-15	64%	20%
3.5	BASELINE	BASELINE-Wet Injection				13.2	231	968	46	2.8	34	11.1	66	2.0	-0.04	236	-0.19	1047	4.2	71	-7	6%	10%
4	Slurry	DL (2gph)- Add 3 (0.05 gph)	2	3	0.05	13.6	257	537	51	2.4	37	10.2	61	2.1	0.01	202	-0.27	480	6.1	638	-12	57%	16%
5	Slurry	DL (3gph)- Add 3 (0.05 gph)	3	3	0.05	13.4	256	467	48	2.7	34	10.1	60	1.4	0.00	208	-0.25	373	5.4	744	-13	67%	18%
6	Slurry	DL (3gph)- Add 3 (0.1 gph)	3	3	0.1	13.4	245	342	62	2.3	46	9.8	58	1.0	0.02	198	-0.40	280	7.0	837	-15	75%	20%
7	Slurry	DL (1gph)- Add 2 (0.1 gph)	1	2	0.1	14.0	283	745	65	2.7	49	10.5	64	1.5	-0.02	235	-0.30	654	8.0	463	-8	41%	11%
8	Slurry	DL (1gph)- Add 2 (0.2 gph)	1	2	0.2	13.8	273	840	68	2.9	52	10.5	64	1.4	0.02	247	-0.41	677	7.6	441	-9	39%	12%
9	Slurry	DL (2gph)- Add 2 (0.2 gph)	2	2	0.2	14.0	275	779	66	2.5	50	10.4	64	1.5	-0.04	235	-0.40	664	8.2	453	-8	41%	11%
9.5	BASELINE	BASELINE-Wet Injection				14.2	280	1077	57	2.5	41	11.6	70	1.4	0.02	267	-0.22	1128	3.6	11	-2	-1%	3%
9.5	BASELINE	BASELINE-Wet Injection				13.7	278	1190	49	2.5	36	11.7	72	3.5	-0.05	230	-0.12	1210	-2.9	0	0	0%	0%
10	Slurry	DL (1gph)- No Add	1	-		13.5	274	579	62	2.7	45	10.3	58	1.7	-0.03	236	-0.36	534	1.2	676	-14	56%	19%
11	Slurry	DL (1gph)- Add 4 (0.1 gph)	1	4	0.1	13.5	275	549	63	2.6	46	10.2	56	1.0	-0.03	236	-0.23	496	0.6	714	-16	59%	22%
12	Slurry	DL (1gph)- Add 4 (0.5 gph)	1	4	0.5	13.5	275	534	63	2.7	46	10.3	56	0.8	-0.03	230	-0.34	496	1.3	714	-16	59%	23%

Condition No.	Wet/Dry Injection	Product Designation	Base Sorbent Rate, gph	Additive (liquid as separate stream, solid mixed in)	Additive Rate, gp	CO2, % (CEM)	NO ppm (CEM)	SO2 ppm (CEMS)	CO ppm (CEM)	O2 % (1) (CEMS)	CO ppm (FTIR)	CO2 % (FTIR)	HCl ppm (FTIR)	HF ppm (FTIR)	NH3 % (FTIR)	NO ppm (FTIR)	NO2 % (FTIR)	SO2 ppm (FTIR)	SO3 ppm (FTIR)	dSO2, from base run	dHCl, from base run	% SO2 Reduction	% HCl Reduction
12.5	BASELINE	BASELINE-Dry Injection				14.0	229	1184	27	2.6	20	11.9	74	3.3	0.03	203	-0.19	1246	-3.0	0	0	0%	0%
13	Powder	DL (3#/hr)- No Add	3	-		14.0	232	1211	31	2.2	23	12.0	74	3.4	0.01	197	-0.21	1181	-2.6	65	0	5%	-1%
14	Powder	DL (9#/hr)- No Add	9	-		13.7	239	917	34	3.1	24	11.4	70	3.3	0.03	218	-0.12	835	-1.2	411	-4	33%	6%
15	Powder	BASELINE-Dry Injection									24	11.9	74	3.1	0.06	202	-0.11	1217	-0.8	29	0	2%	0%
16	Powder	DL (3#/hr)- Add 3 (mix w solid)	3	3	mix w solid	14.2	228	1014	35	2.3	27	11.2	70	3.2	0.03	226	-0.11	904	-0.9	342	-4	27%	5%
17	Powder	DL (9#/hr)- Add 3 (mix w solid)	9	3	mix w solid	14.1	235	722	41	2.4	30	11.6	70	2.9	0.00	214	-0.16	699	-0.7	547	-3	44%	5%
18	Powder	BASELINE-Dry Injection				14.2	229	1213	31	2.2	22	11.9	74	3.2	0.08	204	-0.07	1212	-0.8	33	0	3%	-1%
19	Powder	DL (3#/hr)- Add 2 (mix w solid)	3	2	mix w solid	14.0	230	1094	30	2.5	20	11.9	74	3.3	0.10	201	-0.12	1133	-1.3	113	0	9%	0%
20	Powder	DL (9#/hr)- Add 2 (mix w solid)	9	2	mix w solid	13.8	238	951	27	2.6	18	11.8	72	3.2	0.01	208	-0.14	958	-1.3	288	-1	23%	2%
21	Powder	BASELINE-Dry Injection				14.1	228	1160	27	2.5	18	11.9	74	3.4	0.04	195	-0.23	1217	-1.6	29	0	2%	-1%
22	Powder	DL (3#/hr)- Add 4 (mix w solid)	3	4	mix w solid	14.0	233	1100	29	2.5	19	12.0	75	3.6	-0.02	188	-0.17	1126	-1.4	120	1	10%	-1%
23	Powder	DL (9#/hr)- Add 4 (mix w solid)	9	4	mix w solid	13.7	238	1014	27	2.5	20	11.7	73	3.5	0.03	208	-0.20	981	-1.3	265	-1	21%	1%
24	Powder	BASELINE-Dry Injection				14.5	218	1197	29	2.4	20	12.0	74	3.6	0.01	199	-0.24	1225	-0.9	21	1	2%	-1%
25	Powder	DL (3#/hr)- Add 1 (mix w solid)	3	1	mix w solid	14.6	222	1030	28	2.8	20	11.6	72	3.6	0.02	218	-0.16	979	-1.5	267	-2	21%	2%
26	Powder	DL (9#/hr)- Add 1 (mix w solid)	9	1	mix w solid	14.5	231	899	31	2.5	24	11.6	71	3.5	0.08	215	-0.18	831	-0.5	415	-3	33%	4%
27	Powder	BASELINE-Dry Injection				14.0	209	1241	28	2.3	20	11.5	73	3.4	0.03	189	-0.09	1242	-0.9	4	-1	0%	2%

[086] **Example 3**

[087] This example reports tests made with dry materials that showed the best results for dry injection in Example 1.

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[088] A rotary mixer was typically utilized to prepare the dry compositions, where liquid solutions were applied with a spraying system in a slow, controlled manner as to minimize agglomeration. The materials were added as-is in that no additional drying was performed on the mixture materials.

[089] For dry injection, the samples were added to a rotary screw feeder which had been previously calibrated for addition rate of each material. The screw feeder exits into the entry of an eductor system which injects directly into the desired entry point of the combustor or downstream flue. In the present study, dry injection was performed into Port 2 of the combustor, facing upward.

[090] **Table 7** relates lbs/hr sorbent feed rate to lbs per ton fuel rate

Feed Rate Conversion (Dry injection)
1lb/hr sorbent=9lbs/ton fuel

lbs/hr	lbs/ton fuel
3	27
9	81

[091] In addition to the SO_2 reduction study, a set of samples were also injected by dry injection into the flue gas stream for potential usage for HCl reduction additives. The temperature selected for this trial was about 500°F. This is denoted as "Recap 2/3" in the tables. Injection rates were selected from 3 and 9 lbs/h.

[092] During select time periods, a flue gas isokinetic particulate sample was obtained. The procedure uses "Method 17" as the basis for collection, but the process is modified to ideally collect the particulate sample only. Typically, 20-60 minutes is required to collect sufficient sample for further analysis. Due to the extended period of time required to collect the modified "Method 17" samples, several samples were taken directly from the baghouse catch by skimming the top layer from the drum.

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[093] **Table 8** – Dry Feed Data

Condition No.	Wet/Dry Injection	Product Designation	Base Sorbent Rate, #/hr	Additive (liquid as separate stream, solid mixed in)	Additive Rate, gpm	CO2, % (CEMS)	NO ppm (CEMS)	SO2 ppm (CEMS)	CO ppm (CEMS)	O2 % (1) (CEMS)	CO ppm (FTIR)	CO2 % (FTIR)	HCL ppm (FTIR)	HF ppm (FTIR)	NH3 % (FTIR)	NO ppm (FTIR)	NO2 % (FTIR)	SO2 ppm (FTIR)	SO3 ppm (FTIR)	dSO2, from base run	dHCl, from base run	% SO2 Reduction	% HCL Reduction
35	BASELINE	BASELINE-Back End				13.6	251	1235	30	2.8	16	11.5	63	3.7	0.01	179	-0.21	1086	-3.3	0	0	0%	0%
36	Powder	RN (3#/hr)- No Add	3	-		13.2	298	1220	29	2.5	15	11.2	61	3.8	-0.05	202	-0.24	1058	-2.8	-28	-2	3%	3%
37	Powder	RN (9#/hr)- No Add	9	-		13.3	323	1197	29	2.6	15	11.1	48	3.8	0.01	245	-0.17	1026	-2.8	-60	-15	6%	24%
38	Powder	RN (3#/hr)- Add 2 (mix w solid)	3	2	mix w solid	13.9	225	1230	27	2.2	14	11.4	61	4.3	-0.03	167	-0.22	1095	-3.4	9	-2	-1%	3%
39	Powder	RN (9#/hr)- Add 2 (mix w solid)	9	2	mix w solid	13.2	261	1167	26	2.4	14	10.7	47	4.0	-0.01	202	-0.15	994	-3.0	-92	-16	9%	26%
40	Powder	RN (3#/hr)- Add 3 (mix w solid)	3	3	mix w solid	13.7	278	1207	25	2.1	12	11.2	50	4.2	-0.04	207	-0.21	1072	-3.2	-13	-14	1%	21%
41	Powder	RN (9#/hr)- Add 3 (mix w solid)	9	3	mix w solid	13.7	284	1218	25	2.2	12	10.9	46	4.0	-0.01	205	-0.15	1024	-3.0	-62	-17	6%	27%
42	Powder	RN (3#/hr)- Add 4 (mix w solid)	3	4	mix w solid	13.3	248	1230	24	2.5	12	11.2	50	4.3	-0.13	193	-0.32	1058	-3.5	-28	-14	3%	21%
43	Powder	RN (9#/hr)- Add 4 (mix w solid)	9	4	mix w solid	13.5	267	1215	24	2.6	12	11.1	47	4.2	0.01	203	-0.22	1051	-3.5	-35	-16	3%	25%
43.5	BASELINE	BASELINE-Back End				13.8	246	1236	24	2.5	12	11.3	66	4.6	-0.03	193	-0.20	1086	-3.5	0	0	0%	0%
44	Powder	DL (3#/hr)- Add 3 (mix w solid)	3	3	mix w solid	13.9	235	1245	24	2.3	13	11.6	58	2.5	0.01	175	-0.26	1134	-3.3	47	-8	-4%	12%
45	Powder	DL (9#/hr)- Add 3 (mix w solid)	9	3	mix w solid	13.7	265	1212	24	2.7	10	10.8	52	1.4	0.06	223	-0.16	1040	-2.8	-47	-15	4%	22%
46	Powder	DL (9#/hr)- Add 3 (mix w solid)	9	3	mix w solid	13.5	268	1212	25	2.4	11	11.2	44	1.2	-0.02	200	-0.25	1068	-3.0	-19	-23	2%	34%

[094] We have reviewed all of the data taken and believe that the following conclusions the and observations are borne out by the data:

a. All the grades (and their enhanced blends) of calcium aluminate, cement aggregate, magnesium hydroxide, many of the grades of calcium carbonate (except for one test), Trona (sodium sesquicarbonate) and manganese dioxide did little in the way of reductions (<20%). Unlike everything else tested in the furnace, Trona was tested at 350 °F and 500 °F due to temperature stability limitations.

b. The calcium hydroxides and their enhanced mixtures fared better at 20 to 40% reductions.

c. One combination exceeded the performance of all the others, both wet (slurry) and dry- dolomite hydrate and copper ammonium acetate; the CAA (copper ammonium acetate) being fed at a ratio of from 1 – 6% of the mass of the dolomite hydrate.

d. Two of the three highest performers in terms of SO_2 reduction were a blend of dolomite hydrate and copper ammonium acetate, with the highest performance seen by the dry materials and their blends being the dolomite hydrate-CAA blend at 91% reduction in SO_2. This is well beyond what any other sorbent or

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sorbent blend tried in the complete battery of tests was able to generate, yielding an unexpected result.

e. The three top performers were all dolomite hydrate-CAA blends at various dosages of chemical. The highest performer was the same blend at 75% reduction in SO_2. Again, no other slurried blend performed as well, which was also an unexpected result.

f. The dolomite hydrate plus iron nitrate, copper nitrate and magnetite blends all produced reasonable reductions (~50%), but not as good as the dolomite CAA blends.

g. Prior tests showed that a high quality lime, fed at up to 300 pounds/ton of fuel, yielded not only lower reductions (~65%) in SO_2 than the top performing blends discussed here, but also had relatively inefficient SO_3/CaO ratios that were more similar to baseline chemistry measurements. This is all the more remarkable considering that the dolomite hydrate CAA blend tests were at one-third to one-half the dosage of the other calcium based sorbents.

h. The enhanced SO_3/CaO ratio was observed in the high performing formulations, namely that of dolomitic lime hydrate and CAA. In the below table (Figure 5), the high performing lime sample from the earlier trial is included as a comparison of the chemistry. This comparative data shows the relative inefficiency of the calcium conversion in the lime, in which the SO_3/CaO ratio is just 0.64, a value similar to the base case. XRD data confirmed a significant amount of unreacted CaO was present in the fly ash samples.

i. The results of chemical analysis using X-Ray Diffraction compared to X-Ray Flourescence, shows very good linearity, indicating that both test methods track well in measuring what the end results of the tests show. In general, the lower the level of unreacted calcium oxide in the ash sample, the more efficient the process is. The high performing combination of dolomitic lime hydrate and copper ammonium acetate (CAA) had essentially no unreacted calcium oxide present, and had the highest levels, on average of calcium sulfate present in the ash.

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[095] The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the invention. It is not intended to detail all of those obvious modifications and variations, which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the invention which is defined by the following claims. The claims are meant to cover the claimed components and steps in any sequence that is effective to meet the objectives there intended, unless the context specifically indicates the contrary.

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Claims

1. A process for reducing emissions of SO_x and/or HCl from a combustor, comprising: identifying locations within a combustor for feeding a dolomite hydrate sorbent and a sorbent doping agent; determining the physical form and injection parameters for the sorbent and the sorbent doping agent; injecting both the dolomite hydrate sorbent and the sorbent doping agent into combustion gases containing SO_x and/or HCl, the introduction being under conditions effective to capture sulfur oxides and/or HCl with the sorbent at a greater rate than achievable by the same sorbent without the sorbent doping agent; and collecting the spent sorbent.

2. A process according to claim 1, wherein the sorbent is introduced at a temperature within the range of from about 2200° to 1500°F as a slurry in droplets having a mean diameter of from about 25 to about 300 microns.

3. A process according to claim 2, wherein the sorbent is introduced at a temperature within the range of from 1900° to about 1600°F.

4. A process according to claim 1, wherein the sorbent is introduced to reduce HCl at a temperature of less than about 1600°F.

5. A process according to claim 1, wherein the sorbent is introduced to reduce HCl at a temperature lower than 900°F.

6. A process according to claim 1, wherein the sorbent is introduced a as droplets having a mean diameter of from about 25 to about 350 microns.

7. A process according to claim 1, wherein the sorbent is introduced at feed rates within the range of from about 25 to about 100 pounds of dolomite hydrate per ton of fuel.

8. A process according to claim 1, wherein the dolomite hydrate is employed at a weight ratio of dolomite hydrate to weight of SO_2 in the flue gases of from about 0.15:1 to about 1.4:1.

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9. A process according to claim 1, wherein the sorbent doping agent will be employed with the dolomite hydrate sorbent at a weight ratio (dry basis) of dolomite hydrate to sorbent doping agent within the range of from about 100:1 to about 1:1.

10. A process according to claim 1, wherein the sorbent doping agent is a water-soluble or water-dispersible composition of copper and/or iron.

11. A process according to claim 1, wherein the sorbent doping agent comprises a copper composition selected from the group consisting of copper ammonium acetate, copper diammonium diacetate, copper ammonium triacetate, copper triammonium acetate, copper tetra ammonium sulfate, copper gluconate (and hydrates thereof), and mixtures of any of these. From another perspective, the doping agent can be a member selected from the group consisting of compositions defined by the formula $Cu(NH_3)_x$(lower carboxylate)$_y$, wherein the lower carboxylate is selected from the group consisting of formate, acetate and propionate, x is an integer from 0 to 4, y is an integer from 0 to 2, and x+y is equal to or greater than 1.

12. A process according to claim 1, wherein the sorbent doping agent comprises an aqueous cuprammonium lower carboxylate complex of copper lower carboxylate and ammonium lower carboxylate.

13. A process according to claim 1, wherein the sorbent doping agent comprises an aqueous cuprammonium lower carboxylate complex of copper lower carboxylate and ammonium lower carboxylate containing weight proportions of about 13 parts of copper lower carboxylate as measured as the dihydrate to about 2 parts of ammonium lower carboxylate, and about 10 parts of 29 percent aqueous ammonia, said solution being at a pH in the range of about 7.1 to 7.4.

14. A process according to claim 1, wherein the sorbent doping agent comprises a member selected from the group consisting of: copper acetylacetonate (and hydrates thereof), copper citrate (and hydrates thereof, *e.g.*, hemipentahydrate), copper formate (and hydrates thereof), copper acetate monohydrate, copper nitrate (and hydrates thereof), copper 2,4-pentandionate (and hydrates thereof), copper sulfate (and hydrates thereof), copper gluconate (and hydrates thereof), copper soaps of fatty acids, and mixtures of any of these.

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15. A process according to claim 1, wherein the sorbent doping agent comprises copper diammonium diacetate.

16. A process according to claim 1, wherein the sorbent doping agent comprises a copper ammonium complex having an empirical formula of $C_2H_7CuNO_2$.

17. A process according to claim 1, wherein the sorbent is injected as a slurry containing from about 25 to about 45% dolomite hydrate solids by weight in water.

18. A process according to claim 1, wherein the sorbent has a mass average particle size of from about 1 to about 5 microns (μ).

19. A process according to claim 1, wherein the dolomite hydrate sorbent is preferably mixed with water to form a slurry at a concentration of at least about 25% solids by weight.

20. An process according to claim 1, wherein the dolomite sorbent hydrate and the sorbent doping agent are injected by injection means comprising a plurality of nozzles within an introduction zone, and the nozzles are positioned to achieve at least 90% coverage within the introduction zone.

21. An apparatus for reducing SO_x and/or HCl in a gas stream, comprising: injection means positioned at locations on a passage for flue gases generated by the combustion of fuel, said injection means capable of feeding a dolomite hydrate sorbent and a sorbent doping agent at predetermined rates relative to a concentration of SO_x and/or HCl in said flue gases, and said injection means further capable of introducing the dolomite hydrate sorbent and a sorbent doping agent in a predetermined physical form and with predetermined injection parameters for the sorbent and the sorbent doping agent including droplet size, momentum and concentration; whereby the dolomite hydrate sorbent with the sorbent doping agent captures sulfur oxides with high efficiency.

22. An apparatus according to claim 21, wherein the injection means comprise a plurality of nozzles within an introduction zone and the nozzles are positioned to achieve at least 90% coverage within the introduction zone.

23. A system for reducing SO_x and/or HCl in a gas stream, comprising: computer modeling means for identifying locations within a combustor and its duct work for feeding a dolomite

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hydrate sorbent and a sorbent doping agent and determining the physical form and injection parameters for the dolomite hydrate sorbent and the sorbent doping agent injection means positioned at locations on a passage for flue gases, said injection means capable of feeding a dolomite hydrate sorbent and a sorbent doping agent at predetermined rates relative to a measured concentration of SO_x and/or HCl in said passage, and said injection means further capable of introducing the dolomite hydrate sorbent and a sorbent doping agent in a predetermined physical form and with predetermined injection parameters for the sorbent and the sorbent doping agent including droplet size, momentum and concentration; whereby the dolomite hydrate sorbent with the sorbent doping agent can have the characteristics of any of claims 6-20 to capture sulfur oxides and/or HCl with high efficiency.

24. A composition for reducing SO_x and/or HCl in a gas stream, comprising: dolomite hydrate sorbent and a sorbent doping agent comprising copper and/or iron which will dehydrate and be caused to shatter into fine particles within the size range of from about 0.01 to about 0.2 microns upon introduction into a hot gas stream containing SO_x and/or HCl, wherein the weight ratio (dry basis) of dolomite hydrate to sorbent doping agent is within the range of from about 500:1 to about 25:1 and the sorbent doping agent is selected from water-soluble or water-dispersible copper and/or iron compositions that release active species when heated *in situ* by the flue gases being treated.

25. A composition for reducing SO_x and/or HCl in a gas stream, comprising: dolomite hydrate sorbent and a sorbent doping agent comprising copper and/or iron having characterizing features described in any of claims 6-20.

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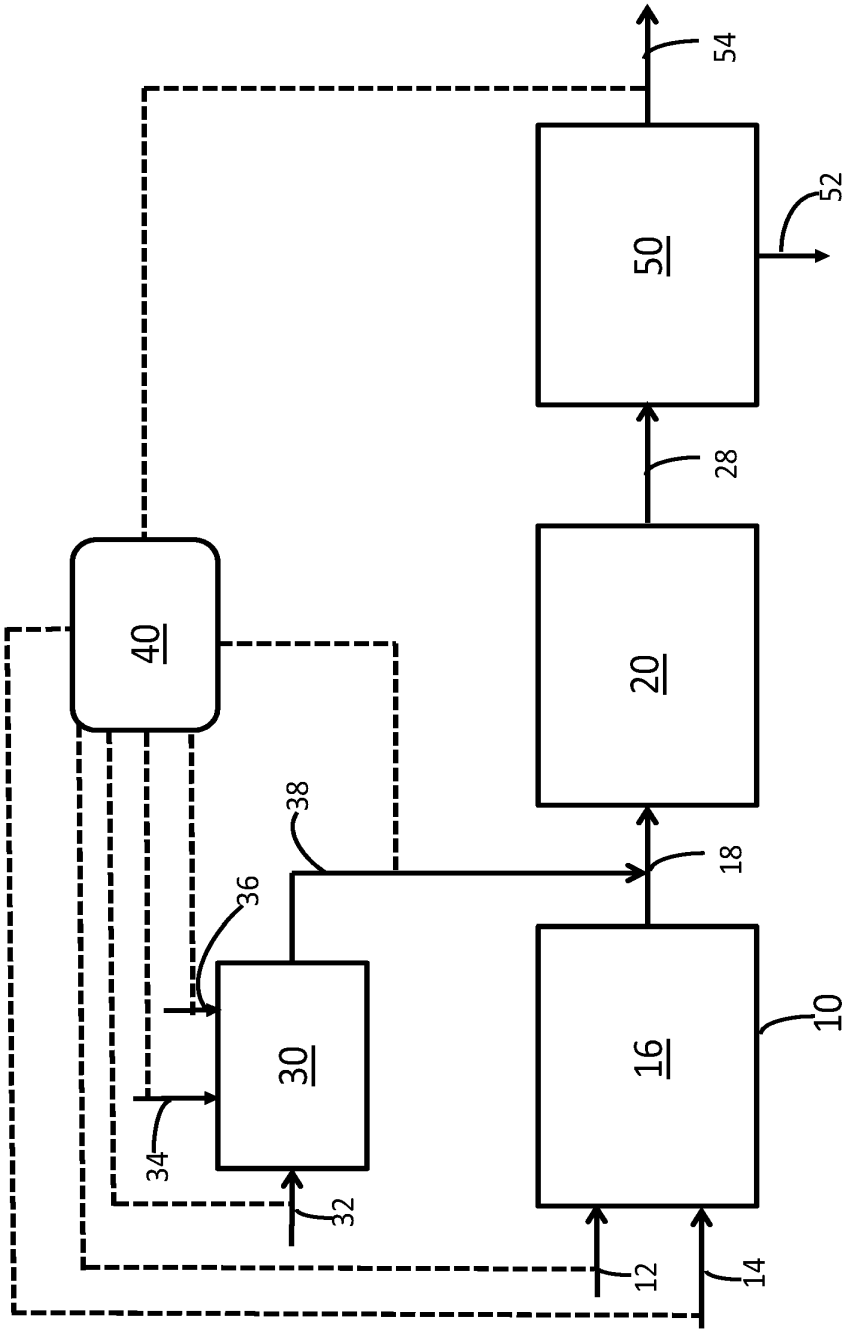


Fig. 1

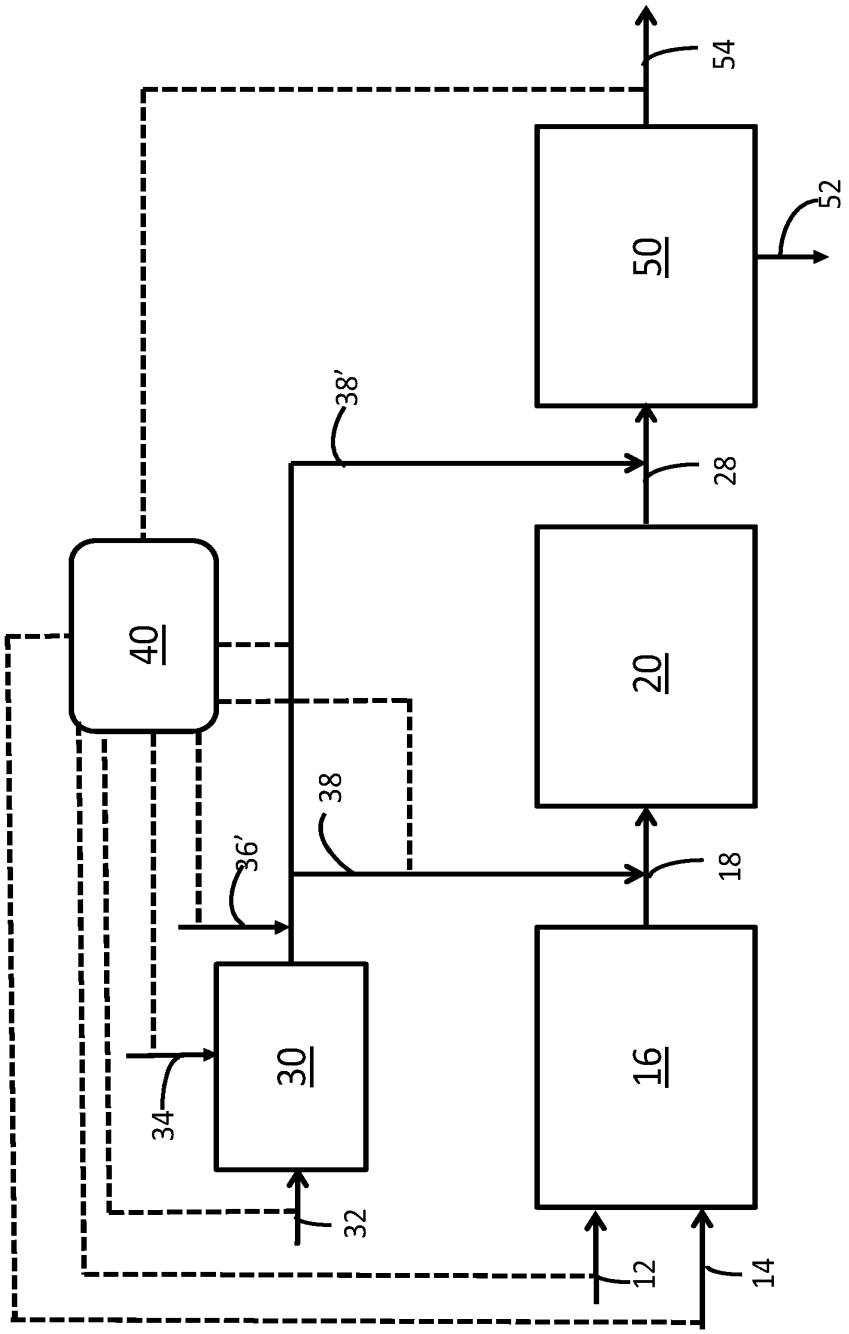


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/034807

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 53/00 (2013.01)
USPC - 423/244.07
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - B01D 53/00, 53/02, 53/14, 53/34, 53/50, 53/68, 53/81; B01J 8/00, 20/00, 20/04, 20/06 (2013.01)
USPC - 110/345; 422/177; 423/175, 210, 240R, 242.1, 243.08, 244.05, 244.07, 244.08; 504/400

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - B01D 53/50, 53/501, 53/508; B01J 20/04, 20/041, 20/043 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Orbit, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,724,130 A (STATNICK et al) 09 February 1988 (09.02.1988) entire document	1, 9, 10, 25 --- 1-9, 11-24
Y	US 4,795,586 A (THOMPSON et al) 03 January 1989 (03.01.1989) entire document	1-3, 6-9, 17-19
Y	US 7,666,374 B2 (GROCHOWSKI) 23 February 2010 (23.02.2010) entire document	4, 5
Y	WO 02/16026 A2 (IRETSKAYA et al) 28 February 2002 (28.02.2002) entire document	11
Y	US 4,020,180 A (WOERNER) 26 April 1977 (26.04.1977) entire document	12, 13, 15
Y	WO 2011/143517 A1 (SMYRNIOTIS et al) 17 November 2011 (17.11.2011) entire document	14, 21-24
Y	US 4,081,253 A (MARION) 28 March 1978 (28.03.1978) entire document	16
Y	US 6,453,830 B1 (ZAUDERER) 24 September 2002 (24.09.2002) entire document	20, 22

☐ Further documents are listed in the continuation of Box C. ☐

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LIME-BASED SORBENT COMPOSITION FOR MERCURY REMOVAL AND ITS MANUFACTURING PROCESS

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Abstract of WO2016185033 (A1)

Sorbent composition containing core-shell particles for removing heavy metals, in particular, mercury from gases, wherein the core comprises a calcium-magnesium compound fitting the formula aCaCO3.bMgCO3.xCaO.yMg0.zCa(OH)2.tMg(OH)2.ul, wherein I represents impurities, a, b, x, y, z and t each being mass fractions > 0 and≤ 100%, u being mass fraction > 0 and < 20 % by weight, and is coated with a shell presenting a thickness comprised in the range of 50 nm to 20 µm, and comprising at least a metal salt and a sulfur-based compound and its manufacturing process.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00420

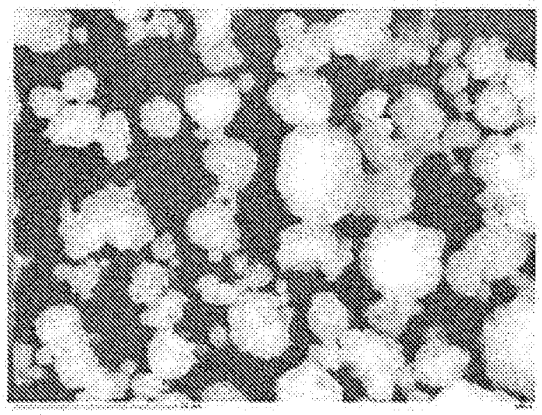


Fig. 1

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(54) Title: LIME-BASED SORBENT COMPOSITION FOR MERCURY REMOVAL AND ITS MANUFACTURING PROCESS

(57) Abstract: Sorbent composition containing core-shell particles for removing heavy metals, in particular, mercury from gases, wherein the core comprises a calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMg0.zCa(OH)_2.tMg(OH)_2.ul$, wherein I represents impurities, a, b, x, y, z and t each being mass fractions > 0 and≤ 100%, u being mass fraction > 0 and < 20 % by weight, and is coated with a shell presenting a thickness comprised in the range of 50 nm to 20 μηι, and comprising at least a metal salt and a sulfur-based compound and its manufacturing process.

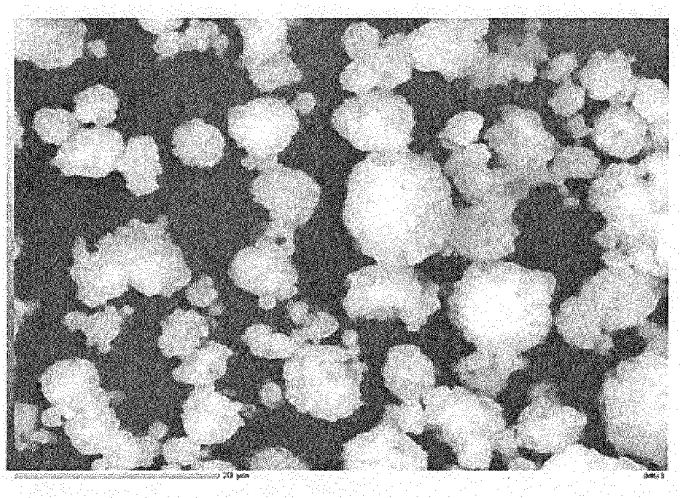


Fig. 1

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« LIME-BASED SORBENT COMPOSITION FOR MERCURY REMOVAL AND ITS MANUFACTURING PROCESS »

The present invention relates to a sorbent composition containing particles for removing heavy metals, in particular mercury, from flue gases.

Sorbent composition containing solid particles are well known in the art.

Document US7923397B2 discloses a modified activated carbon sorbent (with a powder of elementary sulfur) to remove heavy metals from flue gases. While activated carbon is the best available sorbent technique up to now in terms of mercury uptake (quantity of mercury adsorbed per gram of sorbent), carbon is susceptible to combustion inside the flue gas stream, which is one of the main drawbacks of this sorbent (see also US 2002/0035925).

Further, the use of activated carbon sorbent increases the total organic carbon content in the dusts present at the discharge of these flue gases, which carbon content is nowadays strictly regulated.

Additionally, the carbon colors the gypsum produced from wet desulfurization process black while the whiteness of this material determines its valorization value when selling it to gypsum manufacturer.

Further, activated carbon is naturally retained in the fly ash waste stream. However, activated carbon can adversely interact with the additives used in cement and concrete formulations precluding by consequence the utilization of said fly ash containing activated carbon as additive in the cement industry that must therefore rather be disposed of, at significant cost.

For those reasons, there is a need to provide alternatives to the use of activated carbon, which should be more competitive in terms of costs, for acquiring it, but also for handling by-products and valorizing the residual material of the flue gases treatment.

Document US2014/0050641A1 relates to an aqueous mercury sorbent composition. Such composition is produced by mixing

(a) an aqueous solution of a silica containing precursor (such as silicic acid, colloidal silica);

(b) an aqueous solution of metal species (such as copper salts); and

(c) a solution of a sulfur-based species (such as (poly)sulfide salts or dithiocarbamates) with

(d) process water.

Unfortunately, such impregnated silica involves quite complex manufacturing process and is sold on the market as being a quite expensive specialty product, especially, where the silica has to be highly porous for good capture properties, while on the other hand it is intended to treat waste product. Therefore, even if this solution is quite well accepted on the market, notably because up to now no other mineral sorbent composition efficient enough has been proposed, it remains a problem for industrial actors to use expensive silica to treat flue gases being a waste.

In addition, according to this document, the sorbent composition is intended to be used under aqueous suspension in two different applications. In the first application, the aqueous suspension is designed to be used in wet flue gas desulfurizer units, where it is stable enough. In the second application, the aqueous suspension is injected in the dry and hot flue gas. However, in the latter case, the aqueous suspension is dried in the hot flue gas causing likely in such a case a loss of efficiency due to sensitivity towards thermal decomposition and a lack of reproducibility since the drying process of the sorbent is only undergone and not controlled. Indeed, tests conducted in our study have proven that spray-dried colloidal silica particles have a tendency to trap active chemical compounds into the particle core during the spray-drying step, thus reducing overall efficiency.

Also, the lack of reproducibility from one plant to another, as well as the difficulties linked with the handling and injection of liquid additive

in a process dealing with hot gas, are other issues encountered with this type of product.

Document WO2014/164975A1 discloses also a sorbent for removing mercury or sulfur from gas stream. Such composition is disclosed as being a solid state composition of

(a) an inorganic base (such as calcium hydroxide, sodium sesquicarbonate, sodium (bi)carbonate, potassium carbonate and/or calcium carbonate); and

(b) a sulfide (such as ammonium sulfide, alkali metal sulfide, alkali-earth metal sulfide and/or transition metal sulfide); and

(c) optionally a support (such as silicate, aluminate, aluminosilicate, and/or carbon) carrying the admixture. Other admixtures are also disclosed in WO2014/164980 containing silicate sorbents.

From US2013/089479, US2011/012422, WO2015/057420, US6719828 or US 7288499 are also known sorbent compositions based on clays or other silicate sorbents.

Unfortunately, all the sorbent compositions for mercury removal available on the market present drawbacks since either they consist of organic sorbent material and have accordingly a high efficiency in terms of mercury removal but present ignition risks, or they are globally mineral but have a poor efficiency in terms of mercury removal and/or typically are expensive.

There is still therefore a need to provide a mineral sorbent composition, powerful for mercury removal from flues gases, chemically stable, affordable on a cost basis and compatible with fly ash valorization.

The present invention relates more precisely to sorbent composition containing particles for removing heavy metals, in particular mercury, from flue gases, wherein said particles are core-shell particles with the aim to solve at least a part of the aforementioned drawbacks by providing a composition for an oxidative sorbent material used in the capture of heavy metals, and more specifically mercury, in both ionic and metallic form, and its method of manufacturing. The heavy metals can be removed from a fluid,

preferentially a gaseous fluid, notably from flue gas, wherein the heavy metals are usually gaseous, in coal-fired plants, municipal solid waste incinerators, and/or cement kilns and/or other industries exhaust gases.

To solve this problem, it is provided according to the present invention, a lime-based sorbent composition wherein the core comprises a calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.uI$, wherein I represents impurities, a, b, z and t each being mass fractions > 0 and ≤ 100 %, x and y each being mass fractions ≥ 0 and ≤ 50%, u being mass fraction ≥ 0 and ≤ 20 %, the total a, b, x, y, z, t and u being 100 % by weight, based on the total weight of said at least one calcium-magnesium compound, characterized in that said core is coated with a shell comprising a metal salt and a sulfur-based compound, said sulfur based compound being present in an amount sufficient for allowing a shielding effect of the composition, preferably of the core and presenting a thickness of less than 20 µm and more than 50 nm.

According to the present invention, the $CaCO_3$, $MgCO_3$, CaO, MgO, $Ca(OH)_2$ and $Mg(OH)_2$ contents in calcium-magnesium compounds may easily be determined with conventional methods. For example, they may be determined by X-ray fluorescence analysis, the procedure of which is described in the EN 15309 standard, coupled with a measurement of the loss on ignition and a measurement of the CO_2 volume according to the EN 459-2:2010 E standard.

The impurities I notably comprise all those which are encountered in natural limestones and dolomites, such as clays of the silico-aluminate type, silica, impurities based on iron or manganese,... or those coming from the manufacturing process of the calcium-magnesium compound.

Tests conducted in our study have proven, when experimenting mixture of hydrated lime with sulfur-based compound, that lime, when in contact with the flue gases, either present on the surface or in mixture with the sulfur-based compound, has a strong tendency to reduce ionic mercury into elemental mercury, thereby yielding to a loss of efficiency in mercury

removal since mercury must be in the ionic form to react with the sulfur compound. In the present document, hydrated lime means an industrial calcium-magnesium compound made essentially of calcium dihydroxide $Ca(OH)_2$ with impurities.

Surprisingly, according to the present invention, due to the core-shell structure of the calcium-magnesium particles coated with a shell presenting a thickness of more than 50 nm and less than 20 µm, the negative effect of lime is reduced, thereby increasing drastically the mercury removal capacity of the composition according to the present invention.

Indeed, in the product of the present invention, the core of calcium-magnesium particles is shielded from the mercury compounds by the shell layer of the sulfur-based compound.

The core of the calcium-magnesium particles is coated with a shell comprising a sulfur-based compound in an amount sufficient for allowing a shielding effect of the composition, preferably of the core. By the terms "shielding effect of the composition", it is meant that not necessarily 100 % of the particles composing the composition are entirely coated by the shell layer of sulfur-based compound. The amount of particles which are coated by the shell layer of sulfur-based compound could be 30 weight %, advantageously 35 weight %, preferably 40 weight %, more preferably 45 weight %, in particular 50 weight %, advantageously 55 weight %, preferably 60 weight %, more preferably 65 weight %, in particular 70 weight %, even more preferably 75 weight %, particularly advantageously 80 weight %, preferably 85 weight %, more preferably 90 weight %, advantageously 95 weight %, in particular 100 weight %, with respect to the lime-based composition.

The coating of the particles by the shell layer of sulfur-based compound can also be total or partial, provided that a shielding effect of the composition, especially of the core, is reached. This means that some coated particles of the composition can present some portions of their surface which are coated while other portions of their surface do not present any coating while allowing to avoid reduction of ionic mercury to elemental mercury and

thereby providing the shielding effect of the composition according to the invention.

Consequently, lime-based sorbent composition can contain particles which are effectively totally coated by the shell layer of sulfur-based compound, particles which are partially coated by the shell layer of sulfur-based compound, particles which are not coated by the shell layer of sulfur-based compound and which are therefore only composed of calcium magnesium compound and particles which are totally composed of the sulfur-based compound. The particles which are totally composed of the sulfur-based compound result from the precipitation and the agglomeration of the sulfur-based compound.

Moreover, the presence of an alkaline lime core (calcium-magnesium compound) helps to improve the stability of the sulfur-based compound in the shell layer in its most reactive form being S^{2-} while at the same time preventing H_2S emissions resulting from acidic conditions.

Therefore the sulfur-based compound in the shell can react with ionic mercury present in the flue gases and form HgS.

In a preferred embodiment, in the lime-based sorbent composition according to the present invention, said sulfur-based compound is fitting the formula $A_\alpha S_\beta O_\gamma$ wherein α, β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture. In particular, said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture.

Therefore, the lime-based composition according to the present invention is mainly from inorganic nature, thereby helping to reduce the global carbon content in the fly ash.

In a particular embodiment of the present invention, in the lime-based sorbent composition according to the invention, said metal salt is

chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

In a preferred embodiment, said metal salt is a copper sulfide or a copper polysulfide.

In an alternative embodiment according to the present invention the lime-based sorbent composition according to the invention further comprises a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.

Further, in another preferred embodiment according to the present invention, the lime-based sorbent composition according to the invention further comprises a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docecyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and their mixtures.

In an advantageous lime-based sorbent composition according to the invention, in the calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.ul$, $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

In another advantageous lime-based sorbent composition according to the invention, in the calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.ul$, $z \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

Therefore, most of the core particles in the lime-based sorbent composition are made from hydrated lime, also called slaked lime, meaning that some particles might have a core being entirely slaked lime particles or a mixture of slaked and quicklime in the same core or even partially slaked lime

particles; to a level such that the amount of slaked lime with respect to the calcium-magnesium particles is greater than 60 w%.

Said at least one calcium-magnesium compound according to the present invention is therefore at least formed with slaked lime, slaked dolomitic lime, magnesium slaked lime or burnt dolime from the calcination of natural limestones or dolomites.

The composition according to the invention may therefore also comprise calcium or magnesium carbonates such as unburnt materials from the calcination of natural limestones or dolomites or else further products from the recarbonation of calcium-magnesium compounds. Finally it may also comprise calcium or magnesium oxides due to the partial hydration (slaking) of calcium-magnesium compounds.

In another variant according to the present invention, the calcium-magnesium compound of the lime-based sorbent composition presents a particle size distribution wherein d_{10} is comprised in the range from 0,5 to 2 µm; d_{90} is comprised in the range from 2 to 50 µm, preferably from 5 to 40 µm, d_{50} is comprised in the range from 0,5 to 50 µm, preferably from 1 to 30 µm.

The notation d_X represents a diameter expressed in µm, relatively to which X % by mass of the measured particles are smaller or equal.

In yet another advantageous embodiment of the lime-based sorbent composition according to the present invention, said shell presents a thickness of less than 10 µm, preferably less than 5 µm, in particular less than 2 µm, advantageously less than 1 µm, more preferably less than 700 nm, and greater than 75 nm, preferably greater than 100 nm, in particular greater than 150 nm.

It is well understood that the smaller the core particle, the higher is its external surface, enabling therefore a higher amount of sulfur additive to be available in the outer layer, for a given sulfur/calcium-magnesium compound (core) ratio. This should improve the global mercury uptake.

In a particularly advantageous embodiment according to the present invention, the ratio between calcium-magnesium compound (core) and sulfur in the form of sulfide ranges from 15:1 w/w to 1:1 w/w, preferably 10:1 to 2:1 and preferably is of 5:1, advantageously is of 4:1, more preferably is of 3:1, preferentially is of 2,5:1 w/w, with respect to the lime-based sorbent composition, in the lime-based sorbent composition.

The quantity of the sulfur-based compound with respect to the composition according to the present invention has to be sufficient to allow a shielding effect of the composition, preferably of the core of the particles.

In another advantageous embodiment, the ratio between calcium-magnesium compound (core) and said metal salt ranges from 15:1 w/w to 1:1 w/w, preferably from 10:1 to 2:1, advantageously from 8:1 to 3:1, preferentially from 7:1 to 4:1 and preferably is of 5:1 w/w with respect to the lime-based sorbent composition, in the lime-based sorbent composition according to the invention.

Other embodiments of the lime-based sorbent composition according to the present invention are mentioned in the appended claims.

The present invention also relates to a process to produce a lime-based sorbent composition comprising the steps of :

i) Feeding an aqueous suspension of calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.uI$, wherein I represents impurities, a, b, z and t each being mass fractions > 0 and ≤ 100%, x and y each being mass fractions ≥ 0 and ≤ 50%, u being mass fraction ≥ 0 and ≤ 20 %, the total a, b, x, y, z, t and u being 100 % by weight, based on the total weight of said at least one calcium-magnesium compound to a spray dryer

ii) Feeding a calcium-magnesium polysulfide solution to said spray dryer,

said feeding of said aqueous suspension of calcium-magnesium compound and the feeding of the calcium-magnesium polysulfide solution being separated or together, optionally under the form of a premix of said calcium-

magnesium polysulfide solution and said aqueous suspension of calcium-magnesium compound

iii) forming a spray dried lime-based composition presenting particles being core-shell particles, wherein the core comprises said calcium-magnesium compound, said core being coated with a shell presenting a thickness of more than 50 nm and less than 20 µm, allowing to provide a shielding effect of the core from the flue gases medium and comprising at least a sulfur-based compound, said process further comprises the step of providing a metal ammonia complex under the form of a solution

(1) to said calcium-magnesium polysulfide solution or to said aqueous suspension of calcium-magnesium compound or to the premix of said calcium-magnesium polysulfide solution and said aqueous suspension of calcium-magnesium compound, said formed spray dried lime-based composition presenting particles being core-shell particles further comprising at least a metal salt in the shell or,

(2) to said spray dryer separately or together with said calcium-magnesium polysulfide solution or with said aqueous suspension of calcium-magnesium compound or with the premix of said calcium-magnesium polysulfide solution and said aqueous suspension of calcium-magnesium compound, said formed spray dried lime-based composition presenting particles being core-shell particles further comprising at least a metal salt in the shell or,

(3) to the spray dried lime-based composition presenting particles being core-shell particles, said shell being formed of a first layer comprising said sulfur based compound and a second layer comprising at least a metal salt.

The spray dryer used in the process according to the invention has the advantage to allow the formation of a dry composition recovering the majority of the components fed during the process. Consequently, the quantity of the different components with respect to the dry composition can be roughly determined by the quantity of these components initially fed during the process.

As previously said, the shielding effect of the spray dried lime-based composition means that not necessarily 100 % of the particles composing the composition are entirely coated by the shell layer of sulfur-based compound. The amount of particles which are coated by the shell layer of sulfur-based compound could be 30 weight %, advantageously 35 weight %, preferably 40 weight %, more preferably 45 weight %, in particular 50 weight %, advantageously 55 weight %, preferably 60 weight %, more preferably 65 weight %, in particular 70 weight %, even more preferably 75 weight %, particularly advantageously 80 weight %, preferably 85 weight %, more preferably 90 weight %, advantageously 95 weight %, in particular 100 weight % with respect to the spray dried lime-based composition.

The coating of the particles by the shell layer of sulfur-based compound can also be total or partial. Meaning that some coated particles of the composition can present some portions of their surface which are coated while other portions of their surface do not present any coating.

Consequently, spray dried lime-based composition can contain particles which are effectively totally coated by the shell layer of sulfur-based compound, particles which are partially coated by the shell layer of sulfur-based compound, particles which are not coated by the shell layer of sulfur-based compound and which are therefore only composed of lime and particles which are totally composed of the sulfur-based compound. The particles which are totally composed of the sulfur-based compound result from the precipitation and the agglomeration of the sulfur-based compound.

Preferably, said metal ammonia complex is obtained by mixing a metal salt with an ammonia solution, where the ratio between said metal salt and said ammonia ranges from 1:2 w/w to 1:10 w/w and preferably is of 1:4 w/w, advantageously is of 1:5 w/w, preferentially is of 1:5,5 w/w, more preferably is of 1:6.

Advantageously, said calcium-magnesium polysulfide solution is obtained by mixing a sulfur-based compound with a calcium-magnesium compound fitting the formula $pCaO.qMgO.rCa(OH)_2.sMg(OH)_2.ul$, wherein l represents impurities, u being mass fractions ≥ 0 and $\leq 20\%$, p, q, r and s each

being mass fractions ≥ 0 and ≤ 100%, with p + q + r + s ≥ 60% by weight, based on the total weight of said at least one calcium magnesium compound to form said calcium-magnesium polysulfide solution.

Particularly, in the process according to the present invention, said aqueous suspension of calcium-magnesium compound, also called milk of calcium-magnesium compound, presents a solid content between 30 and 45 w% with respect to the total weight of the suspension of calcium-magnesium compound.

Advantageously, in the process according to the present invention, the aqueous suspension of calcium-magnesium compound comprises particles having a particle size distribution wherein d_{50} is comprised in the range from 0,5 to 20 μm, preferably from 0,5 to 10 μm and more preferably from 1 to 5 μm.

In a particular embodiment according to the present invention, said sulfur-based compound is fitting the formula $A_\alpha S_\beta O_\gamma$ wherein α, β and γ each being mass fraction with β≠0 and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture. In particular, said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture..

Advantageously, said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

In a preferred embodiment, said metal salt is a copper sulfide or a copper polysulfide.

Preferably, said metal ammonia complex is a copper halide ammonia complex, preferably a coper chloride ammonia complex.

In a variant of the process according to the present invention, the process further comprises a step of adding a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides,

alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.

Such doping agent can be added either to the spray dried lime-based composition, meaning after the spray drying, or to the calcium-magnesium polysulfide solution, preferably to the calcium-magnesium polysulfide solution.

In another variant of the process according to the present invention, the process further comprises a step of adding a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docecyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and their mixtures.

Such dispersing agent is preferably added to the aqueous suspension of calcium-magnesium compound either before, after or simultaneously with the metal ammonia complex.

Preferably, in the calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.uI$, $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

In another advantageous embodiment of the invention, in the calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.uI$, $z \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

More particularly, in the process according to the present invention, said shell presents a thickness of less than 10 µm, preferably less than 5 µm, in particular less than 2 µm, advantageously less than 1µm, preferentially less than 700 nm, and greater than 75 nm, preferably greater than 100 nm, in particular greater than 150 nm.

In a preferred embodiment of the process according to the present invention, the ratio between calcium-magnesium compound and

sulfur in the form of sulfide ranges from 15:1 w/w to 1:1 w/w, preferably 10:1 to 2:1 and preferably is of 5:1, advantageously is of 4:1, more preferably is of 3:1, preferentially is of 2,5:1 w/w, in the calcium-magnesium polysulfide solution.

In another preferred embodiment according to the present invention, the ratio between said calcium-magnesium compound and said metal salt ranges from 15:1 w/w and 1:1 w/w, preferably from 10:1 to 2:1, advantageously from 8:1 to 3:1, preferentially from 7:1 to 4:1 and preferably is of 5:1 w/w with respect to the solid content in the suspension of calcium-magnesium particles onto which the metal is dispersed.

Preferably, the calcium-magnesium compound presents a specific surface area measured by manometry with adsorption of nitrogen after degassing *in vacuo* at 190°C for at least 2 hours and calculated according to the multipoint BET method as described in the ISO 9277:2010E standard comprised between 5 m^2/g and 50 m^2/g.

Other embodiments of the process according to the present invention are mentioned in the appended claims.

Other characteristics and advantages of the present invention will be derived from the non-limitative following description, and by making reference to the examples and the drawings.

Figure 1 represents a SEM picture of the particles of the sample "product 1" (obtained from example 1). The particles exhibit a mean diameter around 5 µm, the particle size measuring typically between 1 and 10 µm.

Figure 2 is a schematic presentation of the device used to measure the mercury capture with the several samples according to the invention and the one of the comparative examples.

Figure 3 represents the results of example 1.

Figure 4 represents the results of example 2.

Figure 5 represents the results of comparative example 1.

Figure 6 represents the results of comparative example 2.

Figure 7 represents the results of comparative example 3.

Figure 8 represents the results of example 3.

In the drawings, the same reference numbers have been allocated to the same or analog elements.

The invention concerns a sorbent under the form of a lime-based composition for the cleaning of waste gases charged with gaseous heavy metal, especially mercury, comprising :

a) a calcium-magnesium compound being a support (for instance calcium-magnesium compound at least formed with slaked lime, slaked dolomitic lime, magnesium slaked lime, but which may also comprise calcium or magnesium carbonates or oxides),

b) a metal salt (such as salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture and preferably copper sulfide or copper polysulfide), and

c) a sulfur-containing compound (such as sulfide salts, dithiocarbamates, sulfate salts, polymer-based dithiocarbamate, polysulfide salts and their mixture; preferably calcium sulfide, calcium polysulfide, calcium sulfate and their mixture and more preferably calcium polysulfide).

Advantageously, a doping agent (such as alkali metal halides, alkali earth metal halides, ammonium halides and their mixtures, preferably sodium, potassium, calcium or magnesium halides) can be added either to the spray dried lime-based composition or to the calcium-magnesium polysulfide solution, preferably to the calcium-magnesium polysulfide solution.

Optionally, a dispersant can be mixed with the suspension of calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.ul$ (such as (poly)sulfates, (poly)sulfonates, (poly)phosphates, (poly)phosphonates, polyols, and their mixtures, preferably diethylenetriamine-penta(methylene phosphonic acid) (DTPMP)or sodium docecyl sulfate).

The sorbent is a powder in particular synthetized through spray drying and comprises notably spherical particles exhibiting a core-shell structure wherein the calcium-magnesium compound making the support is the core and wherein the metal salt and sulfur-compound compose the shell.

The particle size distribution of this sorbent shown in Figure 1 is preferably as follows: d_{10}=1µm and d_{90}=10 µm, with d_{50} equal to 5µm.

The preferred embodiment of the process according to the present invention is as follows:

i) a calcium polysulfide solution is prepared separately. This chemical compound has been well known for a number of years. Its production requires a basic mix of lime and elemental sulfur, both being dissolved in boiling water (80°C-100°C), stirred at 300 rpm for 2 hours. The ratios between lime and sulfur can vary (from 1:1 w/w to 1:2). Additional chemicals can be used as well (polyphosphonate for example). For this step process, any hydrated lime or quicklime can be used (standard hydrated lime or with high surface area and/or high pore volume).

ii) Copper chloride is dissolved in water with ammonia (1:3 to 1:6 w/w) to form copper ammonia complex, stable at high pH. This solution is then mixed with a milk of lime (aqueous suspension of hydrated lime in water) for several hours to ensure complete dispersion of copper on the lime particles. For this step process, it is advantageous to use fine milk of lime (meaning with a particle size distribution with a d_{10} between 0,5 and 1,5 µm; a d_{50} between 1 and 4 µm and a d_{90} between 2 and 10 µm) and highly concentrated with solid content of between 30 wt% and 45 wt% based on the total weight of the milk of lime suspension.

iii) When both preparations are completed, the two are mixed and high-shear stirred for a short time (to limit sulfur-copper reactions) then fed into a spray dryer. During the spray-drying, there is a chemical reaction between copper ammonia complex and calcium polysulfide, likely leading to the formation of molecules of copper (poly)sulfide with a portion of unreacted calcium polysulfide. Ammonia is eliminated during the drying process. Part of the chloride counter ions are also present in the final product.

Before the spray drying, the future shell material is mainly made by $Cu(NH_3)_4$ and $CuCl_2/CaS_X$ in excess compared to the amount of copper. After spray-drying, the shell is mainly made by CuS_x and CaS_x (the

amount remaining from the excess) and $CuCl_2/Cu(OH)_2$ (possible traces) as well as $CaCl_2$ (possible traces).

The invention will now be described by virtue of non-limiting examples.

Examples.-

In the following examples, calcium polysulfide solutions have been prepared according to the following general procedure: lime and elemental sulfur, both being dissolved in boiling water (80°C-100°C), are mixed together and stirred at 300 rpm for 2 hours. The ratios between lime and sulfur can vary (from 1:1 w/w to 1:2). Additional chemicals can be optionally used (polyphosphonate for example). For this step process, any hydrated lime or quicklime can be used (standard hydrated lime or with high surface area and/or high pore volume).

Example 1.-

About 523 g of a milk of lime according to WO2014/064234 with a solid content of 45% was mixed with 50 g of copper chloride (grade 97% from Alfa Aesar) and 300 ml of ammonia (25% solution from VWR) and stirred at 300 rpm for 3 hours to form the milk of lime suspension n°1.

Calcium polysulfide solution was synthetized using the aforementioned process proposed with a lime/sulfur ratio of 1:1,5 w/w until the water was completely saturated with polysulfide. The sulfur powder (99%) has been bought from VWR Chemicals. The solution was then filtered.

487.5 ml of this saturated calcium polysulfide solution was then mixed with the milk of lime suspension n°1 and spray dried to obtain product 1.

The spray drier was the Atomizer Model MOBILE MINOR, from the Brand GEA. The tank has about a 500 dm^3 capacity, the air pressure can vary between from approximately 0 to 5,5 bar. The injection rate depends on the peristaltic pump used.

The spray drier parameters were as follows:

Mode : counter-current,

Entry pressure : 1 bar,

Entry flow rate : 25 ml/min,

Entry temperature : 210°C

Carbon-sulfur analysis of this product (performed on an Eltra CS 2000 using the prescription of the manufacturer with a high temperature furnace at 1450°C, using 100 mg of product 1 + 100 mg of iron phosphate to enhance the combustion) showed a total sulfur content of 11%, which was close to our expectation (11-14%).

The sorbent capacity of this product was then evaluated on a mercury bench illustrated on Figure 2.

Figure 2 gives a schematic representation of the mercury bench used to evaluate sorbents performances.

The mercury bench 1 used and illustrated in Figure 2 is composed of a few devices connected together. An exhaustive list is given below:

-Mercury and flue gas generator (illustrated under number 2) is the bench's central equipment designed to regulate the flow of gases 3, 4, 5, 6 (respectively N_2, O_2, HCl and SO_2). It also controls the mercury solution 7 (aqueous solution of diluted $HgCl_2$ in HCl) flow to the evaporator 8 with a peristaltic pump.

-Evaporator 8 is an essential device and the start of the circuit, designed to turn the liquid mercury solution 7 into vapor in the gas flow composed at this point of N_2 (illustrated under number 3) and O_2 (illustrated under number 4).

-Mercury reducing unit 9, 9' is a piece of equipment similar to the evaporator 8, filled with catalyst material to reduce ionic mercury into metallic mercury.

-The oven (not illustrated) is the reactor 10 heating unit. The temperature inside the reactor 10 is set around 180°C.

-Reactor 10 is a metallic cylinder of low width. It is plugged to a T connection allowing access to the gas flow and a thermocouple for a precise recording of the temperature inside the reactor 10. It is completed by a 2 µm metallic filter located at the exit of the reactor 10.

-Bypass 11 is located between the central valves. It helps stabilizing the metallic and ionic mercury levels before the test begins.

-The Coolers (illustrated under number 12) are dedicated to the elimination of water in the gas flow which is a mandatory operation due to the analyzers 13 sensibility to water. Their temperature is set to 1°C.

-Flow meters 14 are devices used to measure and control the gas flow. Their function is to make sure that the flow is equally divided between the 2 lines.

-Mercury Analyzers (illustrated under number 13) are the analyzers (one on each line) for detecting metallic mercury only in the gas flow after the flow meters. The first one (main line, equipped with Mercury reducing unit 9') shows the concentration of total mercury (as ionic mercury has been reduced just before). The second one shows the concentration of metallic mercury only, which leads to the concentration of ionic mercury by simple subtraction.

The mercury bench was used to measure the mercury removal according to the following experimental procedure:

The tested sorbent is first mixed with purified sand (washed with HCl, triple rincing with deionized water, size between 125 µm and 250 µm) and poured into a fixed bed cylindrical reactor. Then a flue gas having the following composition is injected at a total flow rate of 5.8×10^{-5} Nm^3/s so as to cross this bed:

Mercury: 800µg/Nm^3

Sulfur dioxide: 70 ppm

Hydrogen chloride: 60 ppm

Dioxygen: 11%

Dinitrogen balance

With two Mercury Analyzers, it is possible to measure both the ionic and the metallic mercury levels at the outlet of the reactor. To achieve that, the gas flow is equally divided in two lanes. Prior to its arrival at the detector/analyzer, the gas flowing in the first lane crosses a mercury reduction unit so as to convert into metallic mercury the possible fraction of

mercury present in ionic form. In this way, the totality of the mercury is measured. On the other lane, only the metallic mercury is detected, which enables the calculation of the level of ionic mercury by simple substraction. With this device, it is possible to evaluate the capacity of mercury reduction by a solid by applying the principle of the breakthrough curve. The reduction capacity is expressed in (µg Hg)/g of solid.

The test starts with a 10-minutes stabilization period, then the gas is redirected through the reactor and the test begins. It ends when the total mercury level ("Hg tot" in figures 3 to 7) is back to its baseline.

From this test, calculations were made by integration of the total mercury curve to access the mercury uptake value, in µg Hg/g of sorbent used. Also, a ratio between the mercury level baseline and the minimum mercury stable level was calculated (maximum removal rate, in %).

About 100 mg of product 1 was mixed with 6,5 g of purified sand and poured into the fixed bed reactor. The mercury uptake was found to be 2000 µg/g. About 98% of total mercury was removed during the first 15 minutes of the test. The test results are shown Figure 3, where it can be seen that product n°1 shows fast kinetics of mercury capture, allowing product 1 to reach its highest removal rate in seconds. After roughly two hours, mercury is still captured in the gas phase but at a much smaller rate, which is likely caused by a diffusion process of the mercury inside the sorbent particles.

Example 2.-

About 523 g of a milk of lime according to WO2014/064234 with a solid content of 45% was mixed with 12,5 g of copper chloride (grade 97% from Alfa Aesar) and 75 ml of ammonia (25% solution from VWR) and stirred at 300 rpm for 3 hours to form the milk of lime suspension n°2.

Calcium polysulfide solution was synthetized using the aforementioned process proposed with a lime/sulfur ratio of 1:1,5 w/w until the water was completely saturated with polysulfide. The sulfur powder (99%) has been bought from VWR Chemicals. The solution was then filtered.

About 122 ml of this saturated calcium polysulfide solution was then mixed with the milk of lime suspension n°2 and spray dried to obtain product 2.

The sorbent capacity of this product was then evaluated on a mercury bench according to the experimental procedure disclosed in example 1.

About 100 mg of product 2 was mixed with 6,5 g of purified sand and poured into the fixed bed reactor. The mercury uptake value was found to be 850 µg/g. About 95% of total mercury was removed during the first 5 minutes of the test.

The test results are shown in Figure 4 where it can be seen that product n°2 has a similar behavior compared to product 1 during the first 15 minutes of the test. After this period of time, the gap between the total mercury value detected and the baseline is much smaller and is reducing faster than for product 1, showing therefore limited diffusion due to the thinner shell layer of sulfur. The total uptake is interesting (850 µg/g vs 2000 µg/g, with 4 times less copper and sulfur).

Comparative example 1.-

The sorbent capacity of activated carbon according to prior art was also evaluated on the same mercury bench and according to the same experimental procedure as disclosed in example 1.

For this test, about 50 mg of commercial product Darco Hg-LH was mixed with 6,5 g of purified sand and poured into the fixed bed reactor.

The mercury uptake value was found to be 8000 µg/g. About 95% of total mercury was removed during 70 minutes, after a 1-hour period of stabilization.

The test results are shown Figure 5 where it can be seen that, as expected, activated carbons have great mercury uptake values, with however slower kinetics, as it takes almost 1 hour to reach the maximum removal rate. No stabilization of the total mercury level under the baseline was observed, which means that no diffusion is encountered, probably

because of the highly porous structure of activated carbon and good accessibility of those pores.

Comparative example 2.-

About 10 g of bentonite was mixed with 7,8 g of copper chloride and 40 ml of ammonia and stirred at 300 rpm for 5 hours. The slurry was then filtered using a Buchner filter. The solid phase was then mixed with a solution of 20,65 g Na_2S in 100 ml H_2O and stirred for 5 hours. After a second Buchner filtration, the solid phase was dried overnight to obtain a copper sulfide-impregnated bentonite sample.

The sorbent capacity of this product was then evaluated on a mercury bench according to the experimental procedure disclosed in example 1.

About 100 mg of copper sulfide-impregnated bentonite was mixed with 6,5 g of purified sand and poured into the fixed bed reactor. The mercury uptake value was found to be 100 µg/g. About 80 % of total mercury was removed during the first 5 minutes of the test.

The test results are shown in Figure 6, where it can be seen that bentonite, which is known as a good cation exchanger, helps copper being accessible and has a good mercury oxidation capacity but the resulting total mercury uptake is weak.

Comparative example 3.-

About 625 g of Ludox HS-40 (colloidal silica available from Sigma-Aldrich, solid content 40%) was mixed with 50 g of copper chloride and 300 ml of ammonia (25% solution) in 2 kg of deionized water and stirred for 3 hours at 300 rpm so as to form a suspension of colloidal silica.

Calcium polysulfide solution was synthetized using the process proposed with a lime/sulfur ratio of 1:1,5 w/w until the water was completely saturated with polysulfide. The solution was then filtered.

600 ml of this saturated calcium polysulfide solution were then mixed with said suspension of colloidal silica and spray dried to obtain the spray dried colloidal silica product.

The sorbent capacity of this product was then evaluated on a mercury bench according to the experimental procedure disclosed in example 1.

About 100 mg of spray dried colloidal silica was mixed with 6,5 g of purified sand and poured into the fixed bed reactor.

The mercury uptake value was found to be 500 µg/g. About 93 % of total mercury was removed during the first 15 minutes of the test.

The test results are shown in Figure 7, where it can be seen that the spray dried colloidal silica sample has good kinetics and removal rate, but weak total mercury uptake compared with product 1 due to the amount of impregnant trapped between colloidal silica particles in the core of the sorbent.

Example 3.-

Test has been made to evaluate the shielding effect of the lime-based sorbent compositions according to the present invention.

Indeed, as previously mentioned, lime, when in contact with flue gases, tends to reduce Hg^{2+} into Hg°, complicating significantly the task of capturing mercury in flue gas.

The present invention has allowed to significantly reduce this undesirable effect by producing core-shell particles in which lime is shielded by a shell comprising a sulfur-based compound.

To evaluate this shielding effect, a test has been developed in order to measure and compare the propensity of three different sorbents to reduce ionic mercury present in a gas into metallic mercury. These three different sorbents consist of:

- Sorbent 1 : (S1) standard powdery slaked lime composition (comparative example 1).
- Sorbents 2 : (S2) solid admixtures of standard slaked lime and calcium polysulfide (comparative example 2).
- Sorbents 3 : (S3) composition comprising core-shell particles with the core being slaked lime and the shell being calcium polysulfide (according to the invention).

Sorbent 3 was prepared according to the following procedure. A calcium polysulfide solution was synthetized using the aforementioned process with a lime/sulfur ratio of 1:1.5 w/w. Then, different amounts of this solution were then mixed with a milk of lime (aqueous suspension of standard slaked lime in water) for 1 hour then fed into a spray dryer to obtain core-shell particles with different amounts of calcium polysulfide. During the spray-drying, it is believed that most of the calcium polysulfide molecules are deposited on the surface of lime, creating a shell. A source of metal salt was intentionally not added in this process in order to avoid distorting the results of the test due to the oxidative character of this compound (which would then oxidize Hg° into Hg^{2+}).

Sorbent 2 (S2) was prepared by spray-drying the same calcium polysulfide solution, alone, for obtaining pure spray-dried polysulfide particles. The resulting product was then mixed with standard powdery slaked lime (S1) to create a solid admixture with the same amounts of polysulfide as for the sorbents 3 (S3).

The shielding effect test was performed on the mercury bench described in Example 1, according to the following experimental procedure:

The tested sorbent is first mixed with purified sand (washed with HCl, triple rincing with deionized water, size between 125 µm and 250 µm) and poured into a fixed bed cylindrical reactor. Then a flue gas having the following composition is injected at a total flow rate of 9.33×10^{-5} Nm^3/s so as to cross this bed:

Mercury: 800µg/Nm^3

Sulfur dioxide: 500 ppm

Hydrogen chloride: 90 ppm

Dioxygen: 7%

Dinitrogen balance

The test starts with a 10-minutes stabilization period, then the gas is redirected through the reactor and the test begins. It ends when the metallic mercury level is back to its baseline.

From this test, calculations were made by integration of the metallic mercury curve to access the mercury reduction propensity, expressed in µg Hg/g of sorbent used.

The results are shown in Figure 8 where it can be seen that a standard powdery slaked lime composition (sorbent 1) presents a propensity to reduce ionic mercury into metallic mercury ($Hg^{2+} \rightarrow Hg^{0}$) which is equal to 110 µg/g.

It can also be seen in this Figure that the core-shell particles (sorbent 3) present a lower propensity to reduce ionic mercury than standard slaked lime, due to the shielding effect generates by calcium polysulfide shell covering the lime core.

Further, it can be seen that solid admixtures of standard slaked lime and calcium polysulfide (sorbent 2) do not present a shielding effect as good as with the core-shell particles since for a given amount of calcium polysulfide, the value obtained with sorbent 2 is almost always higher than the one obtained with sorbent 3. Moreover, such solid admixture, depending on the amount of calcium polysulfide, can even have a propensity to reduce more the ionic mercury than standard powdery slaked lime since the value obtained with sorbents 2 can be even higher than the reference (sorbent 1).

It should be understood that the present invention is not limited to the described embodiments and that variations can be applied without going outside of the scope of the appended claims.

« CLAIMS »

1. Lime-based sorbent composition containing particles for removing heavy metals, in particular mercury, from flue gases, said particles being core-shell particles characterized in that the core comprises a calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.uI$, wherein I represents impurities, a, b, z and t each being mass fractions > 0 and ≤ 100%, x and y each being mass fractions ≥ 0 and ≤ 50%, u being mass fraction ≥ 0 and ≤ 20 %, the total a, b, x, y, z, t and u being 100 % by weight, based on the total weight of said at least one calcium-magnesium compound, characterized in that said core is coated with a shell comprising a metal salt and a sulfur-based compound, said sulfur-based compound being present in a amount sufficient for allowing a shielding effect of the composition, preferably of the core and presenting a thickness of less than 20 µm and more than 50 nm.

2. Lime-based sorbent composition according to claim 1, wherein said sulfur-based compound is fitting the formula $A_\alpha S_\beta O_\gamma$ wherein α, β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture.

3. Lime-based sorbent composition according to claim 1 or claim 2, wherein said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture.

4. Lime-based sorbent composition according to anyone of the claims 1 to 3, wherein said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

5. Lime-based sorbent composition according to anyone of the claims 1 to 4, wherein said metal salt is a copper sulfide or a copper polysulfide.

6. Lime-based sorbent composition according to anyone of the claims 1 to 5, further comprising a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.

7. Lime-based sorbent composition according to anyone of the claims 1 to 6, further comprising a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docecyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and their mixtures.

8. Lime-based sorbent composition according to anyone of the claims 1 to 7, wherein $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

9. Lime-based sorbent composition according to anyone of the claims 1 to 8, wherein the calcium-magnesium compound presents a particle size distribution wherein d_{10} is comprised in the range from 0,2 to 3 µm, preferably from 0,5 to 2 µm; d_{90} is comprised in the range from 2 to 50 µm, preferably from 5 to 40 µm, d_{50} is comprised in the range from 0,5 to 50 µm, preferably from 1 to 30 µm.

10. Lime-based sorbent composition according to anyone of the claims 1 to 9, wherein said shell presents a thickness of less than 10 µm, preferably less than 5 µm, in particular less than 2 µm, advantageously less than 1 µm, more preferably less than 700 nm, and greater than 75 nm, preferably greater than 100 nm, in particular greater than 150 nm.

11. Lime-based sorbent composition according to anyone of the claims 1 to 10, wherein the ratio between calcium-magnesium compound and sulfur in the form of sulfide ranges from 15:1 w/w to 1:1 w/w, preferably 10:1 to 2:1 and preferably is of 5:1, advantageously is of 4:1, more preferably is of 3:1, preferentially is of 2,5:1 w/w with respect to the lime-based sorbent composition.

12. Lime-based sorbent composition according to anyone of the preceding claims, wherein the ratio between calcium-magnesium compound and said metal salt ranges from 15:1 w/w and 1:1 w/w, preferably from 10:1 to 2:1, advantageously from 8:1 to 3:1, preferentially from 7:1 to 4:1 and preferably is of 5:1 w/w with respect to the lime-based sorbent composition.

13. Process to produce a lime-based sorbent composition comprising the steps of :

i) Feeding an aqueous suspension of calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.uI$, wherein I represents impurities, a, b, z and t each being mass fractions > 0 and ≤ 100%, x and y each being mass fractions ≥ 0 and ≤ 50%, u being mass fraction ≥ 0 and ≤ 20 %, the total a, b, x, y, z, t and u being 100 % by weight, based on the total weight of said at least one calcium-magnesium compound to a spray dryer

ii) Feeding a calcium-magnesium polysulfide solution to said spray dryer,

said feeding of said aqueous suspension of calcium-magnesium compound and the feeding of the calcium-magnesium polysulfide solution being separated or together, optionally under the form of a premix of said calcium-magnesium polysulfide solution and said aqueous suspension of calcium-magnesium compound,

iii) forming a spray dried lime-based composition presenting particles being core-shell particles, wherein the core comprises said calcium-magnesium compound, said core being coated with a shell presenting a thickness of more than 50 nm and less than 20 µm, allowing to provide a shielding effect of the composition from the flue gases medium and comprising at least a sulfur-based compound,

said process further comprises the step of providing a metal ammonia complex under the form of a solution

(1) to said calcium-magnesium polysulfide solution or to said aqueous suspension of calcium-magnesium compound or to the premix of said

calcium-magnesium polysulfide solution and said aqueous suspension of calcium-magnesium compound, said formed spray dried lime-based composition presenting particles being core-shell particles further comprising at least a metal salt in the shell or?

(2) to said spray dryer separately or together with said calcium-magnesium polysulfide solution or with said aqueous suspension of calcium-magnesium compound or with the premix of said calcium-magnesium polysulfide solution and said aqueous suspension of calcium-magnesium compound, said formed spray dried lime-based composition presenting particles being core-shell particles further comprising at least a metal salt in the shell or,

(3) to the spray dried lime-based composition presenting particles being core-shell particles, said shell being formed of a first layer comprising said sulfur based compound and a second layer comprising at least a metal salt.

14. Process according to claim 13, wherein said aqueous suspension of calcium-magnesium compound presents a solid content between 30 and 45 w% with respect to the total weight of the aqueous suspension of calcium-magnesium compound.

15. Process according to claim 13 or claim 14, wherein the aqueous suspension of calcium-magnesium compound comprises particles having a particle size distribution wherein d_{50} is comprised in the range from 0,5 to 20 µm, preferably from 0,5 to 10 µm and more preferably from 1 to 2,5 µm.

16. Process according to anyone of the claims 13 to 15, wherein said sulfur-based compound is fitting the formula $A_\alpha S_\beta O_\gamma$ wherein α, β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture.

17. Process according to anyone of the claims 13 to 16, wherein said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as

calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture.

18. Process according to anyone of the claims 13 to 17, wherein said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

19. Process according to anyone of the claims 13 to 18, wherein said metal salt is a copper sulfide or a copper polysulfide.

20. Process according to anyone of the claims 13 to 19 wherein said metal ammonia complex is a copper halide ammonia complex, preferably a coper chloride ammonia complex.

21. Process according to anyone of the claims 13 to 20, further comprising a step of adding a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.

22. Process according to claim 21 wherein said doping agent is added to the calcium-magnesium polysulfide solution.

23. Process according to claim 21 wherein said doping agent is added to the spray dried lime-based composition.

24. Process according to anyone of the claims 13 to 23, further comprising a step of adding a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docecyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and their mixtures to the aqueous suspension of calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.ul$.

25. Process according to anyone of the claims 13 to 24, wherein in the calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.ul$, $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by

weight, based on the total weight of said at least one calcium magnesium compound.

26. Process according to anyone of the claims 13 to 25, wherein said shell presents a thickness of less than 10 µm, preferably less than 5 µm, in particular less than 2 µm, advantageously less than 1µm, preferentially less than 700 nm, and greater than 75 nm, preferably greater than 100 nm, in particular greater than 150 nm.

27. Process according to anyone of the claims 13 to 26, wherein the ratio between calcium-magnesium compound and sulfur in the form of sulfide ranges from 15:1 w/w to 1:1 w/w, preferably 10:1 to 2:1 and preferably is of 5:1, advantageously is of 4:1, more preferably is of 3:1, preferentially is of 2,5:1 w/w in the calcium-magnesium polysulfide solution.

28. Process according to anyone of the claims 13 to 27, wherein the ratio between said calcium-magnesium compound and said metal salt ranges from 15:1 w/w and 1:1 w/w, preferably from 10:1 to 2:1, advantageously from 8:1 to 3:1, preferentially from 7:1 to 4:1 and preferably is of 5:1 w/w with respect to the solid content in the suspension of calcium-magnesium particles onto which the metal is dispersed.

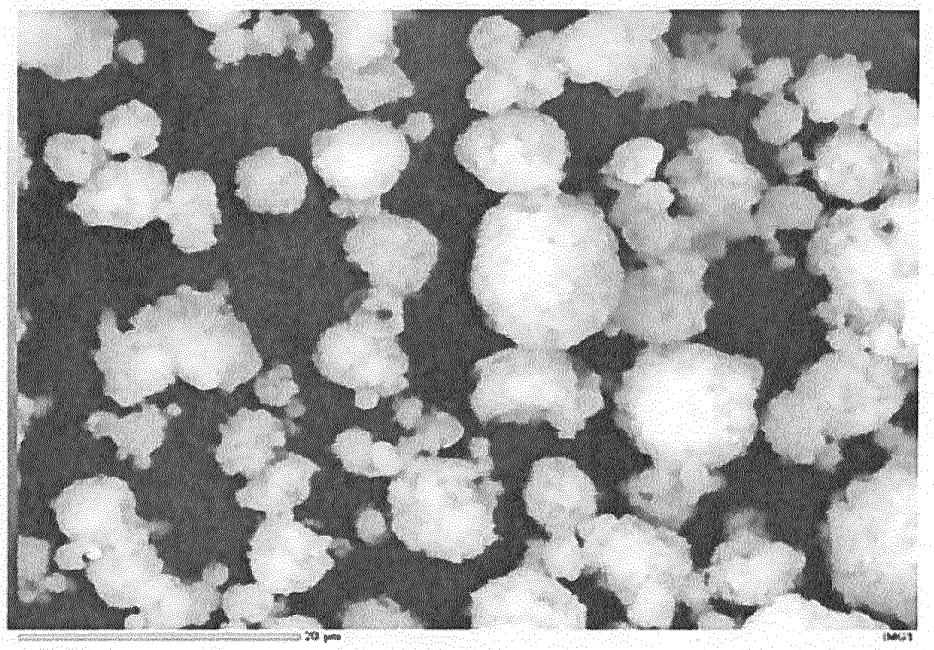


Fig. 1

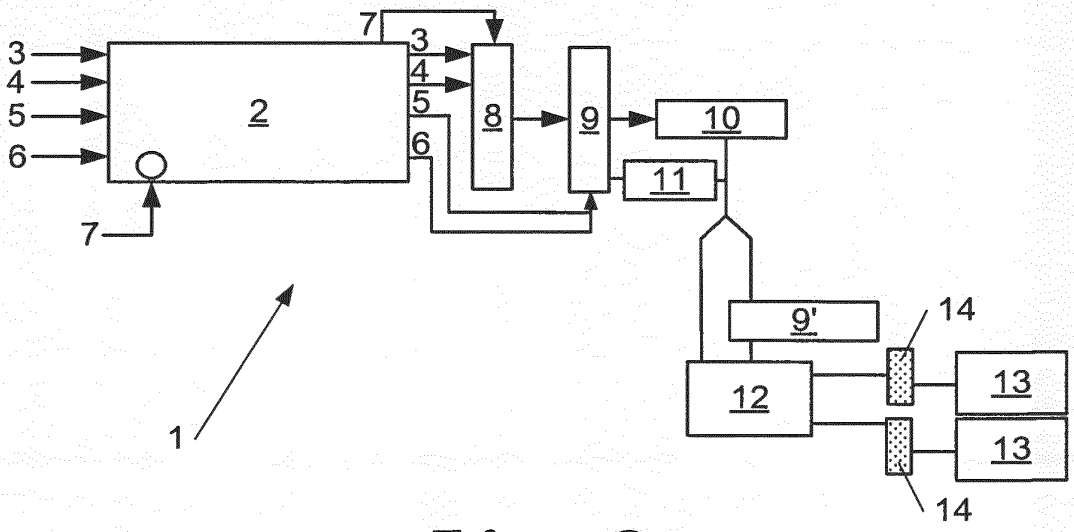


Fig. 2

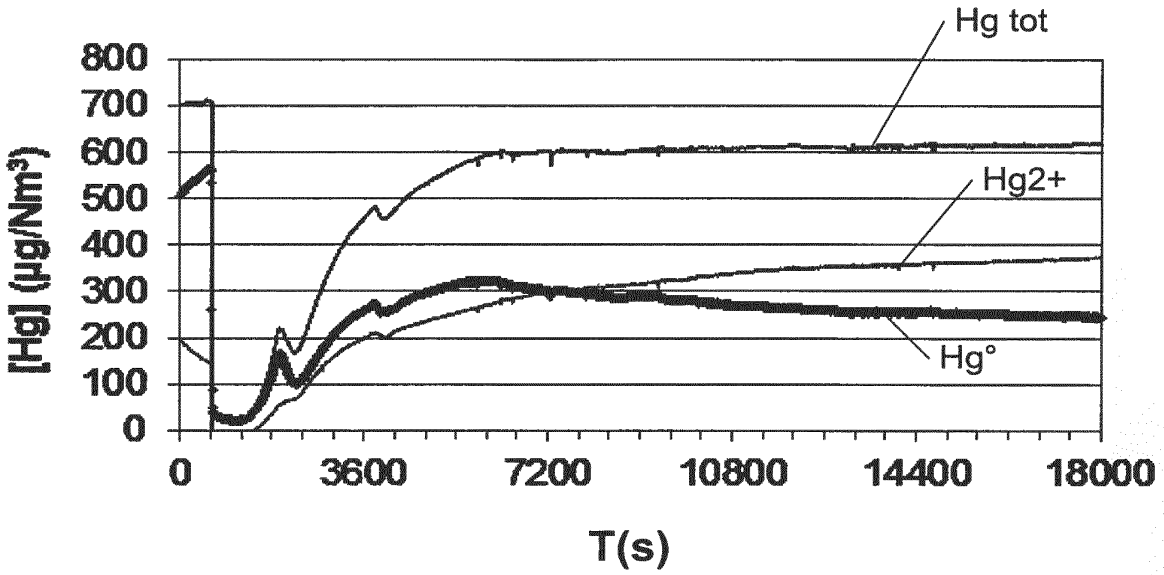

Hg tot
Hg2+
Hg°
[Hg] (µg/Nm³)
800
700
600
500
400
300
200
100
0
0
3600
7200
10800
14400
18000
T(s)

Fig. 3

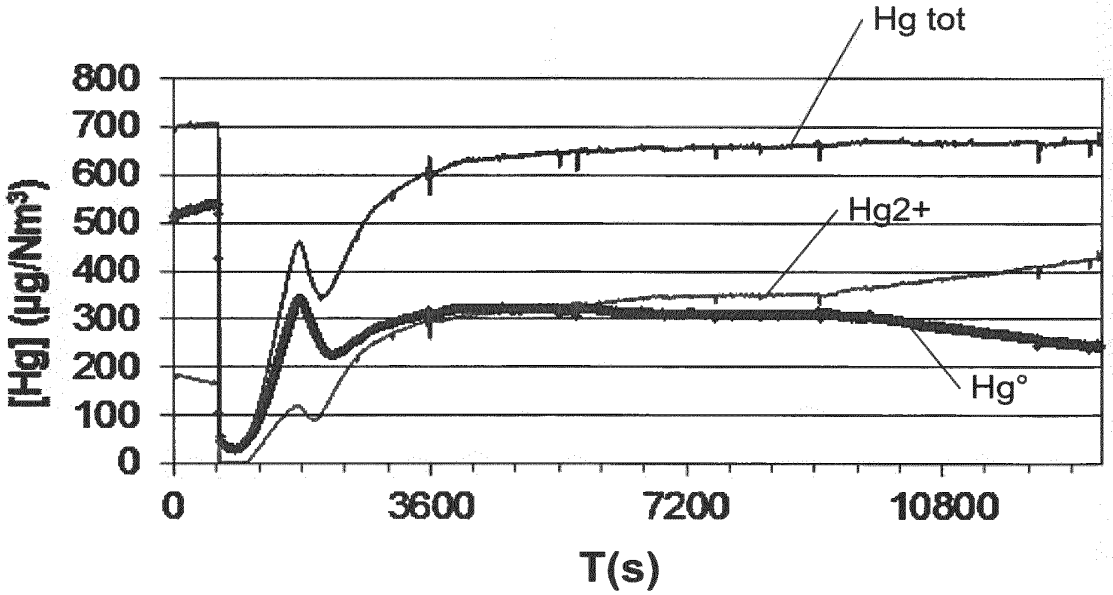

Hg tot
Hg2+
Hg°
[Hg] (µg/Nm³)
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700
600
500
400
300
200
100
0
0
3600
7200
10800
T(s)

Fig. 4

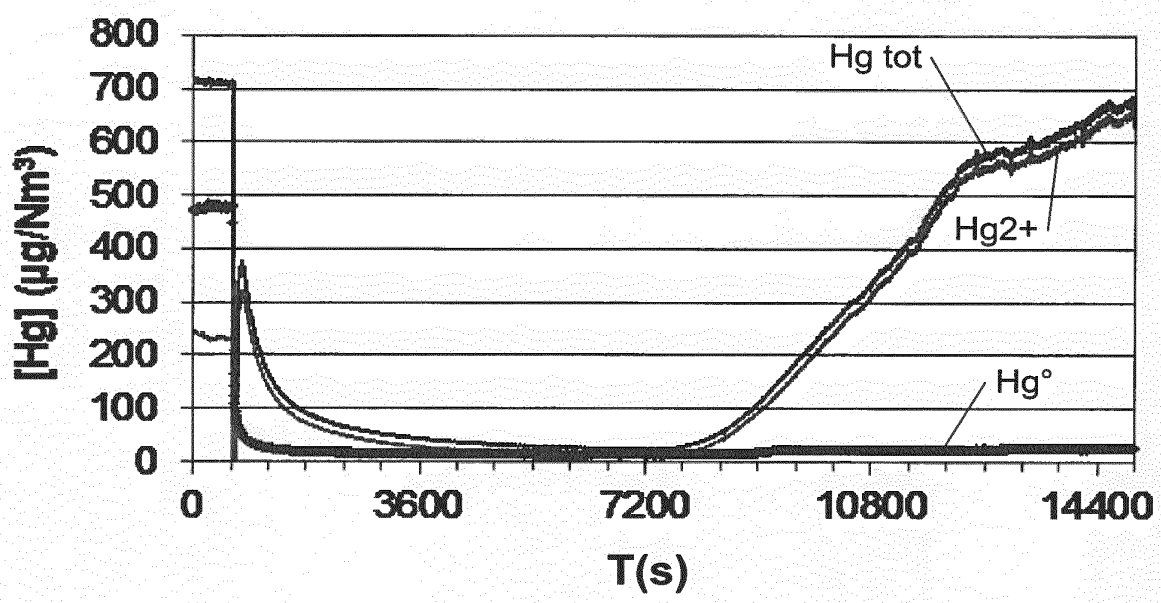

800
700
600
500
400
300
200
100
0
[Hg] (µg/Nm³)
Hg tot
Hg2+
Hg°
0
3600
7200
10800
14400
T(s)

Fig. 5

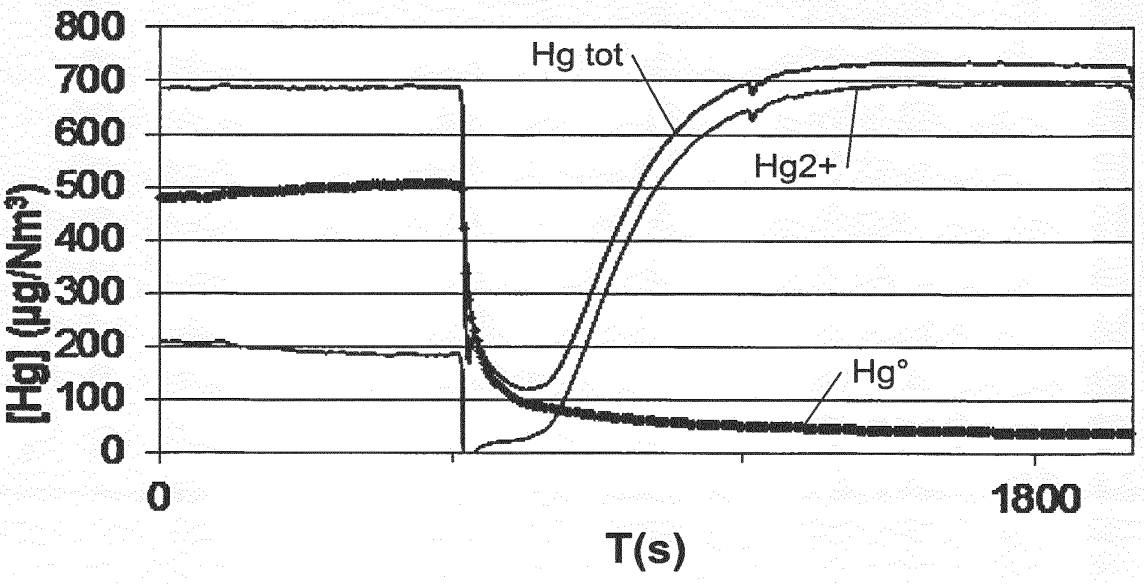

800
700
600
500
400
300
200
100
0
[Hg] (µg/Nm³)
Hg tot
Hg2+
Hg°
0
1800
T(s)

Fig. 6

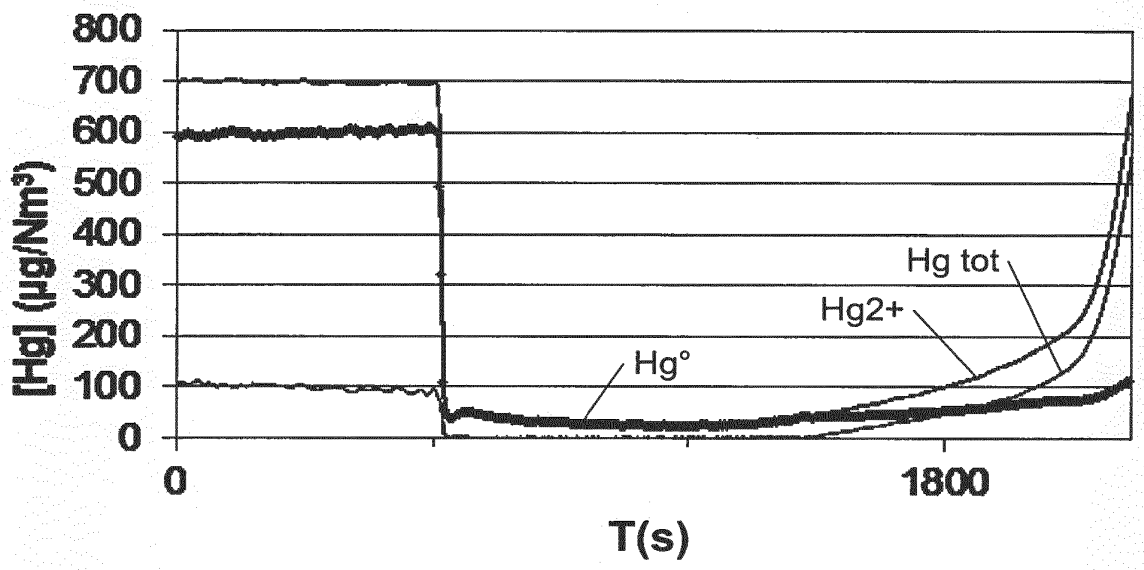

800
700
600
500
400
300
200
100
0
[Hg] (µg/Nm³)
Hg tot
Hg2+
Hg°
0
1800
T(s)

Fig. 7

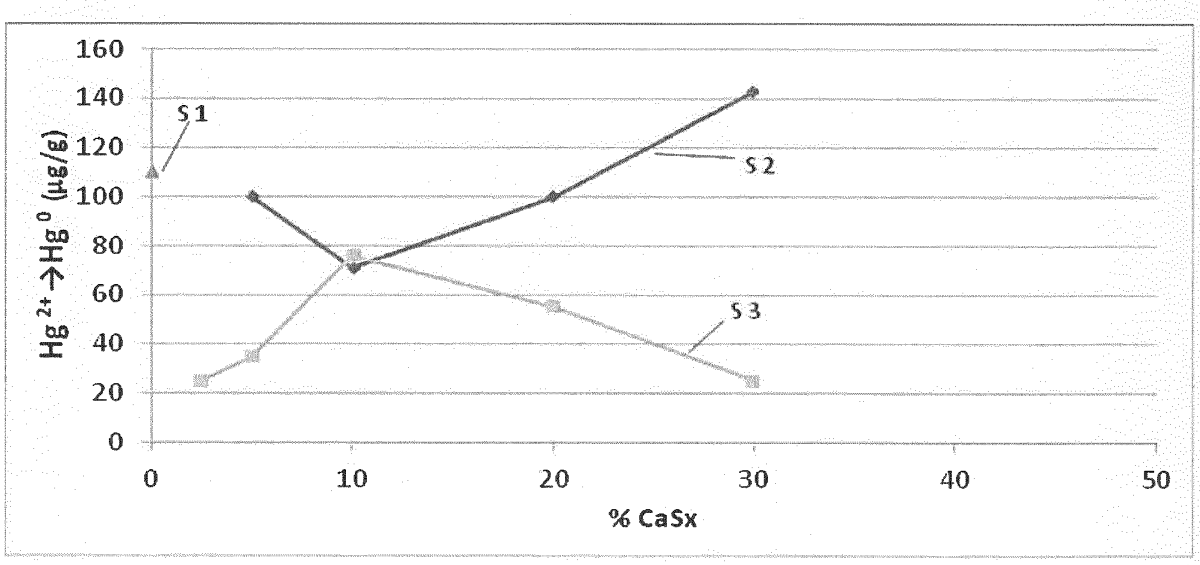

160
140
120
100
80
60
40
20
0
Hg 2+ → Hg 0 (µg/g)
S 1
S 2
S 3
0
10
20
30
40
50
% CaSx

Fig. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/061480

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/04 B01J20/32 B01J20/02 B01J20/28
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/089479 A1 (ERGANG NICHOLAS S [US] ET AL) 11 April 2013 (2013-04-11) cited in the application	1-12
A	paragraph [0059] - paragraph [0060] paragraph [0068] - paragraph [0069] paragraph [0101] paragraph [0103] - paragraph [0115]; examples 1-4 paragraph [0067]	13-28
A	US 2011/123422 A1 (WANG ZHEN [US]) 26 May 2011 (2011-05-26) the whole document	1-28
A	US 2002/035925 A1 (EL-SHOUBARY YOUSSEF [US] ET AL) 28 March 2002 (2002-03-28) the whole document	1-28

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 July 2016	05/08/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Klemps, Christian

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/061480

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013089479 A1	11-04-2013	US 2013089479 A1	11-04-2013
		US 2014084209 A1	27-03-2014
		WO 2013052876 A1	11-04-2013
US 2011123422 A1	26-05-2011	AU 2011357684 A1	27-06-2013
		CA 2820097 A1	09-08-2012
		CN 103313770 A	18-09-2013
		EP 2670510 A1	11-12-2013
		EP 2870990 A1	13-05-2015
		JP 5923526 B2	24-05-2016
		JP 2014508638 A	10-04-2014
		KR 20130141591 A	26-12-2013
		US 2011123422 A1	26-05-2011
		WO 2012106007 A1	09-08-2012
US 2002035925 A1	28-03-2002	NONE	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00460

Electronic Acknowledgement Receipt

EFS ID:	45186653
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
Filer Authorized By:	Nicholas Charalambos Kokkinos
Attorney Docket Number:	123450.013001
Receipt Date:	09-MAR-2022
Filing Date:	03-APR-2020
Time Stamp:	15:49:07
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		123450-013001_Transmittal-IDS.pdf	110304 b2b09691ff63b49a7277a87e3ec864da7b5ea2c4	yes	2

	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Transmittal Letter		1	1	
	Letter specifying the conditions for filing under 37 CFR 1.97		2	2	
Warnings:					
Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	123450-013001_SB08.pdf	1080646 c34685efe0613c0e3e2a1e98bc51287dbd63db00	no	4
Warnings:					
Information:					
3	Foreign Reference	WO2013096281A1.pdf	1284290 ab0277f8879530ed4f1feb96976e9ed2269b053d	no	24
Warnings:					
Information:					
4	Foreign Reference	WO2013149241A1.pdf	1897033 b9c073924f1796d200b779d2911d551b82030f30	no	36
Warnings:					
Information:					
5	Foreign Reference	WO2016185033A1.pdf	7523998 546f653d5deb7b77e91b7c40e1e1be4720382a41	no	41
Warnings:					
Information:					
		Total Files Size (in bytes):	11896271		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Attorney Docket No.: 123450-013001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Application of:	:	Rebecca L. DISTEFANO et al.
Application No:	:	16/839,862
Filed:	:	April 3, 2020
Group Art Unit:	:	1731
Confirmation No.:	:	5111
Examiner:	:	Yong Liang CHU

Title: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with the provisions of 37 C.F.R. §§ 1.56, 1.97 and 1.98, the attention of the Patent and Trademark Office is hereby directed to the documents listed on the attached form PTO/SB/08a. It is respectfully requested that the documents be expressly considered and that the documents be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

Statement under 37 C.F.R. §1.97(c)(1) / Fee Authorization

This Information Disclosure Statement is submitted under 37 C.F.R. §1.97(c)(1) after the mailing of a first Office Action on the merits, but before the mailing date of a Final Office Action or a Notice of Allowance. The undersigned asserts in accordance with 37 C.F.R. §1.97(e)(1) that each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. Therefore, applicant holds that no fee is due. However, the Commissioner is hereby authorized to charge any additional fees which may be required for this submission, or credit any overpayment to Deposit Account No. 60-4406.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00464

Attorney Docket No.: 123450-013001

Statement under 37 C.F.R. §1.704(d)(i) / Patent Term Adjustment

The applicant states that each item of information contained in the information disclosure statement was first cited in any communication from a patent office in a counterpart foreign or international application or from the Office, and this communication was not received by any individual designated in § 1.56 (c) more than thirty days prior to the filing of the information disclosure statement. Thus, the applicant holds that the submission of this Statement does not affect any patent term adjustment.

Respectfully submitted,

DLA PIPER LLP (US)

/Nicholas Kokkinos/

Nicholas C. Kokkinos
Reg. No. 76,979

DLA PIPER LLP (US)
1650 Market Street, Suite 5000
Philadelphia, PA 19103-7348
Telephone: (215) 656-3300
Date: March 9, 2022

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00465

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450.013001	5111

93724 7590 03/03/2022

DLA Piper LLP/ CCC-Pittsburgh
1650 MARKET ST
STE 5000
PHILADELPHIA, PA 19103-7348

EXAMINER	
CHU, YONG LIANG	

ART UNIT	PAPER NUMBER
1731	

NOTIFICATION DATE	DELIVERY MODE
03/03/2022	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

ip.pitt@us.dlapiper.com

Office Action Summary	Application No. 16/839,862	Applicant(s) DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	AIA (FITF) Status Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTHS FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☑ Responsive to communication(s) filed on 11/23/2021.

☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

2a)☐ This action is **FINAL.** 2b) ☑ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims*

5) ☑ Claim(s) 1-13 is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6) ☐ Claim(s) _____ is/are allowed.

7) ☑ Claim(s) 1-13 is/are rejected.

8) ☐ Claim(s) _____ is/are objected to.

9) ☐ Claim(s) _____ are subject to restriction and/or election requirement

* If any claims have been determined allowable, you may be eligible to benefit from the **Patent Prosecution Highway** program at a participating intellectual property office for the corresponding application. For more information, please see http://www.uspto.gov/patents/init_events/pph/index.jsp or send an inquiry to **PPHfeedback@uspto.gov.**

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☑ The drawing(s) filed on 04/03/2020 is/are: a)☑ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

Certified copies:

a)☐ All b)☐ Some** c)☐ None of the:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

** See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☑ Notice of References Cited (PTO-892)

2) ☑ Information Disclosure Statement(s) (PTO/SB/08a and/or PTO/SB/08b) Paper No(s)/Mail Date _____.

3) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date _____.

4) ☐ Other: _____.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00467

DETAILED ACTION

The present application, filed on or after March 16, 2013, is being examined under the first inventor to file provisions of the AIA.

Claims 1-13 are pending in the instant application.

Priority

This application claims priority to U.S. Provisional Application Serial No. 62/828,790 filed on April 3, 2019.

Information Disclosure Statements

Applicants' Information Disclosure Statements, filed on 11/23/2021, 07/27/2020, and 06/26/2020, have been considered. Please refer to Applicant's copies of the PTO-1449 submitted herewith.

Status of the Claims

Claims 1-13 are under examination on the merits.

Claim Rejections - 35 USC § 112

The following is a quotation of 35 U.S.C. 112(b):

> (b) CONCLUSION.—The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the inventor or a joint inventor regards as the invention.

The following is a quotation of 35 U.S.C. 112 (pre-AIA), second paragraph:

> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

Claims 1-13 are rejected under 35 U.S.C. 112(b) or 35 U.S.C. 112 (pre-AIA), second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject

matter which the inventor or a joint inventor, or for pre-AIA the applicant regards as the invention.

Specifically, claim 1 contains a phrase "a first sorbent material including about 0.5 wt.% to about 25 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof". This phrase renders claim 1 indefinite because it is not clear what "about 0.5 wt.% to about 25 wt.%" is relevant to? An ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof **each** has its specific molecular weight, and a weight percentage (wt.%) of Mg having molecular weight of 24.3 is different from a weight percentage (wt.%) of $MgCl_2$ having molecular weight of 95.2. In addition, a carbonate of magnesium salt ($MgCO_3$) is encompassed by a salt of magnesium. Because claim 1 contains both narrowly defined species of $MgCO_3$ and broadly defined species of magnesium salts (e.g. $MgCO_3$, $MgCl_2$, $MgBr_2$, $MgSO_4$), the metes and bounds of claim 1 are not clear. Therefore, claim 1 is indefinite. Claims 2-13 depending on claim 1 are rejected accordingly.

Claim Rejections - 35 USC § 102

In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (a)(1) the claimed invention was patented, described in a printed publication, or in public use, on sale or otherwise available to the public before the effective filing date of the claimed invention.

Claims 1-3, 7, 13, and 14 are rejected under 35 U.S.C. 102(a)(1) as being anticipated by Wang *et al*., *Chemosphere*, (**2015)**, v.131, p.178-183.

Applicants' claim 1 is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material including about 0.5 wt.% to about 25 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and contacting the first sorbent material with a liquid or gas containing the PFAS.

Wang *et al*. discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM comprising a step of mixing 1g of sludge B1 (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration, see "2.3 *Aqueous solution composition*" at page 180. The Ca^{2+} ion was prepared from $CaCl_2$, and Mg_{2+} was prepared from $MgCl_2$, see "*2.1 Chemicals*" at page 179. The sorbent of sludge B1 was prepared through drying at 105 °C overnight and further burned in an oven under 300 °C for 1 h, see the procedure under "2.2 Sorbents" at page 179. The sorbent of sludge B1 includes carbonaceous char or activated carbon formed by burning in an oven under 300 °C for 1 h, and evidenced by the characteristics of sludge samples in Table 1, Sludge 1B, page 179. In terms of the concentration of Ca^{2+} ion made from $CaCl_2$ (Mw=110.98) having concentration up to 100 mM, the molar concentration can be converted to weight concentration: (0.1x110.98/1000)x100%=1.1098 wt%. In terms of the concentration of Mg^{2+} ion made from $MgCl_2$ (Mw=95.21) having concentration up to 100 mM, the molar concentration can be converted to weight concentration:

(0.1x95.21/1000)x100%=0.9521 wt%. Therefore, Wang *et al.* anticipates Applicant's claims 1-3, and 9-10.

Claim Rejections - 35 USC § 103

In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102 of this title, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

The factual inquiries set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103 are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

Claims 4-8 and 11-13 are rejected under 35 U.S.C. 103 as being unpatentable over Appleman *et al.*, *Water Research*, (**2014)**, v.51, p.246-255 in view of Wang *et al.*, *Chemosphere*, (**2015)**, v.131, p.178-183.

Applicants' claim 4 is drawn to a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising: providing a first sorbent material

including about 0.5 wt.% to about 25 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and contacting the first sorbent material with a liquid or gas containing the PFAS, wherein the first sorbent material is reactivated carbon.

Determination of the scope and content of the prior art (MPEP §2141.01)

Appleman *et al.* discloses a method of treatment of poly- and perfluoroalkyl substances in 18 raw drinking water sources and 2 treated wastewater effluents for the attenuation of PFASs. The method applied anion exchange and granular activated carbon (GAC) treatment to remove longer-chain PFAS, see Abstract at page 246. The detail analysis of the GAC treatment was disclosed in Figs. 1-2, and "*3.2.5 GAC treatment*" at pages 250-252.

Wang *et al*. discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous solution comprising PFAS in the presence of Ca^{2+} ion and Mg^{2+} at a concentration up to 100 mM comprising a step of mixing 1g of sludge B1 (sorbent) with 50 nL of perfluoroalkyl substances of PFHxS and PFHpA mixture (5 ppb each) solution containing different cation concentration, see "2.3 *Aqueous solution composition*" at page 180. The Ca^{2+} ion was prepared from $CaCl_2$, and Mg_{2+} was prepared from $MgCl_2$, see "*2.1 Chemicals*" at page 179. The sorbent of sludge B1 was prepared through drying at 105 °C overnight and further burned in an oven under 300 °C for 1 h, see the procedure under "2.2 Sorbents" at page 179. The sorbent of sludge B1 includes carbonaceous char or activated carbon formed by burning in an oven under 300 °C for 1 h, and evidenced by the characteristics of sludge samples in Table 1, Sludge 1B, page 179. In terms of the concentration of Ca^{2+} ion made from $CaCl_2$ (Mw=110.98) having concentration up to 100 mM, the molar concentration can be converted to weight concentration of 1.1098 wt%. In terms of the concentration of Mg^{2+}

ion made from $MgCl_2$ (Mw=95.21) having concentration up to 100 mM, the molar concentration can be converted to weight concentration of 0.9521 wt%.

Ascertainment of the difference between the prior art and the claims (MPEP §2141.02)

The difference between the instantly claimed method and the method of Appleman *et al.* is that the prior art does not teach the first sorbent material including about 0.5 wt.% to about 25 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to PFAS.

Finding of prima facie obviousness--rational and motivation (MPEP §2142-2413)

However, instantly claimed method of claims 4 and 12-13 would have been obvious over the method disclosed by Appleman *et al.* because the difference is further taught by Wang *et al*. which teaches divalent ions prompt stronger effects of sorbent (e.g. sludge B1) on PFAS sorption caused by the potential bridging effects, see "4. *Conclusions*" at page 182. One ordinary skilled in the art would have been motivated to use a sorbent such as granular activated carbon (GAC) mixing with divalent ions (e.g. Ca^{2+} and Mg^{2+}) for removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from an aqueous liquid, wherein reactivated carbon is activated carbon.

In terms of claim 5 wherein the first sorbent material is a deagglomerated activated carbon, Appleman *et al. teaches the sorbent is GAC, and* Wang *et al*. teaches the sorbent was burned at 300 C, which teaches and/or suggests the sorbent of active carbon could be a deagglomerated activated carbon.

In terms of claim 6 wherein further comprising providing a second sorbent material that includes one or more of carbonaceous char, activated carbon.., it would not be a inventive optimization, but a repeating step of the known procedure taught by Appleman *et al. and* Wang

et al., because one ordinary skilled in the art would known that a repeating adsorption would cause further removal of the PFAS.

In terms of claims 7-8, using an oxide of Mg or Ca as divalent ions are suggested by Wang *et al.* for improving the sorbents adsorption capability of PFAS.

In terms of claim 11, wherein the first sorbent material includes about 2 wt.% to about 8 wt.% of an ion, salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof, because claim 11 is indefinite for failing to define the scope of the claim (see the 112(b) rejection); and because it would have been obvious over Wang *et al.* for improving the sorbents adsorption capability of PFAS.

Optimization of the concentration with known mechanism is an obvious to try. The decision *In re Aller*, 220 F.2d 454, 456,105 USPQ 233, 235 (CCPA 1955) goes into significant detail about changes in concentration and clearly indicates that the burden is on applicant to show criticality of these changes as a result that is different in kind and not merely different in degree:

"Normally, it is to be expected that a change in temperature, or in concentration, or in both, would be an unpatentable modification. Under some circumstances, however, **changes such as these may impart patentability to a process if the particular ranges claimed produce a new and unexpected result which is different in kind and not merely in degree from the results of the prior art**. *In re Dreyfus*, 22 C.C.P.A. (Patents) 830, 73 F.2d 931, 24 USPQ 52; *In re Waite et al*, 35 C.C.P.A. (Patents) 1117, 168 F.2d 104, 77 USPQ 586. **Such ranges are termed "critical" ranges, and the applicant has the burden of proving such criticality.** *In re Swenson et al.*, 30 C.C.P.A. (Patents) 809, 132 F.2d 1020, 56 USPQ 372; *In re Scherl*, 33 C.C.P.A. (Patents) 1193, 156 F.2d 72, 70 USPQ 204.

However, **even though applicant's modification results in great improvement and utility over the prior art, it may still not be patentable if the modification was within the**

capabilities of one skilled in the art. *In re Sola*, 22 C.C.P.A. (Patents) 1313, 77 F.2d 627, 25 USPQ 433 ; *In re Normann et al.*, 32 C.C.P.A. (Patents) 1248,150 F.2d 708, 66 USPQ308; *In re Irmscher*, 32 C.C.P.A. (Patents) 1259,150 F.2d 705, 66 USPQ 314 . **More particularly, where the general conditions of a claim are disclosed in the prior art, it is not inventive to discover the optimum or workable ranges by routine experimentation.** *In re Swain et al.*, 33 C.C.P.A. (Patents) 1250, 156 F.2d 239, 70 USPQ 412; *Minnesota Mining and Mfg. Co. v. Coe*, 69 App. D.C. 217, 99 F.2d 986, 38 USPQ 213 ; *Allen et al. v. Coe,* 77 App. D. C. 324, 135 F.2d 11, 57 USPQ 136 ." See *In re Aller*, 220 F.2d 454, 456, 105 USPQ 233, 235 (CCPA 1955)" In the absence of unexpected results, one of ordinary skill in the art at the time of the invention would have been motivated to optimize the process in view of the teachings in the combined references, and said optimization could have been accomplished by one of ordinary skill in the art through routine experimentation.

Conclusions

- Claims 1-13 are rejected.

Telephone Inquiry

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Yong Chu, whose telephone number is (571)272-5759. The examiner can normally be reached on M-F 8:00am-5:00pm.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Bryan D. Ripa can be reached on 571-270-7875. The fax phone number for the organization where this application or proceeding is assigned is (571) 273-8300.

Status Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for

unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

/YONG L CHU/
Primary Examiner, Art Unit 1731

Notice of References Cited	Application/Control No. 16/839,862	Applicant(s)/Patent Under Reexamination DISTEFANO et al.	
	Examiner YONG L CHU	Art Unit 1731	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
	A					
	B					
	C					
	D					
	E					
	F					
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	K					
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FOREIGN PATENT DOCUMENTS

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	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Appleman et al., Water Research, (2014), v.51, p.246-255.
*	V	Wang et al., Chemosphere, (2015), v.131, p.178-183. (Disclosed in IDS)
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00477

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	**Art Unit**
	YONG L CHU	1731

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS										
☐ Claims renumbered in the same order as presented by applicant					☐ CPA		☐ T.D.		☐ R.1.47	
CLAIM		**DATE**								
Final	Original	02/25/2022								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
	10	✓								
	11	✓								
	12	✓								
	13	✓								

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00478

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

CPC - Searched*		
Symbol	**Date**	**Examiner**
B01J20/20; 041; 3028	02/25/2022	YC
B01D53/02	02/25/2022	YC
C02F1/283	02/25/2022	YC

CPC Combination Sets - Searched*		
Symbol	**Date**	**Examiner**

US Classification - Searched*			
Class	**Subclass**	**Date**	**Examiner**

* See search history printout included with this form or the SEARCH NOTES box below to determine the scope of the search.

Search Notes		
Search Notes	**Date**	**Examiner**
EAST	02/25/2022	YC
STN	02/25/2022	YC
Patent global Dossier of 16/839,862	02/25/2022	YC
Google scholar search--PFAS removal from wastewater Ca2+ Mg2+--02252022	02/25/2022	YC
The PCT search report "Y" references are not good prior art. Much better prior art references are found and cited by this examiner. A lot of search time spent	02/25/2022	YC
ODP search (PALM inventor name and assignee, EAST and STN search)	02/25/2022	YC

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
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00479

Search Notes	Application/Control No.	Applicant(s)/Patent Under Reexamination
	16/839,862	DISTEFANO et al.
	Examiner	Art Unit
	YONG L CHU	1731

Interference Search			
US Class/CPC Symbol	US Subclass/CPC Group	Date	Examiner

/YONG L CHU/ Primary Examiner, Art Unit 1731	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00480

Under-reporting Potential of Perfluorooctanesulfonic Acid (PFOS) under High-Ionic Strength Conditions

SD Steffens, EK Cook, DL Sedlak... - ... Science & Technology ..., 2021 - ACS Publications

... , potassium, magnesium, and **calcium** with an initial PFOS ... of shorter and longer chain **PFAS** (eg, perfluorohexanesulfonic ... of enhancing the **removal** of PFOS and other **PFAS** from ...

☆ Save 99 Cite Cited by 1 Related articles »

Permeability of lime-activated pulverised fuel ash to metal-containing permeants

Y Awe, C Cheeseman... - Waste management & ..., 2001 - journals.sagepub.com

... **PFA** and **PFA**-sand mixtures have been used for lining **wastewater** lagoons and landfills where permeabilities a low as 1.4x10–10 m/s ... A mix of class F **PFA**, lime-kiln dust and **calcium** ...

☆ Save 99 Cite Cited by 8 Related articles All 12 versions

Layered metal chalcophosphate (K-MPS-1) for efficient, selective, and ppb level sequestration of Pb from water

E Rathore, P Pal, K Biswas - The Journal of Physical Chemistry C, 2017 - ACS Publications

... evaporation, are unable to selectively and effectively **remove** the heavy metal ions up to the mark ... Samples were introduced using a 100 mL/min **PFA** nebulizer connected to a peristaltic ...

☆ Save 99 Cite Cited by 29 Related articles All 4 versions »

Groundwater quality assessment in a volcanic region, Iran

M Mosaferi, M Mahmoudi, M Pourakbar... - Proceedings of the ..., 2015 - researchgate.net

... Based on **PFA**, two factors for these data were obtained, ... of rainfall and somewhat agricultural **wastewater** and their return ... the case of available **removal** technologies and the existing ...

☆ Save 99 Cite Cited by 3 Related articles »

Passive and Active *In Vitro* Resorption of **Calcium** and Magnesium Phosphate Cements by Osteoclastic Cells

C Großardt, A Ewald, LM Grover, JE Barralet... - ... Engineering Part A, 2010 - liebertpub.com

... The samples were fixed for 5 min in 2% paraformaldehyde (**PFA**) at 4C and permeabilized for 5 min in ... **Removal** of phosphate, magnesium and **calcium** from swine **wastewater** through ...

☆ Save 99 Cite Cited by 116 Related articles All 7 versions »

Solid phase extraction based on the use of Agaricus arvensis as a fungal biomass for the peconcentrations of Pb and Al prior to their determination in ...

E Kilinc, A Dündar, S Özdemir, V Okumuş - 2013 - researchgate.net

... to **remove** contaminants and finally dried at room temperature. The dried fungal biosorbent was ground in a porcelain mortar to obtain a fine powder. It was then oven-dried at 80 ºC for ...

☆ Save 99 Cite Cited by 22 Related articles All 5 versions »

Valorización de cenizas volantes para la síntesis de zeolitas mediante extracción de sílice y conversión directa: aplicaciones ambientales

N Moreno Palmerola - 2002 - upcommons.upc.edu

... A review of potential applications of different zeolitic products for **waste water** ... **removal** of dry-bottom furnaces. • Boiler slag is a vitreous grained material derived from wet ash **removal** of ...

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00481

Identification of most susceptible soil parameters for Latosol under simulated acid rain stress using principal component analysis

DJ Ling, QC Huang, Y Ouyang - Journal of Soils and Sediments, 2010 - Springer

... The **effluent** and soil samples from the columns were collected ... **PFA** techniques to environmental management and protection studies. The aim of this study is to apply the PCA and ...

☆ Save 99 Cite Cited by 4 Related articles All 10 versions »

Identifying groundwater-surface water interactions and groundwater geochemistry in the Upper Murrumbidgee Catchment using surface water surveys

SS Gray, CL Moore, BN Opdyke, CE Hughes - 2019 - dspace101.ansto.gov.au

... ionic strength but oxic deionized **wastewater** is triggering pyrite oxidation. ... **calcium** concentrations of the deionized **wastewater** injectate. Under the low ionic strength conditions **calcium** ...

☆ Save 99 Cite Related articles All 2 versions »

Nuclear magnetic resonance studies on bentonite in complex mixed systems

AS Goryan - 2012 - diva-portal.org

... relative concentration of **calcium** ions in the ... **calcium** phosphate complexes. Above pH 8 the amount of phosphate that is sorbed increases drastically through precipitation as a **calcium** ...

☆ Save 99 Cite Related articles »

Related searches

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference 123450-13002	**FOR FURTHER ACTION**	See item 4 below
International application No. PCT/US2020/026661	International filing date *(day/month/year)* 03 April 2020 (03.04.2020)	Priority date *(day/month/year)* 03 April 2019 (03.04.2019)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant CALGON CARBON CORPORATION		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 *bis*.1(a).

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44*bis*.3(c) and 93*bis*.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44*bis* .2).

	Date of issuance of this report 28 September 2021 (28.09.2021)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Miki Kobayashi e-mail pct.team8@wipo.int

Form PCT/IB/373 (revised January 2020)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To: NICHOLAS C. KOKKINOS
PEPPER HAMILTON LLP
501 GRANT STREET, SUITE 300
UNION TRUST BUILDING
PITTSBURGH, PA 15219-4429

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing *(day/month/year)*	30 JUN 2020

Applicant's or agent's file reference	FOR FURTHER ACTION
123450-13002	See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US 20/26661	03 April 2020 (03.04.2020)	03 April 2019 (03.04.2019)

International Patent Classification (IPC) or both national classification and IPC

IPC - B01D 53/70, B01D 71/02, B01J 20/20, C02F 1/58, C02F 1/68, C07C 19/08, C08F 6/12 (2020.01)

CPC - B01D 53/70, B01D 53/68, B01D 71/02, B01D 71/024, B01D 71/028, B01D 2257/2066, C02F 1/28, C02F 1/583, C02F 1/68, C02F 1/683, C02F 5/08, C02F 2003/003, C02F 2101/14, B01D 15/36, B01J 20/04, B01J 20/20, B01J 20/0288, B01J 2523/22, B01J 2523/23, B01J 2523/24, B01J 2523/25, B01J 2531/20, C07C 17/389, C07C 19/08, C08F 6/12, C08F 214/182

Applicant CALGON CARBON CORPORATION

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA/US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	08 June 2020	Lee Young PCT Help Desk Telephone No. 571-272-4300

Form PCT/ISA/237 (cover sheet) (revised January 2019)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/26661

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed.

   ☐ a translation of the international application into _____ which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(b)).

3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the international application as filed:

      ☐ in the form of an Annex C/ST.25 text file.

      ☐ on paper or in the form of an image file.

   b. ☐ furnished together with the international application under PCT Rule 13*ter*.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.

   c. ☐ furnished subsequent to the international filing date for the purposes of international search only:

      ☐ in the form of an Annex C/ST.25 text file (Rule 13*ter*.1(a)).

      ☐ on paper or in the form of an image file (Rule 13*ter*.1(b) and Administrative Instructions, Section 713).

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that forming part of the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/26661

Box No. V **Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Claims	1-13	YES
	Claims	none	NO
Inventive step (IS)	Claims	none	YES
	Claims	1-13	NO
Industrial applicability (IA)	Claims	1-13	YES
	Claims	none	NO

2. Citations and explanations:

Claims 1-13 lack an inventive step under PCT Article 33(3) as being obvious over US 2013/0316433 A1 (Huang), in view of US 2013/0168321 A1 (The Penn State Research Foundation).

Regarding Claim 1, Huang discloses a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas (para [0006], remediating groundwater of perfluoroalkyl compounds.), the method comprising: providing a first sorbent material of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof (Fig. 14; para [0006], [0040], [0080], a catalyst immobilized on activated carbon with a cofactor of calcium peroxide.) to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate (para [0081], [0085], [0086], sorption of PFOA on granular activated carbon... enhanced by cofactor.); and contacting the first sorbent material with a liquid or gas containing the PFAS (para [0041], [0085], [0086], absorption of PFOA from groundwater using sorbent column.); but does not specifically disclose including about 0.5 wt.% to about 25 wt.%. However, The Penn State Research Foundation discloses a method of removing substances from liquid (para [0005], [0043]) using a first sorbent material (para [0010], [0044], [0045], [0096], activated carbon treated with nitrogen compound for absorption of halide compounds including fluoride.) with a material including about 0.5 wt.% to about 25 wt.% (para [0074], [0078], [0106], loading of 4.9% N and on GAC.). To a person of ordinary skill in the art, varying amount of sorbent material as taught by The Penn State Research Foundation would have been obvious for use in the method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas as in Huang in order to improve removal of desired species from water, because Huang and The Penn State Research Foundation are directed towards methods of removing contaminants from liquid using activated carbon.

Regarding Claim 2, Huang further discloses the method of claim 1, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon (para [0066]), reactivated carbon, and carbon black.

Regarding Claim 3, The Penn State Research Foundation further discloses the method of claim 2, wherein the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood (para [0006]), wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, com husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.

Regarding Claim 4, The Penn State Research Foundation further discloses the method of claim 2, wherein the first sorbent material is reactivated carbon (para [0072]).

Regarding Claim 5, The Penn State Research Foundation further discloses the method of claim 2, wherein the first sorbent material is an aggregated activated carbon (para [0009]); but does not specifically disclose a reagglomerated activated carbon. To a person of ordinary skill in the art, selecting among known species of activated carbon would have been obvious in order to optimize the cost or efficiency of removing desired species from a liquid.

Regarding Claim 6, Huang further discloses the method of claim 1, further comprising: providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica (para [0066], [0080], sand and activated carbon.), silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and contacting the second sorbent material with the liquid or gas containing the PFAS (Fig. 14; para [0080]).

Regarding Claim 7, Huang further discloses the method of claim 1, wherein the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium (Fig. 14; para [0006], [0040], [0080], a catalyst immobilized on activated carbon with a cofactor of calcium peroxide.), an oxide of strontium, or an oxide of barium.

Regarding Claim 8, Huang further discloses the method of claim 7, wherein the first sorbent material includes a calcium peroxide (para [0038]) and an oxide (para [0009]); but does not specifically disclose one or more of MgO or CaO. To a person of ordinary skill in the art, selecting among species of calcium and oxides would have been obvious through routine experimentation to optimize catalysis of desired compounds for removal from liquid (Huang: para [0038]).

-- Please See Supplemental Box --

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US 20/26661

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of:
Box V.2., Citations and explanations,

Regarding Claim 9, Huang further discloses the method of claim 1, wherein the ion, salt, oxide, hydroxide, or carbonate of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation (para [0038], [0047], [0070], cofactors included in mixture used to treat sorbent material.) used to chemical vapor deposition, or physical vapor deposition.

Regarding Claim 10, The Penn State Research Foundation further discloses the method of claim 1, wherein the first sorbent material includes about 1 wt.% to about 20 wt. % of a compound (para [0074], [0078], [0106], loading of 4.9% N and on GAC.); but does not specifically disclose that said compound is an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof. However, Huang discloses a first sorbent material of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof (Fig. 14; para [0006], [0040], [0080], a catalyst immobilized on activated carbon with a cofactor of calcium peroxide.). To a person of ordinary skill in the art, varying amount of sorbent material as taught by The Penn State Research Foundation would have been obvious for use in the method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas as in Huang in order to improve removal of desired species from water, because Huang and The Penn State Research Foundation are directed towards methods of removing contaminants from liquid using activated carbon.

Regarding Claim 11, The Penn State Research Foundation further discloses the method of claim 10, wherein the first sorbent material includes about 2 wt.% to about 8 wt.% of a compound (para [0074], [0078], [0106], loading of 4.9% N and on GAC.); but does not specifically disclose an ion, salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof. However, Huang discloses a first sorbent material of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof (Fig. 14; para [0006], [0040], [0080], a catalyst immobilized on activated carbon with a cofactor of calcium peroxide.). To a person of ordinary skill in the art, varying amount of sorbent material as taught by The Penn State Research Foundation would have been obvious for use in the method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas as in Huang in order to improve removal of desired species from water, because Huang and The Penn State Research Foundation are directed towards methods of removing contaminants from liquid using activated carbon.

Regarding Claim 12, The Penn State Research Foundation further discloses the method of claim 1, wherein the first sorbent material is a reactivated carbon (para [0072]) comprising ions, oxides or carbonates of calcium, magnesium, sodium (para [0072]), potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, potassium and zinc (para [0072], [0095], [0099], activated carbon was regenerated prior to processing groundwater.).

Regarding Claim 13, The Penn State Research Foundation further discloses the method of claim 12, wherein the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, and zinc (para [0072], [0095], [0099], activated carbon was regenerated prior to processing groundwater and acid washing is absent.).

Claims 1-13 have industrial applicability as defined by PCT Article 33(4) because the subject matter could be made or used in industry.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00487

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1736
Examiner Name	Not Yet Assigned
Attorney Docket Number	123450.13001

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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	9199862	B2	2015-12-01	Kuramitsu et al.	

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.13001

	1	McNamara et al., "Comparison of Activated Carbons for Removal of Perfluorinated Compounds from Drinking Water", American Water Works Association, January 2018 (13 pages)	
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Examiner Signature	/YONG L CHU/	Date Considered	02/23/2022

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Doc code: IDS
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Art Unit	OPAP
Examiner Name	Not Yet Assigned
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Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00495

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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	Attorney Docket Number	123450.013001

	10	2011127323	WO	A2	2011-10-13	Calgon Carbon Corp		☐
	11	2013063490	WO	A1	2013-05-02	Ada Carbon Solutions, LLC		☐
	12	2014082076	WO	A1	2014-05-30	Ecolab Usa Inc		☐
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	17	2020028839	WO	A1	2020-02-06	Calgon Carbon Corp		☐
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00501

EAST Search History

EAST Search History (Prior Art)

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	4,412	B01J20/20.cpc.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:22
L2	1,399	B01J20/041.cpc.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:22
L3	540	B01J20/3028.cpc.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:23
L4	5,881	l1 or l2 or l3	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:23
L5	5,227	B01D53/02.cpc.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:23
L6	5,659	C02F1/283.cpc.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:23
L7	66	l5 and l6	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:23
L8	44	l7 and l4	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:23
L9	1	l8 and (PFAS or perfluoroalkyl or perfluoroalkyl)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:24
L10	1	l8 and ($4fluoroalkyl or perfluoroalkyl)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 16:25
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S2	1	"20130316433".pn.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/23 17:33
S4	97	("20130316433" | "20050167367" | "20070272080" | "20160346723" | "20200039809" | "5338458" | "5352274" | "7547350" | "7879136" | "20030188663" | "20110030592" |	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/23 17:47

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S6	0	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) WITH (magnesium ADJ1 oxide$2 or MgO)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:50
S7	0	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) WITH (magnesium ADJ1 hydroxide$2 or MgOH)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:51
S8	0	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) and (magnesium ADJ1 hydroxide$2 or MgOH)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:51

S9	84	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:51
S10	40	S9 and magnesium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:52
S11	1	S9 and (magnesium ADJ1 oxide$2)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:52
S12	0	S9 and (magnesium ADJ1 hydroxide$2)	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:53
S13	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) WITH magnesium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:54
S14	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) WITH calcium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:55
S15	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) WITH strontium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:55
S16	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) WITH barium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:55
S17	1	S13 or S14 or S15 or S16	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:56
S18	0	S17 not S11	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:56
S19	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) SAME magnesium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:57
S20	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) SAME calcium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:57
S21	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) SAME barium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:57
S22	1	(polyfluoroalkyl$2 or perfluoroalkyl$2) WITH (sorbent$2 or absorbent$2) SAME strontium	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:58
S23	1	S19 or S20 or S21 or S22	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:58

S24	0	S23 not S11	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/24 10:58
S25	3	WO-2017180346-$.did.	US-PGPUB; USPAT; USOCR; FPRS; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2022/02/25 11:00
S26	1	"10287185".pn.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 11:01
S27	1	"9199862".pn.	US-PGPUB; USPAT; USOCR	OR	ON	2022/02/25 11:05

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Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1736
Examiner Name	Not Yet Assigned
Attorney Docket Number	123450.013001

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	2	20130316433	A1	2013-11-28	Huang	

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	1	3077069	FR	A1	2019-07-26	Commissariat Energie Atomique	w/English Abstract	X
	2	2017180346	WO	A1	2017-10-19	Emerging Compounds Treatment Technologies, Inc		☐

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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1736
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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	1	JOHNSON et al., "Advanced Filtration Membranes for the Removal of Perfluoroalkyl Species from Water", American Chemical Society, ACS Omega, May 2, 2019, Vol. 4(5), pp. 8001-8006	

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Norit Americas, Inc. v. Calgon Carbon Corporation
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                  and TEMA Add Numeric Property Search
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                  Property Searching and SLART Improvements
 NEWS 17  SEP 11  September 2021 Update to Emtree(R) Now Available on STN
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 NEWS 19  NOV  9  RDISCLOSURE Reload Expands Searching Capabilities and
                  Introduces Numeric Property Searching
 NEWS 20  NOV 12  PATGENE database provides updated BLAST and GETSIM versions,
                  new searching capabilities and data quality improvements
 NEWS 21  DEC 16  Latest INPADOCDB and INPAFAMDB Enhancements Focus on Patent
                  Status Information
 NEWS 22  DEC 20  CAplus SM Coverage of Claims Expanded to Include JP, EP and
                  KR and Enhanced for US, WO and CN
 NEWS 23  JAN  4  Reloaded GENESEQ database provides updated BLAST and GETSIM
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L1            1 FILE USPATFULL
L2            0 FILE USPATOLD
L3            0 FILE USPAT2

TOTAL FOR ALL FILES
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L4   ANSWER 1 OF 1  USPATFULL on STN
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              [I]; C02F0001-28 [I]

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                          PATENT      KIND   DATE
                    ----------------- ---- --------
OS    CA 173:660505 * WO   2020206317  A1  20201008
* CA Indexing for this record included
CC    59-2 (Air Pollution and Industrial Hygiene)
ST    perfluoroalkyl and polyfluoroalkyl sorbent materials
IT    Clays
        (alumina, sorbent; perfluoroalkyl and polyfluoroalkyl sorbent materials
        and methods of use)
IT    Chars
        (carbonaceous, sorbent; perfluoroalkyl and polyfluoroalkyl sorbent
        materials and methods of use)
IT    Bagasse
      Carbon nanotubes
      Macadamia
      Peat
      Petroleum pitch
      Rice husk
      Sawdust
      Sorbents
      Wood
      Wood chips
        (perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of
        use)
IT    Perfluoroalkyl and polyfluoroalkyl substances
        (perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of
        use)
IT    Anthracite
      Bituminous coal
```

Lignite
Polymers
Resins
Subbituminous coal
Synthetic polymeric fibers
(perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of use)
IT Cocos nucifera
(shell; perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of use)
IT Carbon black
Diatomite
Oxides (inorganic)
Silica gel
Zeolite-group minerals
Zeolites, synthetic
(sorbent; perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of use)
IT 7440-44-0, Carbon, uses
(activated, sorbent; perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of use)
IT 9005-53-2, Lignin, uses 1034343-98-0, Graphenes
(perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of use)
IT 471-34-1, Calcium carbonate, uses 497-19-8, Sodium carbonate, uses 513-77-9, Barium carbonate 546-93-0, Magnesium carbonate 584-08-7, Potassium carbonate 1304-28-5, Barium oxide, uses 1305-78-8, Calcium oxide, uses 1309-48-4, Magnesium oxide, uses 1314-11-0, Strontium oxide, uses 1314-23-4, Zirconia, uses 1344-28-1, Alumina, uses 1633-05-2, Strontium carbonate 3486-35-9, Zinc carbonate 7631-86-9, Silica, uses
(sorbent; perfluoroalkyl and polyfluoroalkyl sorbent materials and methods of use)

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L5            1 7440-44-0/RN

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ED   Entered STN:  16 Nov 1984
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OTHER NAMES:
CN   1204YL
CN   1262R97
CN   207A
CN   207A (carbon)
CN   207E3
CN   208SR
CN   20SPD
CN   2C98
CN   340F
CN   3GX
CN   3K172
CN   3M 6001
CN   3M 6004
CN   3M 6006
CN   4GCX
CN   4GM
CN   4GS
CN   601D
CN   601D (carbon)
CN   606R97
CN   6MW-K
CN   7144EL
CN   755125-1G
CN   76-CoMoCAT
CN   7GX
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CN   A-BAC SP
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CN   A-BAC-PW 15
CN   A-MW-CNT 1020
CN   A-Supra EUR
CN   ABEKR 1
CN   AC 0
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CN   AC 100
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CN   AC 40
CN   AC 40 (adsorbent)
CN   AC 43765
CN   AC 43767
CN   AC-FE 000082-001
CN   ACP-W
CN   Acticarbon 25K
CN   Acticarbon ENO
CN   Acticarbon TK
CN   Acticarbone 2SW
CN   Actitex CS 1501
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=> s l5 or l6

L7      396537 L5 OR L6

=> s 471-34-1/rn

L8           1 471-34-1/RN

=> S 471-34-1/CRN

L9         164 471-34-1/CRN

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L10        165 L8 OR L9

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=> s l7 and l10

            1782457 L7
          255941 L10
L11        15955 L7 AND L10

=> s l11 and perfluoroalkyl

           24433 PERFLUOROALKYL
              69 PERFLUOROALKYLS
           24471 PERFLUOROALKYL
                 (PERFLUOROALKYL OR PERFLUOROALKYLS)
L12           18 L11 AND PERFLUOROALKYL

=> S L11 AND polyFLUOROALKYL

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              10 POLYFLUOROALKYLS
            4893 POLYFLUOROALKYL
                 (POLYFLUOROALKYL OR POLYFLUOROALKYLS)
L13            2 L11 AND POLYFLUOROALKYL

=> s l12 or l13

L14           18 L12 OR L13

=> s l18 and l11

L18 NOT FOUND

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of L-numbers, enter DISPLAY HISTORY at an arrow prompt (=>).

=> s l14 and l11

L15           18 L14 AND L11

=> s l15 and sorbent

           65293 SORBENT
           47368 SORBENTS
           85265 SORBENT
                 (SORBENT OR SORBENTS)
L16            2 L15 AND SORBENT

=> s l15 and sorbents

           47368 SORBENTS
L17            2 L15 AND SORBENTS

=> s l15 and clay

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          182955 CLAYS
          355993 CLAY
                 (CLAY OR CLAYS)
L18            3 L15 AND CLAY
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=> s l18 not l17

L19          2 L18 NOT L17

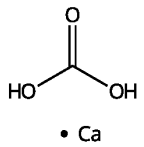
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L17  ANSWER 1 OF 2  CAPLUS  COPYRIGHT 2022 ACS on STN
ACCESSION NUMBER:         2020:1999684  CAPLUS Full-text
DOCUMENT NUMBER:          173:660505
TITLE:                    Perfluoroalkyl and polyfluoroalkyl sorbent
                          materials and methods of use
INVENTOR(S):              Distefano, Rebecca L.; Mimna, Richard A.
PATENT ASSIGNEE(S):       Calgon Carbon Corporation, USA
SOURCE:                   PCT Int. Appl., 31pp.
                          CODEN: PIXXD2
DOCUMENT TYPE:            Patent
LANGUAGE:                 English
FAMILY ACC. NUM. COUNT:   1
PATENT INFORMATION:
     PATENT NO.           KIND  DATE        APPLICATION NO.          DATE
     ---------------      ----  --------    ---------------------    --------
     WO 2020206317         A1   20201008    WO 2020-US26661          20200403
     CA 3136123            A1   20201008    CA 2020-3136123          20200403
     US 20200316560        A1   20201008    US 2020-16839862         20200403
     AU 2020256256         A1   20211111    AU 2020-256256           20200403
     CN 113727774          A    20211130    CN 2020-80031028         20200403
     KR 2021149108         A    20211208    KR 2021-7035369          20200403
     EP 3946690            A1   20220209    EP 2020-784622           20200403
PRIORITY APPLN. INFO.:                      US 2019-62828790     P   20190403
                                            WO 2020-US26661      W   20200403
PATENT STATUS PATENT INFORMATION:
     PATENT NO.           KIND  STATUS          STATUS DATE
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     WO 2020206317         A1   Alive           20201203
     CA 3136123            A1   Alive           20211125
     US 20200316560        A1   Alive           20201120
     AU 2020256256         A1   Alive           20211126
     CN 113727774          A    Alive           20211209
     KR 2021149108         A    Alive           20220113
ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
AB   Sorbent materials that are treated with ions, salts, oxides, hydroxides,
     or carbonates of calcium, magnesium, strontium, or barium are useful in
     removing perfluoroalkyl and polyfluoroalkyl substances (PFAS),
     perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS),
     2,3,3,3,-tetrafluoro-2-(heptafluoropropoxy)propanoate and
     heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether, and similar compds. from
     liqs. and gases are disclosed.  The sorbent materials with the disclosed
     treatments offer improved performance as measured against untreated
     sorbent materials.
IT   7440-44-0, Carbon, uses
     RL: TEM (Technical or engineered material use); USES (Uses)
        (activated, sorbent; perfluoroalkyl and
        polyfluoroalkyl sorbent materials and methods of use)
RN   7440-44-0  CAPLUS
CN   Carbon  (CA INDEX NAME)



       C


IT   471-34-1, Calcium carbonate, uses
     RL: TEM (Technical or engineered material use); USES (Uses)
        (sorbent; perfluoroalkyl and polyfluoroalkyl
        sorbent materials and methods of use)
RN   471-34-1  CAPLUS
CN   Carbonic acid calcium salt (1:1)  (CA INDEX NAME)
```



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L17 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2022 ACS on STN
ACCESSION NUMBER: 2014:449238 CAPLUS Full-text
DOCUMENT NUMBER: 160:474953
TITLE: Continuous destabilization of emulsions
INVENTOR(S): Schabron, John F.; Adams, Jeramie J.; Rovani, Joseph F.; Planche, Jean-Pascal
PATENT ASSIGNEE(S): Western Research Institute, USA
SOURCE: PCT Int. Appl., 112pp., Cont. of Appl. No. PCT/US2012/071087.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 9
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2014043404	A1	20140320	WO 2013-US59538	20130912
CA 2887363	A1	20140320	CA 2012-2887363	20121220
WO 2014042666	A1	20140320	WO 2012-US71087	20121220
EP 2895575	A1	20150722	EP 2012-884399	20121220
CA 2889424	A1	20140320	CA 2013-2889424	20130912
US 20150218461	A1	20150806	US 2015-14427974	20150312
US 10808183	B2	20201020	US 2015-14427975	20150312
US 20150225655	A1	20150813		

PRIORITY APPLN. INFO.:

US 2012-61700090	P1	20120912
WO 2012-US71087	A1	20121220
US 2013-61775924	P	20130311
WO 2013-US59538	W	20130912

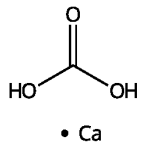
PATENT STATUS PATENT INFORMATION:

PATENT NO.	KIND	STATUS	STATUS DATE
WO 2014043404	A1	Dead	20201202
CA 2887363	A1	Dead	20201120
WO 2014042666	A1	Dead	20201202
EP 2895575	A1	Dead	20201203
CA 2889424	A1	Dead	20201121
US 20150218461	A1	Dead	20201121
US 10808183	B2	Alive	20201120
US 20150225655	A1	Alive	20201121

AB The inventive technol., in at least one embodiment, may be described as a method of destabilizing an aq. hydrocarbon emulsion comprising the steps of: effecting contact between a sorbent and said aq. hydrocarbon emulsion; effecting relative motion between said sorbent and said aq. hydrocarbon emulsion; and destabilizing (perhaps in continuous fashion) the aq. hydrocarbon emulsion. Applications include but are not limited to oil spill clean up, manufg. of emulsions, oil refinery and prodn. operations (anywhere along the prodn. chain).
IT 7440-44-0, Carbon, uses
RL: NUU (Other use, unclassified); USES (Uses)
(activated, sorbent or impregnated material; continuous destabilization of emulsions)
RN 7440-44-0 CAPLUS
CN Carbon (CA INDEX NAME)

C

IT 471-34-1, Calcium carbonate, uses
RL: NUU (Other use, unclassified); USES (Uses)
(continuous destabilization of emulsions)
RN 471-34-1 CAPLUS
CN Carbonic acid calcium salt (1:1) (CA INDEX NAME)



OS.CITING REF COUNT: 2 THERE ARE 2 CAPLUS RECORDS THAT CITE THIS RECORD (2 CITINGS)
REFERENCE COUNT: 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

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L19 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2022 ACS on STN
ACCESSION NUMBER: 2021:2092658 CAPLUS Full-text
DOCUMENT NUMBER: 176:307112
TITLE: Method for manufacturing of the rubber composition with high tensile strength and low volume resistivity
INVENTOR(S): Nagao, Yuji; Takeyama, Yoshihisa
PATENT ASSIGNEE(S): Zeon Corp., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 17pp.
CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 2021147474	A	20210927	JP 2020-48146	20200318

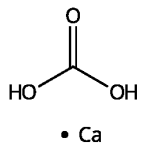
PRIORITY APPLN. INFO.: JP 2020-48146 20200318
PATENT STATUS PATENT INFORMATION:

PATENT NO.	KIND	STATUS	STATUS DATE
JP 2021147474	A	Alive	20211007

AB The present invention relates to produce a rubber compn. contg. rubber and a fibrous carbon nanostructure and having high tensile strength and low vol. resistivity. The method comprises the mixing step of mixing a rubber particle, a fibrous carbon nanostructure, and a poor solvent of the rubber particle to obtain a mixed soln., and a disperser are used to disperse the mixed soln. to obtain a dispersion, the rubber particles include a dispersion step of obtaining and a dispersion medium removing step of removing the poor solvent from the dispersion liq., and the rubber particles are made of rubber having a loss elasticity G'' at 70° of 180 kPa or less, and the av. particle size is 0.01-0.1 mm. Thus, 20 parts of Aflas PM 1100 (fluoro rubber), 4 parts of carbon nanotube and 2000 parts of cyclohexane were admixed in a a disperser to obtain title rubber compositon.
IT 7440-44-0, Carbon, uses
RL: MOA (Modifier or additive use); NANO (Nanomaterial); USES (Uses)
(Zeonano SG 101, nanotube; prodn of rubber compn. contg. rubber particles, fibrous carbon nanostructures and solvents)
RN 7440-44-0 CAPLUS
CN Carbon (CA INDEX NAME)

C

IT 471-34-1, Carbonic acid calcium salt (1:1), uses
RL: MOA (Modifier or additive use); USES (Uses)
(prodn of rubber compn. contg. rubber particles, fibrous carbon nanostructures and solvents)
RN 471-34-1 CAPLUS
CN Carbonic acid calcium salt (1:1) (CA INDEX NAME)



L19 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2022 ACS on STN
ACCESSION NUMBER: 2016:187828 CAPLUS Full-text
DOCUMENT NUMBER: 164:293329
TITLE: Filter medium coated with fluorine-based compoumd, method for manufacturing of it, wastewater treatment module having it, and wastewater treatment device having it
INVENTOR(S): Fujita, Masato; Uotani, Masakazu; Koshiyama, Hiroshi; Kamiya, Takeshi; Honda, Tsunetoshi; Takano, Daisuke
PATENT ASSIGNEE(S): Mitsubishi Materials Corporation, Japan; Mitsubishi Materials Electronic Chemicals Co., Ltd.
SOURCE: PCT Int. Appl., 166pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 6
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2016017754	A1	20160204	WO 2015-JP71635	20150730
JP 5879013	B1	20160308	JP 2015-555304	20150730
CN 106659948	A	20170510	CN 2015-80041456	20150730
CN 106659948	B	20190816		
EP 3175899	A1	20170607	EP 2015-827960	20150730
EP 3175899	B1	20190313		
US 20170247265	A1	20170831	US 2017-15329841	20170127
US 10294125	B2	20190521		

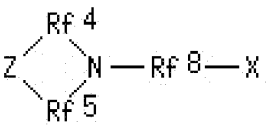
PRIORITY APPLN. INFO.:

JP 2014-155553	A	20140730
JP 2014-155554	A	20140730
JP 2014-206782	A	20141007
JP 2015-104023	A	20150521
WO 2015-JP71635	W	20150730

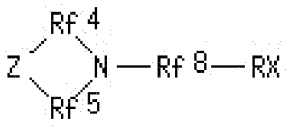
PATENT STATUS PATENT INFORMATION:

PATENT NO.	KIND	STATUS	STATUS DATE
WO 2016017754	A1	Dead	20201201
JP 5879013	B1	Alive	20201121
CN 106659948	A	Alive	20201121
CN 106659948	B	Alive	20201121
EP 3175899	A1	Indeterminate	20201106
EP 3175899	B1	Indeterminate	20201107
US 20170247265	A1	Alive	20201121
US 10294125	B2	Alive	20201121

ASSIGNMENT HISTORY FOR US PATENT AVAILABLE IN LSUS DISPLAY FORMAT
OTHER SOURCE(S): CASREACT 164:293329; MARPAT 164:293329
GI



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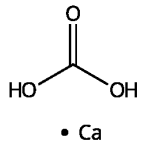


II

AB The title manufg. method comprises the steps of (1) prepg. a coating soln. comprising water and/or an org. solvent and a N-contg. F-based compd., (2) coating a substrate with the coating soln., and (3) removing the coating medium. The title filter medium has the N-contg. F-based compd. selected from Rf1Rf2NRf3X, Rf1Rf2NRf3RX, I, and II (Rf1 - Rf2 = C1-6 linear or branched perfluoroalkyl; Rf3 - Rf6 = C1-6 linear or branched perfluoroalkylene; Z = O, N, CF2, CF; R = divalent linking group; X = anionic, cationic, or amphoteric hydrophilicity-imparting group). The filter medium is used for sepg. a liq. contg. water and oil and excels in soiling and fouling resistance and washability.

IT 471-34-1, Calcium carbonate, uses 7440-44-0, Activated carbon, uses
RL: TEM (Technical or engineered material use); USES (Uses)
(porous, filter; filter coated with hydrophilic oil-repellent F-based compoumd)

RN 471-34-1 CAPLUS
CN Carbonic acid calcium salt (1:1) (CA INDEX NAME)



RN 7440-44-0 CAPLUS
CN Carbon (CA INDEX NAME)

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OS.CITING REF COUNT: 1 THERE ARE 1 CAPLUS RECORDS THAT CITE THIS RECORD (1 CITINGS)
REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

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PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	OPAP
Examiner Name	Not Yet Assigned
Attorney Docket Number	123450.013001

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	2038071		1936-04-21	Wilhelm	
	2	3713281	A	1973-01-30	Asker et al.	
	3	3757488	A	1973-09-11	Austin et al.	
	4	4331639	A	1982-05-25	Hass et al.	
	5	4624937		1986-11-25	Chou	
	6	4921826		1990-05-01	Juntgen et al.	
	7	5016628	A	1991-05-21	Lambert	
	8	5248395	A	1993-09-28	Rastelli et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	9	5322778	A	1994-06-21	Antrim et al.	
	10	5338458		1994-08-16	Carrubba et al.	
	11	5348755	A	1994-09-20	Roy	
	12	5352274	A	1994-10-04	Blakley	
	13	5356849	A	1994-10-18	Matviya et al.	
	14	5500038	A	1996-03-19	Dauber et al.	
	15	5504050	A	1996-04-02	Hayden	
	16	5598721	A	1997-02-04	Rockenfeller et al.	
	17	5754002	A	1998-05-19	Haitko et al.	
	18	5821682	A	1998-10-13	Foust et al.	
	19	5861050	A	1999-01-19	Pittel et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	20	6176897	B1	2001-01-23	Keefer	
	21	6186939	B1	2001-02-13	Forrester	
	22	6342129	B1	2002-01-29	Vaughn et al.	
	23	6406523	B1	2002-06-18	Connor et al.	
	24	6599856	B1	2003-07-29	Uchino et al.	
	25	6699393	B2	2004-03-02	Baker et al.	
	26	6706194	B2	2004-03-16	Baker et al.	
	27	6848374	B2	2005-02-01	Srinivasachar et al.	
	28	7077891	B2	2006-07-18	Jaffe et al.	
	29	7222612	B2	2007-05-29	Hagler et al.	
	30	7278406	B2	2007-10-09	Hagler	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	31	7361280		2008-04-22	Baker	
	32	7547350	B2	2009-06-16	Callahan et al.	
	33	7666507	B2	2010-02-23	Ishikawa et al.	
	34	7704305	B2	2010-04-27	Nishida	
	35	7780765	B2	2010-08-24	Srinivasachar et al.	
	36	7858061	B2	2010-12-28	Varma et al.	
	37	7862725	B2	2011-01-04	Mazyck et al.	
	38	7879136	B2	2011-02-01	Mazyck	
	39	7923410	B1	2011-04-12	Turk et al.	
	40	8034163	B1	2011-10-11	Durham et al.	
	41	8042524	B2	2011-10-25	Elum et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	42	8057576	B1	2011-11-15	Pollack	
	43	8069797	B2	2011-12-06	Srinivasachar et al.	
	44	8080088	B1	2011-12-20	Srinivasachar	
	45	8168147	B2	2012-05-01	Olson et al.	
	46	8263524	B1	2012-09-11	Skandan et al.	
	47	8864877	B2	2014-10-21	Nishita et al.	
	48	9120079	B1	2015-09-01	Dietz et al.	
	49	9120079		2015-09-01	Dietz et al.	
	50	9174205	B2	2015-11-03	Reimerink-Schats et al.	
	51	9732649	B2	2017-08-15	Hiltzik et al.	
	52	10702853		2020-07-07	Mazzoccoli et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	53	RE38844	E	2005-10-25	Hiltzik et al.	

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U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	20020170436	A1	2002-11-21	Keefer et al.	
	2	20030188663	A1	2003-10-09	Barthel et al.	
	3	20040118287	A1	2004-06-24	Jaffe et al.	
	4	20040118387	A1	2004-06-24	Lawrence	
	5	20050081717	A1	2005-04-21	Meiller et al.	
	6	20050167367	A1	2005-08-04	Baker	
	7	20060042467	A1	2006-03-02	Maru	
	8	20060054142	A1	2006-03-16	Burke et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	9	20070169758	A1	2007-07-26	Mills	
	10	20070272080	A1	2007-11-29	Allen et al.	
	11	20080073290	A1	2008-03-27	Ryan et al.	
	12	20080121142	A1	2008-05-29	Comrie et al.	
	13	20080308075	A1	2008-12-18	Allen et al.	
	14	20090172998	A1	2009-07-09	Harris et al.	
	15	20090223370	A1	2009-09-10	Kosugi et al.	
	16	20100178624	A1	2010-07-15	Srinivasachar	
	17	20110030592	A1	2011-02-10	Baldrey et al.	
	18	20110076210	A1	2011-03-31	POLLACK et al.	
	19	20120048110	A1	2012-03-01	Dawes et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	20	20120100054	A1	2012-04-26	Durham et al.	
	21	20120172216	A1	2012-07-05	Bohringer et al.	
	22	20120220451	A1	2012-08-30	Miyata et al.	
	23	20130078169	A1	2013-03-28	LaFlesh et al.	
	24	20130109562	A1	2013-05-02	Wong et al.	
	25	20130269532	A1	2013-10-17	KIMOTO	
	26	20140117054	A1	2014-05-01	RYAN et al.	
	27	20140165542	A1	2014-06-19	Loftin et al.	
	28	20150050202	A1	2015-02-19	Filippelli et al.	
	29	20160023920	A1	2016-01-28	Doyle et al.	
	30	20160166972	A1	2016-06-16	Owens et al.	

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
00526

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	31	20160236169	A1	2016-08-18	DOUGHTY et al.	
	32	20160271555	A1	2016-09-22	Hiltzik et al.	
	33	20160346723	A1	2016-12-01	HONORE et al.	
	34	20170297926	A1	2017-10-19	Nickelsen et al.	
	35	20180030871	A1	2018-02-01	Hiltzik et al.	
	36	20180214816	A1	2018-08-02	GREENBANK	
	37	20190201870	A1	2019-07-04	Kumar Pal et al.	
	38	20190247831	A1	2019-08-15	TRAMPOSCH et al.	
	39	20200038798	A1	2020-02-06	Greenbank et al.	
	40	20200039809	A1	2020-02-06	GREENBANK et al.	
	41	20200040851	A1	2020-02-06	Greenbank et al.	

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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	1	2485103	CA	A1	2003-11-20	Meadwestvaco Corp		
	2	3620425	DE	C1	1987-06-19	Bergwerksverband GmbH, 4300 Essen	U.S. Equivalent 4,921,826	
	3	0433677	EP	A1	1991-06-26	Calgon Carbon Corp		
	4	1413348	EP	A1	2004-04-28	Air Products And Chemicals, Inc		
	5	1336241	GB	A	1973-11-07	Osaka, Soda Co Ltd		
	6	2008023365	JP	A	2008-02-07	Oji Paper Co	w/English Abstract	☒
	7	H-01058331	JP	B2	1989-03-06	Mitsui Mining Co. Ltd.	English Abstract translation provided	☒
	8	2010042321	WO	A1	2010-04-15	Carbonxt Group Ltd		☐
	9	2011038415	WO	A2	2011-03-31	Calgon Carbon Corp		☐

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	OPAP
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

	10	2011127323	WO	A2	2011-10-13	Calgon Carbon Corp		☐
	11	2013063490	WO	A1	2013-05-02	Ada Carbon Solutions, LLC		☐
	12	2014082076	WO	A1	2014-05-30	Ecolab Usa Inc		☐
	13	2014088630	WO	A1	2014-06-12	Hilliard Emission Controls, Inc		☐
	14	2014205200	WO	A1	2014-12-24	Calgon Carbon Corp		☐
	15	2018144588	WO	A1	2018-08-09	Calgon Carbon Corp		☐
	16	2020028703	WO	A2	2020-02-06	Calgon Carbon Corp		☐
	17	2020028839	WO	A1	2020-02-06	Calgon Carbon Corp		☐
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	1	"The Chemistry of Nitrogen and Phosphorous." Purdue Chemistry, Purdue University, (2006) chemed.chem.purdue.edu/genchem/topicreview/bp/ch10/group5.php#negative.	
	2	RAPOSO et al., Mercury Speciation in Fluorescent Lamps by Thermal Release Analysis (2003), Waste Management 23(10):879-886	
	3	Sharifi et al., "Formation of Active Sites for Oxygen Reduction Reactions by Transformation of Nitrogen Functionalities in Nitrogen-Doped Carbon Nanotubes." ACS Nano, vol. 6, no. 10, 2012, pp. 8904-8912, doi:10.1021/nn302906r	

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	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

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The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

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SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2021-11-23
Name/Print	Nicholas C. Kokkinos	Registration Number	76,979

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Bibliographic data: CA2485103 (A1) — 2003-11-20

REMOVAL OF CHLORAMINES FROM DRINKING WATER WITH IMPROVED ACTIVATED CARBON

Inventor(s): BAKER FREDERICK STANLEY [US]; BRYNE JANE FIONA [US] + (BAKER, FREDERICK STANLEY, ; BRYNE, JANE FIONA)

Applicant(s): MEADWESTVACO CORP [US] + (MEADWESTVACO CORPORATION)

Classification: **- international:** ***B01D15/00; B01J20/20; B01J20/30; C01B32/336; C02F1/28; C02F1/76;*** *B01J21/18; B01J37/08; C02F1/72;* (IPC1-7): B01J20/30; B01J21/18; C01B31/10; C02F1/28

- cooperative: **B01J20/20 (EP); B01J20/28042 (EP); B01J20/3042 (EP); B01J20/3078 (EP); C01B32/336 (EP); C02F1/283 (EP);** B01J21/18 (EP); B01J37/084 (EP); C02F1/288 (EP); C02F1/72 (EP); C02F1/722 (EP); C02F1/725 (EP); C02F2101/38 (EP); C02F2103/02 (EP); C02F2303/185 (EP)

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Abstract of CA2485103 (A1)

This application discloses a method for enhanced removal of chloramines from a fluid media by contacting said media with a catalytic activated carbon. The catalytic activated carbons used in the present invention may be prepared fr om carbon materials that have been contacted or otherwise exposed to nitrogen- containing compounds at temperatures above 700~C, and preferably are derived from a lignocelluiosic material and in the form of a solid carbon block. Future, the invention method achieves greater than 65% chloramine removal fr om the fluid media.

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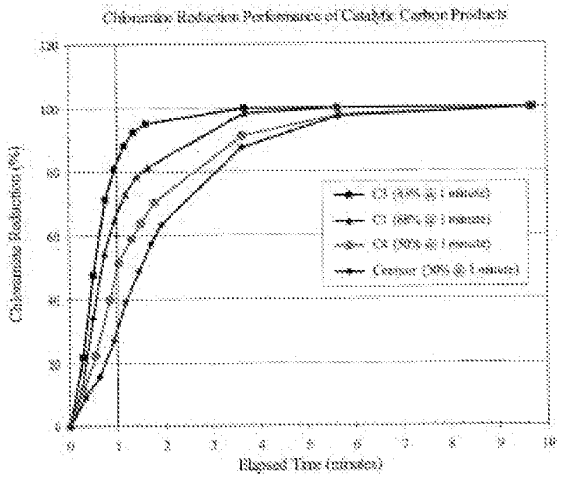


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(51) Int. Cl.[7]: **C02F 1/28**, C01B 31/10, B01J 21/18, B01J 20/30

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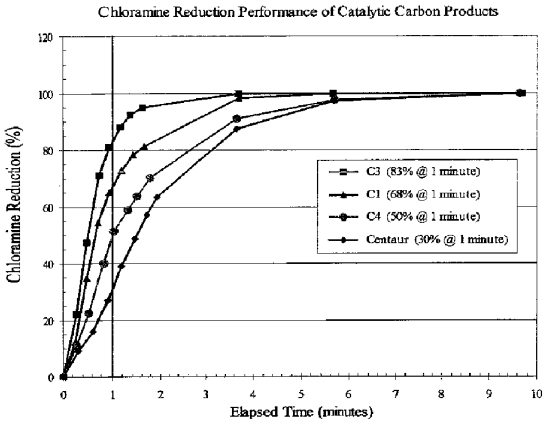
(72) **BAKER, FREDERICK STANLEY (US).**
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(74) **RIDOUT & MAYBEE LLP**

(54) ELIMINATION DE CHLORAMINES D'UNE EAU POTABLE AVEC UN CHARBON ACTIF AMELIORE
(54) REMOVAL OF CHLORAMINES FROM DRINKING WATER WITH IMPROVED ACTIVATED CARBON

(57)

This application discloses a method for enhanced removal of chloramines from a fluid media by contacting said media with a catalytic activated carbon. The catalytic activated carbons used in the present invention may be prepared from carbon materials that have been contacted or otherwise exposed to nitrogen- containing compounds at temperatures above 700~C, and preferably are derived from a lignocellulosic material and in the form of a solid carbon block. Future, the invention method achieves greater than 65% chloramine removal from the fluid media.



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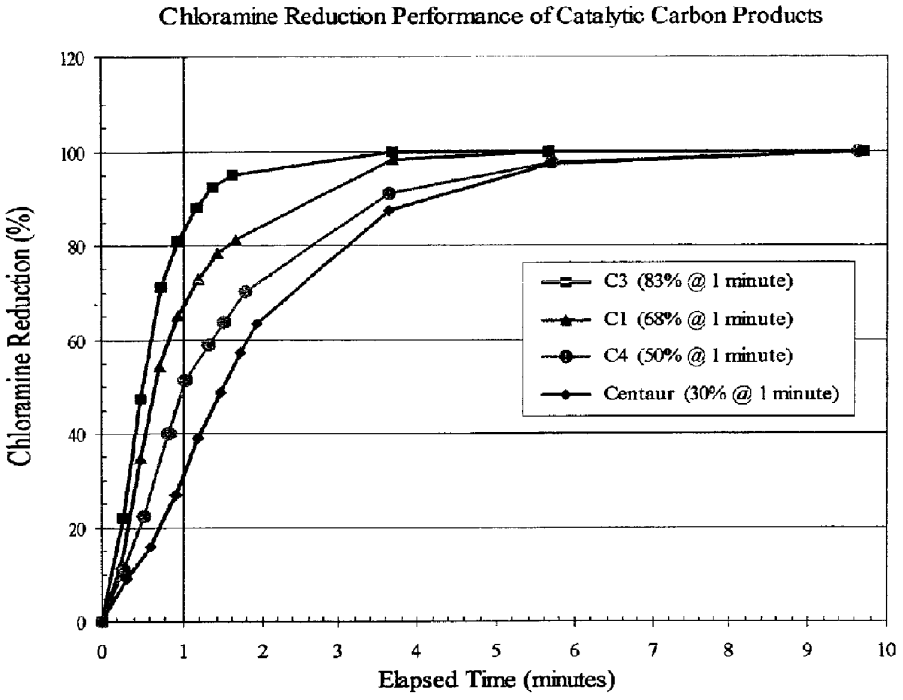
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(71) Demandeur/Applicant:
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(74) Agent: RIDOUT & MAYBEE LLP

(54) Titre : ELIMINATION DE CHLORAMINES D'UNE EAU POTABLE AVEC UN CHARBON ACTIF AMELIORE
(54) Title: REMOVAL OF CHLORAMINES FROM DRINKING WATER WITH IMPROVED ACTIVATED CARBON



(57) Abrégé/Abstract:
This application discloses a method for enhanced removal of chloramines from a fluid media by contacting said media with a catalytic activated carbon. The catalytic activated carbons used in the present invention may be prepared from carbon materials that have been contacted or otherwise exposed to nitrogen-containing compounds at temperatures above 700°C, and preferably

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00536

(57) Abrégé(suite)/Abstract(continued):
are derived from a lignocellulosic material and in the form of a solid carbon block. Future, the invention method achieves greater than 65% chloramine removal from the fluid media.

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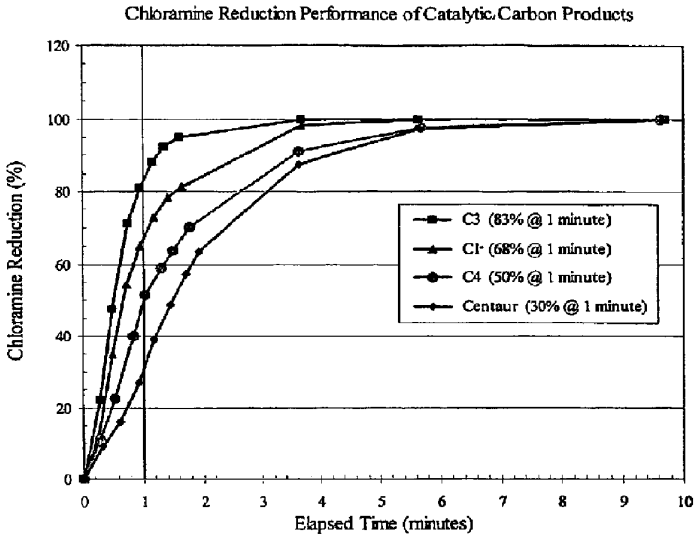
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(54) Title: REMOVAL OF CHLORAMINES FROM DRINKING WATER WITH IMPROVED ACTIVATED CARBON



(57) Abstract: This application discloses a method for enhanced removal of chloramines from a fluid media by contacting said media with a catalytic activated carbon. The catalytic activated carbons used in the present invention may be prepared from carbon materials that have been contacted or otherwise exposed to nitrogen-containing compounds at temperatures above 700°C, and preferably are derived from a lignocellulosic material and in the form of a solid carbon block. Future, the invention method achieves greater than 65% chloramine removal from the fluid media.

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REMOVAL OF CHLORAMINES FROM DRINKING WATER WITH IMPROVED ACTIVATED CARBON

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to improvements in the use of a high-performance, catalytically activated carbon for the removal of chloramines from chloramine-containing fluid streams. In particular, this application relates to the use of high-performance, catalytically activated carbon block filters for the removal of chloramines from chloramine-containing fluid streams.

2. Description of the Prior Art

While chlorination has made the U.S. water supply safe from illness producing bacteria, viruses, and parasites, an unhealthy by-product of chlorinating water that contains natural organics is the production of trihalomethanes, which have been linked to increased risk of cancer. One way to reduce this risk is to change from chlorine disinfection to chloramine disinfection. Chloramines are formed from the reaction between ammonia and chlorine. Thus, adding ammonia (NH_3) to a chlorination system converts chlorine to chloramines. Specifically, monochloramine, hereafter referred to as "chloramine," in low concentrations arise from the disinfection of potable water sources. To improve the taste and odor of the water and to remove the inherently toxic chloramine, the water is typically contacted with activated carbon. The ability of carbonaceous materials, such as activated carbon, to remove chloramine from aqueous streams is generally well known. It is also known that improvements in removal of chloramine can be achieved by reducing the mean particle diameter of the carbon and

by increasing the carbon bed contact time. In some applications, such as in kidney dialysis units, high removal rates of chloramine are particularly important. Although parameters such as contact time and mean particle diameter are known to affect chloramine removal efficiencies, removal performance is neither well understood nor particularly effective.

Activated carbon is used in the treatment of water in the form of powdered actvated carbon, granular activated carbon, or shaped activated carbon, such as pellets or spheres. Another form of shaped activated carbon often recommended for point-of-use (POU) and point-of-entry (POE) water treatment, however, is solid block activated carbon. Block activated carbon is a compressed blend of selected activated carbon and a binder material, such as high-density polyethylene (HDPE), which is capable of adsorbing a wide range of organic materials. Water is forced through the pores of the densely compacted carbon block, where a combination of mechanical filtration, electrokinetic adsorption, and physical/chemical adsorption takes place to reduce or eliminate a wide range of contaminants.

U.S. Patent No. 5,338,458, issued on August 16, 1994 to Carrubba et al., titled "Method for Removing Chloramine with Catalytic Carbon," teaches an improved process for the removal of chloramine from gas or liquid media by contacting said media with a catalytically-active carbonaceous char. In practice, however, a product manufactured according to the patent teaching has been found lacking in effectiveness for chloramine removal from drinking water. Additionally, attempts to replicate even the relatively poor performance of the commercial product based on the '458 patent (Centaur®) in solid block form has not been satisfactory. Apparently, the impact of the

binder component detracts measurably from the prior art carbon's performance for chloramine removal.

Accordingly, it is the object of the present invention to provide an improved method of removal of chloramine from drinking water. It is a further object of the invention to provide an activated carbon that is catalytically active for removal of chloramine apart from factors such as extended contact time, mean particle diameter, and the like which factors are known to affect removal of chloramine. Finally, it is an object of this invention to provide an improved method of chloramine removal using an activated carbon that is catalytically active for removal of chloramine in the form of a solid block activated carbon.

SUMMARY OF THE INVENTION

Generally, the present invention comprises a method for enhanced removal of chloramine from aqueous media by contacting said media with a catalytic activated carbon. The catalytic activated carbons used in the present invention may be prepared from carbon materials that have been contacted or otherwise exposed to nitrogen-containing compounds at temperatures above 700°C.

The carbonaceous feedstocks from which such carbons are produced are relatively nitrogen-poor, naturally occurring materials, such as lignocellulosic materials and coals. The lignocellulosic materials may include carbons derived from wood, olive pits, and various nut shells, including coconut. The nitrogen-poor feedstocks may be processed as low-temperature carbonized chars or as high-temperature carbonized chars such as activated carbons. Either carbon may be oxidized prior to, during, or after carbonization. However, all nitrogen-poor chars must be contacted or otherwise exposed to nitrogen-containing compounds such as ammonia, urea or the like at high

temperatures prior to, during, or after calcination, pyrolysis, and/or activation at high temperatures with a gasifying agent, such as steam or carbon dioxide. Additionally, it is essential that the final products in all cases described above be cooled to temperatures below 400°C, preferably 200°C, in an oxygen-free or otherwise inert atmosphere. In the invention of a block carbon, after treating the carbon it is blended with a binder material and the blend is shaped to a desired form. In a preferred embodiment, the binder material is an organic compound, such as a polymer, which has been heated to a temperature at least above its glass transition temperature (preferably, above its melting point), and the blend is shaped as desired prior to resolidification of the binder. Alternatively, the binder material may also be inorganic, such as one or more clays.

The catalytic activated carbons of the present invention are distinguished from prior art carbons by their ability to extract a greater amount chloramine from drinking water more rapidly. When tested under nearly equivalent conditions of contact time, mean particle diameter, concentration of chloramine, and the like, these catalytic activated carbons remove chloramine much more effectively than prior art carbon materials, which have been used for this application in the past, including the carbonaceous chars of U.S. 5,338,458. Other advantages of the present invention will become apparent from a perusal of the detailed description of the presently preferred embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of chloramine-reduction performance of invention carbon products and prior art carbon product on a gravimetric basis.

FIG. 2 is a graphical representation of chloramine-reduction performance of invention carbon products and prior art carbon product on a volumetric basis.

FIG. 3 is a graphical representation of hydrogen peroxide (H_2O_2) decomposition rates for invention carbon products and prior art carbon product.

FIG. 4 is a graphical representation of the lack of the correlation between the chloramine-reduction performance and the "t-¾ time" of catalytic carbon products.

FIG. 5 is a graphical representation of the correlation between the chloramine-reduction performance and the nitrogen content of catalytic carbon products.

FIG. 6 is a graphical representation of the influence of polyethylene binder on the chloramine-reduction performance of invention carbon product and prior art carbon product.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

As noted above, potential toxicity, unpleasant taste, and odor are associated with the use of chloramine disinfection by potable water-treatment plants. Also, as noted, the prior art teaches that effective removal of chloramine from water requires a catalytically-active carbonaceous char, which has been characterized as a carbon that will rapidly decompose hydrogen peroxide in aqueous solution. It is the object of this invention, more specifically, to provide a catalytic activated carbon that exhibits high performance for chloramine removal from water, yet may possess relatively low activity for hydrogen peroxide decomposition compared to prior art carbons. It is a further objective to demonstrate that the invention process for removal of chloramine employing said catalytic activated carbon is an unexpected and surprising (in light of the prior art teaching) improvement over prior art process performance in removing chloramine employing prior art carbons.

While it is appreciated that the U.S. 5,338,458 patentees disclose "activated carbon" as among their taught "catalytically-active carbonaceous chars," it is noted that

the catalytic activated carbon disclosed herein is distinguished from the '458 teaching and is distinctive in its surprising and unexpected (based on the '458 teaching) properties for the removal of chloramine.

The catalytic activated carbon of the present invention is prepared by the method disclosed in U.S. Patent No. 4, 624,937, which disclosure is incorporated herein, by reference. The '937 patent teaches a method for catalytically oxidizing tertiary amines or secondary amines in the presence of oxygen or an oxygen-containing gas to selectively produce secondary or primary amines, which method comprises the step of treating the carbon catalyst to remove oxides from the surface thereof. In a preferred embodiment of the '937 patent teaching, the surface oxides on the carbon are removed by pyrolyzing the carbon material at a temperature in the range of about 800°C to about 1200°C while simultaneously passing a gas stream of an oxygen-containing gas and NH_3 through the carbon material in a ratio of up to 90:10 for a time sufficient to remove surface oxides from the carbon. More particularly, the '973 patent teaches the carbon treatment gas stream to include a NH_3/oxygen-containing gas mixture from the group consisting of NH_3/CO_2, NH_3/O_2, NH_3/H_2O, and NH_3/NO_x, and preferably the NH_3/oxygen-containing gas mixture is NH_3/H_2O.

Using industry-accepted protocols, the invention catalytic activated carbon product was evaluated against Calgon Carbon's Centaur® catalytic carbonaceous char product (taught in U.S. 5,338,458) for the reduction of chloramine in drinking water. The applicants' found that at chloramine concentrations typical for drinking water the invention carbon has a substantial performance advantage over Centaur with respect to both volumetric capacity and kinetics of eliminating chloramine from drinking water. Furthermore, contrary to the teaching of Calgon Carbon's '458 patent, the applicants

have demonstrated that high performance for removal of chloramine can be obtained using carbons that exhibit relatively low catalytic activity as determined by a surrogate "t-¾ time" test. (In a variation of the t-¾ time test, considered to be equivalent to the t-¾ test procedure patented by Calgon Carbon (U.S. Patent No. 5,470,748), instead of monitoring the rate of decomposition of hydrogen peroxide in the presence of an activated carbon by measuring the temperature of the hydrogen peroxide solution under essentially adiabatic conditions, the applicants measured the weight loss resulting from the evolution of oxygen during the carbon-catalyzed decomposition of the hydrogen peroxide under otherwise similar conditions of hydrogen peroxide concentration, carbon loading, and pH, etc. Reference to this surrogate t-¾ test will be in quotation marks.)

In fact, the "t-¾ time" of some of the carbons that exhibited at least twice the chloramine removal performance of Centaur was over 100 minutes, well outside the broadest claim of the '458 patent (< 15 minutes).

Chloramine Reduction

Data obtained through the applicants' own experiments on the invention catalytic activated carbons and related carbon products confirmed the superior performance of the invention catalytic activated carbon for removal of chloramine from water. The example below was the results of tests run on the carbon products (≥ 90% -325 mesh) using a concentration of chloramine near 3 ppm, a typical level for drinking water, at a temperature of 21°C (70°F). The chloramine solution was prepared by blending one liter of a solution of ammonium chloride (1.500 g NH_4Cl) in water with one liter of a solution containing sodium carbonate (1.250 g Na_2CO_3) and Chlorox household bleach (6% NaOCl, 12 ml) in water. This stock solution, containing about

300 ppm of chloramine (NH_2Cl), was equilibrated at 21°C for one hour. A solution containing about 3 ppm chloramine was prepared by diluting 10.0 ml of the stock solution to one liter with water. The actual concentration of the diluted chloramine solution was determined using the colorimetric procedure described in Example 1 (with the omission of the carbon). This test solution of chloramine was equilibrated at 21°C for one hour before use. All solutions were prepared on the day of the tests using high purity water and, with the exception of the Chlorox bleach, analytical grade reagents.

For the purpose of characterizing the chloramine removal performance of a given carbon product, it can be assumed that, under the conditions of preparation of the chloramine solutions, all the chlorine in the test solution is present in the form of monochloramine, NH_2Cl. The high ratio of NH_4Cl to NaOCl (5:1, compared to a stoichiometric ratio of 1:1) used in the preparation of the solutions ensured that the reaction between the ammonium chloride and the sodium hypochlorite would be driven rapidly towards the production of the monochloramine species. Furthermore, the pH of the test solution was about 8.3, a value consistent with the range in which "chlorine" is present in the solution as the monochloramine species; i.e., not as "free chlorine" (HOCl or OCl^-) or dichloramine ($NHCl_2$) or trichloramine (NCl_3). Supporting documentation in this respect can be found in, for example: the USEPA Guidance Manual "Alternative Disinfectants and Oxidants" (April 1999, pp. 6-1 to 6-35); in the Hach Company's Booklet Number 17, "Current Technology of Chlorine Analysis for Water and Wastewater" by Daniel L. Harp (1995, pp. 1-30); and in the Hach Company's Monochloramine Application Note reprinted from the article, "Specific Determination of Inorganic Monochloramine in Chlorinated Wastewaters" (*Water Environment Research*, **75(6)**, pp. 706-713.

Example 1

An amount of 400 g of water containing chloramine (about 3 ppm) was equilibrated at a temperature of 21°C. An amount of 200 mg (± 1%) of the carbon test sample was added to the stirred solution and a stopwatch started to record elapsed time. 10 ml aliquots of the carbon/water suspension were removed at periodic intervals and immediately filtered to remove the carbon from treated water. The actual time of filtration of an aliquot of the carbon/water suspension was recorded as the elapsed time for that aliquot. The aqueous filtrates were analyzed for chloramine content immediately following collection of all aliquots of the carbon/water suspension. Working with one filtrate at a time, a DPD (N, N-diethyl-p-phenylenediamine) reagent "pillow" for total chlorine determination (Hach Company, Catalog Number 21056-69) was added to the filtrate (10 ml) and the sample vial shaken for 20 seconds to develop the characteristic magenta color of the "Wurster dye" DPD-oxidation product. The absorbance of the filtrate at a wavelength of 515 nm was measured and the concentration of chloramine remaining in the water was calculated using the appropriate calibration. Because the Wurster dye can also be formed through the reaction of free chlorine with DPD, a similar set of measurements was made using a free chlorine reagent "pillow" (Hach Company, Catalog Number 21055-69) instead of the total chlorine reagent "pillow." The absence of color development confirmed that free chlorine was not interfering with the analysis for chloramine. Finally, a "blank" colorimetry measurement was made on water used to prepare the chloramine solutions to ensure that the absorbance at 515 nm was ± 0.001. Chloramine reduction data were normalized to 200.0 mg of carbon (dry weight) to compare data for different products.

Data are shown in Figure 1 and Table I for a series of carbon products isolated from the production process described in the '937 patent under various conditions of ammonia and steam flows. Data for the prior art Centaur product are included for comparison. Figure 1 compares the chloramine reduction curves for representative carbon products over the 10-minute time frame of the test. Table I summarizes the amount of chloramine removed by the carbons at a contact time of one minute, a useful point for comparing the performances of different carbon products.

Table I

Carbon Sample	"t-¾ time" (minutes)	Chloramine Removed (% at 1 minute)
C1	115	68
C2	6.8	81
C3	3.2	83
C4	330	50
C5	14.5	65
C6	4.3	75
Centaur	21	30

It is apparent from Figure 1 and Table I that all the invention catalytic carbon products exhibited much faster kinetics of chloramine removal from water than Centaur. For example, at an elapsed time of one minute, the invention C3 product reduced the chloramine concentration by 83% compared to only a 30% reduction for the Centaur product. Given the low contact time in water-treatment filters, the kinetics of chloramine removal are of considerable importance with respect to point-of-entry (POE) and point-of-use (POU) filters for residential use and commercial use (*e.g.*, restaurants, beverage manufacture).

Example 2

The performance data discussed in Example 1 (Figure 1 and Table I) were determined using equivalent weights of catalytic carbon products, namely 200 mg. However, POE and POU filters for water-treatment applications contain cartridges of certain standard dimensions, and therefore accommodate a certain fixed volume of filtration medium. Depending on the nature of the precursor material from which a carbon product is produced, the density of different catalytic carbon products can vary widely, resulting in different weights of the respective products in a fixed volume of a filter cartridge. For the case in point, the invention carbons were produced from wood,

whereas the Centaur product was produced from coal. For comparable particle sizes, i.e., ≥ 90% -325 mesh, the apparent density of the coal-based Centaur product is about twice that of the wood-based invention carbons. In practice, this means that a cartridge filter of a given volume can hold twice the weight of the Centaur product than of, in this example, a wood-based carbon.

If, for the purpose of illustration only, the Centaur and invention carbons exhibited equal chloramine removal performances on a gravimetric (weight) basis, it would be expected that the denser Centaur product would exhibit about twice the performance of the invention carbon on a volumetric basis. As the data in Figure 1 and Table I demonstrate, however, the gravimetric-based performance of the Centaur product falls far short of the invention carbons at contact times less than one minute. Nevertheless, tests were run on equivalent volumes of the Centaur product and invention carbons to further demonstrate the superior chloramine removal performance of the invention carbons. The tests were run using the procedure described in Example 1, with the exception that the weight of Centaur used in the test was 400 mg, compared to 200 mg of the invention carbons. These weights corresponded to a volume loading of 1.71 ml of carbon per liter of test water. Representative data are shown in Figure 2 for the Centaur product and invention carbon C3. The chloramine removal performances are expressed in the volumetric-based units of g of chloramine removed per liter of carbon.

Clearly, the invention carbon still exhibited substantially superior performance compared to the Centaur product, despite the fact that the Centaur product was present in the test water at twice the weight of the invention carbon. In fact, it is also clear from Figure 2 that the performance of the Centaur product at contact times below one minute

did not increase in proportion to the doubling of the weight of Centaur product present in the test water. Because the removal of chloramine from water is a result of the catalytic reduction of the chloramine by the carbon, it does not necessarily result that twice the weight of a given product doubles the rate of removal of chloramine from the water. The nature of the time-dependent curve in Figure 2 for the Centaur product also reveals another reason why the performance of the Centaur product did not increase in proportion to the weight used. Namely, the "S-shaped" character of the curve at the low contact times relevant to practical use (in POE and POU filters) indicates that the Centaur product was slow to "wet" in the test water, which impeded its ability to catalyze the desired reaction.

Catalytic Activity

The catalytic activity of the catalyst plant products and Centuar was measured using the surrogate "t-¾ time" test. The procedure and results are set forth in Example 3.

Example 3

The t-¾-time is defined (U.S. Patent Nos. 5,338,458, 5,356,849, and 5,470,748) as the time at which three-quarters (75%) of the maximum temperature rise has occurred during the decomposition of hydrogen peroxide by a carbon material. It is assumed that this time corresponds to 75% decomposition of the available hydrogen peroxide. In the surrogate "t-¾ time" test used to characterize the catalytic activity of the invention carbon products, the decomposition of the hydrogen peroxide solution was monitored through the weight loss resulting from the evolution of oxygen. In keeping with Calgon Carbon's definition, the "t-¾ time" was assumed to correspond to the point at which 75% of the theoretical weight loss of oxygen from the available

hydrogen peroxide had occurred. The weight of carbon, volume of hydrogen peroxide solution, and concentration of the hydrogen peroxide solution were similar to those employed in the Calgon Carbon test. Similarly, the reaction medium was buffered at pH 7.

The "t-¾ time" test data are summarized in Table I, above. Examples of the weight loss curves used to calculate the "t-¾ times" for the invention carbon products are shown in Figure 3.

It is clear from Table I that the invention carbon products exhibited a wide range of "t-¾ times," from 3.2 to 330 minutes, yet all exhibited high performance for removal of chloramine from water; *i.e.*, 50-83% reduction, compared to only 30% for Centaur. More to the point, the "t-¾ times" of the C1 and C4 products, 115 and 330 minutes, respectively, were substantially greater than the primary claim in the '458 (chloramine use) patent, which is limited to carbon products exhibiting t-¾ times of less than 15 minutes, which would suggest to one skilled in the art that the invention carbon products C1 and C4 are unsuitable for chloramine removal as compared to the catalytically-active carbonaceous chars of the '458 patent.

The large difference between the catalytic activities of the C1 and C4 invention carbons and the prior art Centaur product is further exemplified in Figure 3, where the weight loss due to the evolution of oxygen during the decomposition of the hydrogen peroxide solution is shown as a function of time. The two lower curves for the C1 and C4 products reflect their relatively low activity towards hydrogen peroxide decomposition compared to the Centaur product. Despite this, the C4 and C1 products exhibited 170-230% of the performance of the Centaur product for removal of chloramine (50 and 70%, respectively, compared to 30% for Centaur). Conversely, the

C3, C6, and C2 products in Table I exhibited fast "t-¾ times," 3.2, 4.3, and 6.8 minutes, respectively, but the performance gains in removal of chloramine were modest relative to the C1 product. Yet, all sample invention activated carbon products exhibited far superior abilities for removal of chloramine over the '458 patent product.

Inasmuch as the surrogate "t-¾ time" test is essentially equivalent to the t-¾ time test of the '458 patent, it appears from the data presented that the time measure of the decomposition of 75% of the theoretical weight loss of oxygen from the available hydrogen peroxide occurring in the presence of a given amount of carbon is not an accurate indication of that carbon's ability to remove chloramine from drinking water. This is exemplified in graphical form in Figure 4, which demonstrates that there is a very poor correlation between "t-¾ time" and the chloramine reduction performance of catalytic carbons (i.e., very low regression coefficient, "R^2," of 0.155). The applicants have shown that carbons with "t-¾ times" well beyond the time taught in the '458 patent to be extremely poor candidates for removing chloramine, in fact, are much better candidates than those taught as excellent candidates in said patent disclosure. The conflict between the date presented herein and the faulty teaching of the '458 patent begs the question, "What carbon material characteristic (or characteristics), then, will provide an accurate indication for enhanced removal of chloramine?"

Though the patentees do not claim to understand fully the chemical and physical mechanisms involved that result in one carbon material being exposed to ammonia or another nitrogen-containing compound in a certain way versus another carbon material being exposed to ammonia or another nitrogen-containing compound in a different way that permits one of said materials to remove chloramine more effectively than the other of said materials; however, one possible theory to explain such a result involves

differing ways the nitrogen enhancement of the carbon occurs. While the applicants do not wish to be bound by any particular theory, it is proposed that the manner of imparting catalytic activity to the carbon material, as claimed herein, results in the nitrogen occurring on the respective catalyzed carbon materials in a different form (*e.g.*, differing functional groups), and the relative success in the carbon's ability to remove chloramine may depend on the presence and amount of a particular nitrogen group or the relative proportions of one particular nitrogen group versus another. Moreover, in some cases nitrogen may be present on the carbon material prior to the exposure to ammonia, wherein the critical processing effect may be in the transformation of the nitrogen present on the carbon into a form more suited to removal of chloramine as well as providing additional such nitrogen forms. Further studies may be required to confirm this hypothesis. Certainly, however, the data shown graphically in Figure 5 indicate that there is a good correlation between the nitrogen content and the catalytic activity of carbon products with respect to chloramine reduction in water (i.e., relatively high regression coefficient, "R^2," of 0.953).

Solid Carbon Block

For various reasons, the water filter industry favors carbon blocks for POE and POU filters. Primarily, in such form they are easy to handle and exhibit lower dust levels. Both of these facts are more conducive to filter change-outs by the consumer. In the manufacture of the carbon blocks, the carbon is blended with a suitable binder, typically high-density polyethylene, and the carbon block formed though a number of distinct, proprietary processes.

Example 4

In a laboratory test, an invention carbon product (50x200 mesh particle size) was melt-blended with high-density polyethylene (HDPE) powder at a level of 20% of the dry carbon weight (1 part binder to 5 parts carbon). The solid block formed from the carbon and HDPE binder was crushed and screened to give material that was > 90% -325 mesh particle size. The Centaur prior art carbon product was similarly melt-blended with HDPE, and the resulting block crushed to –325 mesh particle size. Using a 3 ppm chloramine solution in water, the chloramine reduction performance of each of the powdered, HDPE-treated carbons was determined in a manner similar to that described in Example 1. The amount of sample in each test corresponded to 200 mg of carbon (dry basis). The data obtained are summarized in Table II, together with the corresponding data for the original carbons (not treated with HDPE). The data are also shown graphically in Figure 6 to permit a visual comparison.

Table II

Influence of HDPE Binder on Chloramine Removal Performance of Catalytic Carbons

Contact Time (minutes)	Amount of Chloramine Removed (%)			
	Invention Carbon		Prior Art Carbon (Centaur)	
	Without Binder	With Binder	Without Binder	With Binder
2	83		45	
3		87		26
5	100	100	82	42
10	100	100	100	60
15	100	100	100	69

It is apparent from Figure 6 and Table II that melt-blending the invention carbon with HDPE binder did not impact the chloramine reduction performance of the invention carbon. In a time frame relevant to POU filters, chloramine in the test water was quickly reduced by both the original prior art carbon and the HDPE-treated prior art carbon. In marked contrast, however, it is equally apparent from Figure 6 that the HDPE binder had a pronounced, adverse impact on the chloramine reduction performance of the prior art Centaur product. The performance of the prior art carbon product was reduced by over 50% following melt-blending with the HDPE binder at the 20 wt% level typically used for filter block manufacture. This substantial loss in chloramine reduction performance of the prior art carbon was attributed to, as mentioned earlier, the poor wetability of the Centaur product, which is exacerbated upon addition of a hydrophobic binder such as polyethylene. In fact, although the same test protocol was used for both the invention and prior art carbon products, it was necessary to add a small amount of surfactant to the water containing the prior art carbon to get the carbon to wet at all. In the absence of the surfactant, the HDPE-treated prior art carbon did not wet over the fifteen-minute time frame of the test, resulting in little measurable chloramine reduction in the test water. In marked

contrast, the invention carbon product readily wetted in both the virgin and blended forms, did not require a surfactant, and exhibited substantially superior chloramine removal performance.

In summary, the invention carbon could be formed into blocks, using a standard polyethylene binder, without loss of chloramine reduction capacity.

While presently preferred embodiments of the invention have been described in detail, the invention may be otherwise embodied within the scope of the appended claims.

What is claimed is:

1. A process for the removal of chloramines from fluid solutions or streams comprising the step of contacting said solutions or streams with an activated carbon that has been treated by a process of pyrolyzing the carbon while simultaneously passing a gas stream comprised of a mixture of NH_3 and an oxygen-containing gas through the carbon, wherein the treated activated carbon is derived from lignocellulosic material and the process achieves greater than 65% chloramine removal.

2. The process as set forth in claim 1 wherein the process achieves greater than 75% chloramine removal.

3. The process as set forth in claim 1 wherein the activated carbon is in the form of a solid block.

4. The process as set forth in claim 1 wherein the carbon treatment gas stream includes a NH_3/oxygen-containing gas mixture from the group consisting of NH_3/CO_2, NH_3/O_2, NH_3/H_2O, and NH_3/NO_x.

5. The process as set forth in claim 4 wherein the NH_3/oxygen-containing gas mixture is in a ratio of up to 10:90 for a time sufficient to remove surface oxides from the carbon.

6. The process as set forth in claim 4 wherein the NH_3/oxygen-containing gas mixture is NH_3/H_2O.

7. The process of claim 1 wherein the solutions or streams are aqueous.

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10. The process of claim 1 wherein the pyrolyzing temperature is above about 700°C.

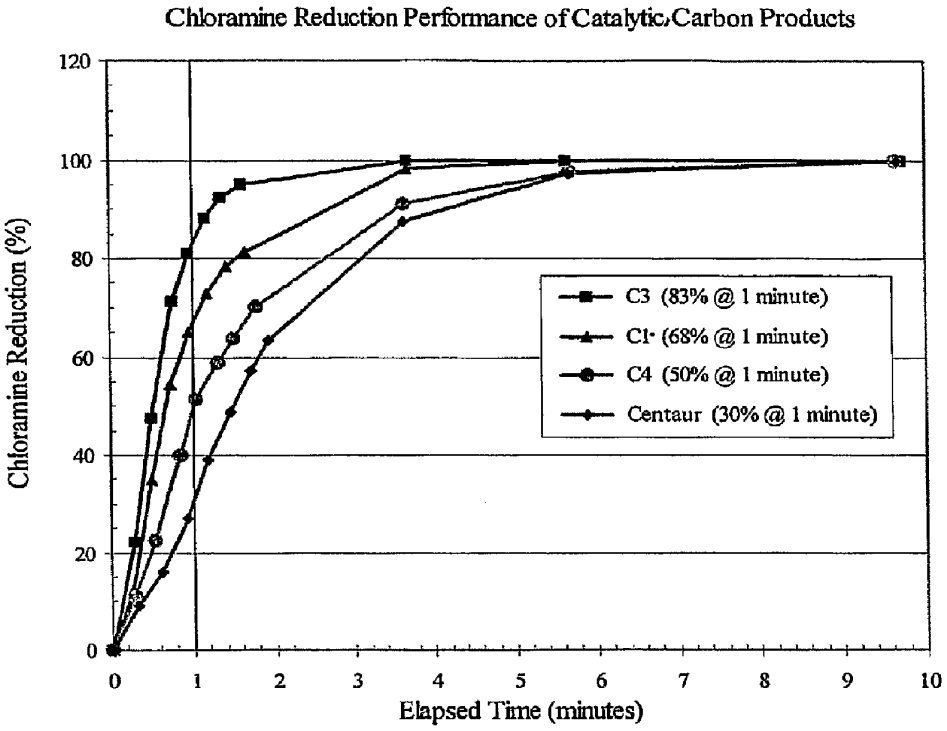
11. The process of claim 1 wherein the solid block of activated carbon is prepared by blending particles of carbon with a binder and shaping the blend.

12. The process of claim 11 wherein the binder is a polymeric material and the blending occurs at elevated temperature and the shaping occurs prior to cooling.

13. The process of claim 12 wherein the binder is a high-density polyethylene and the blending occurs at a temperature above its glass transition temperature.

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Figure 1



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Figure 2

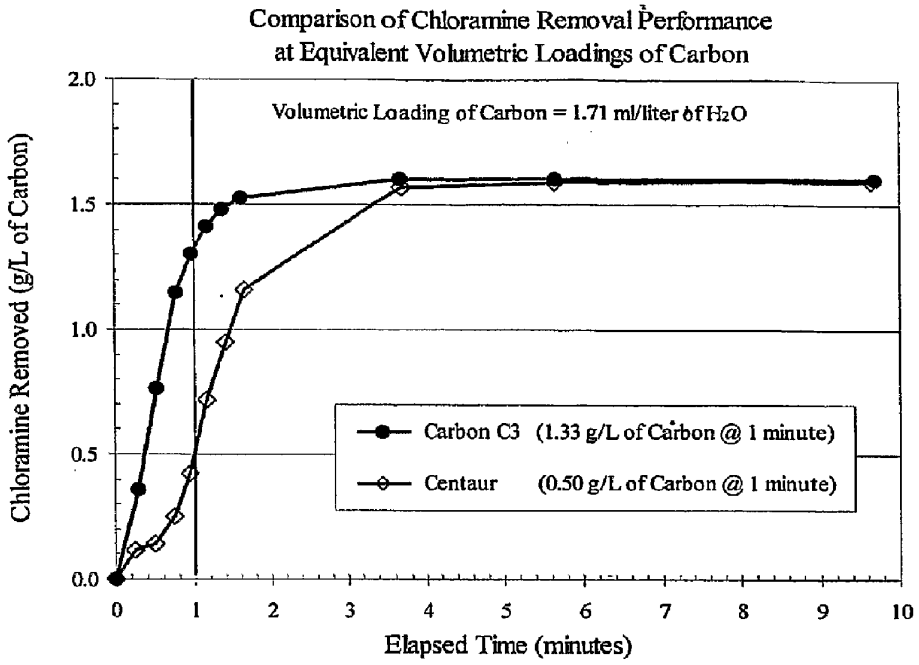


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Figure 3

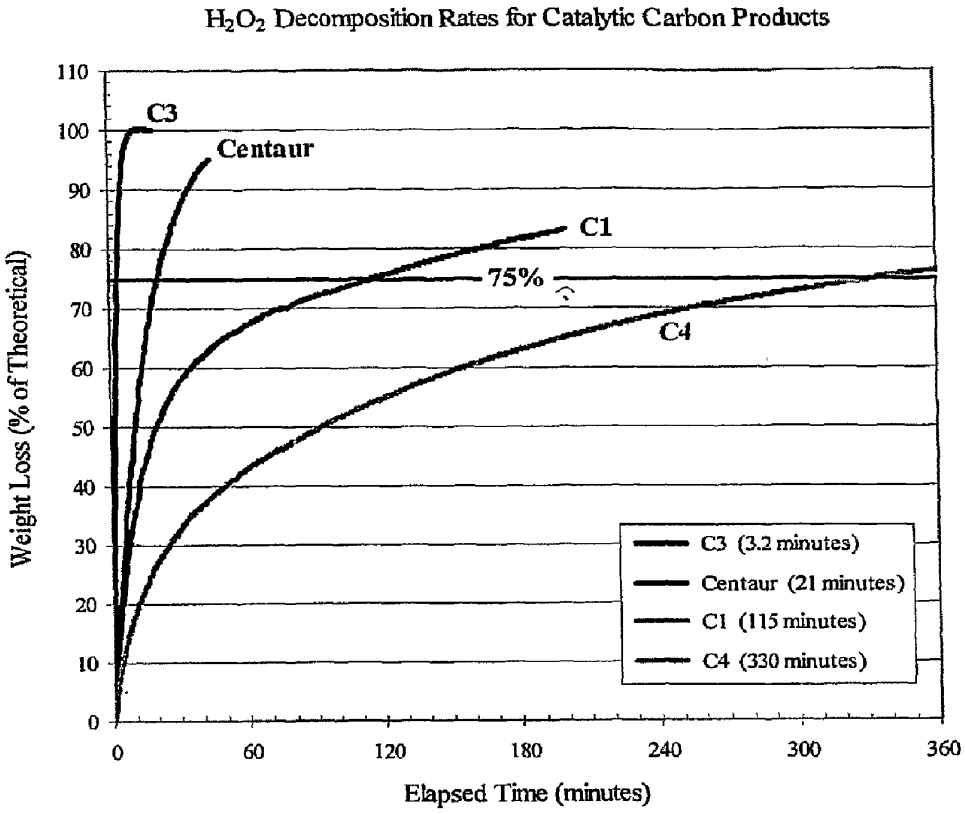


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Figure 4

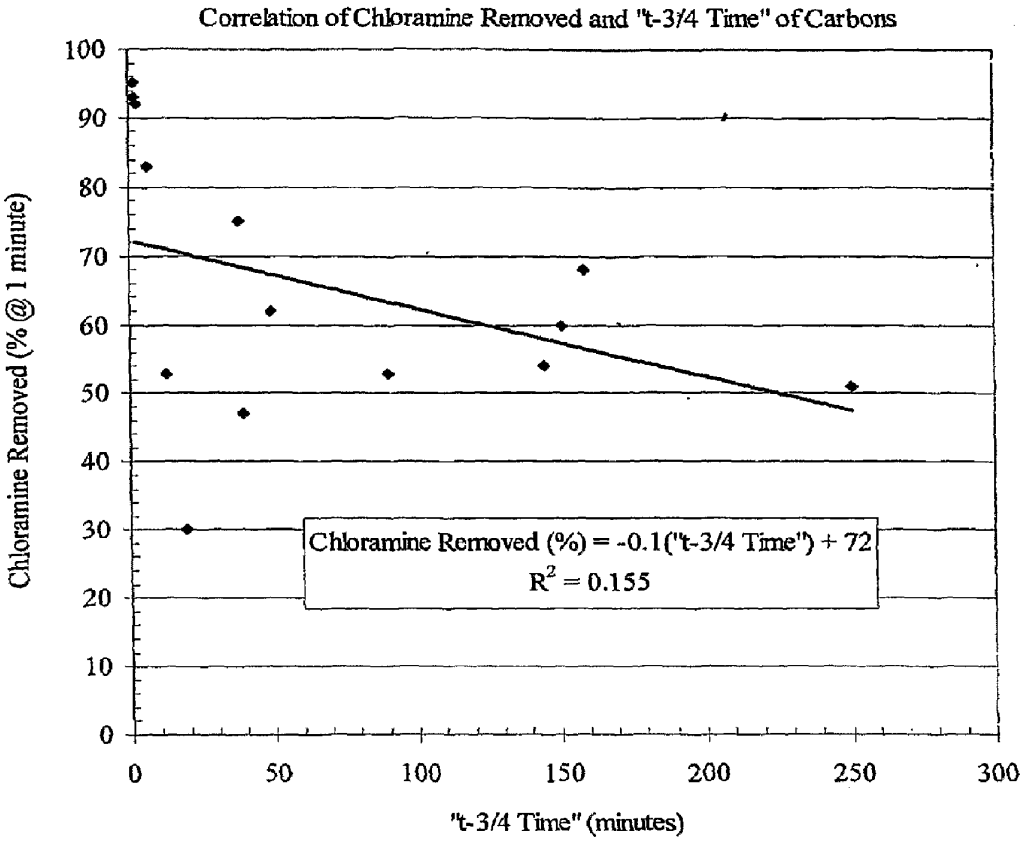


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Figure 5

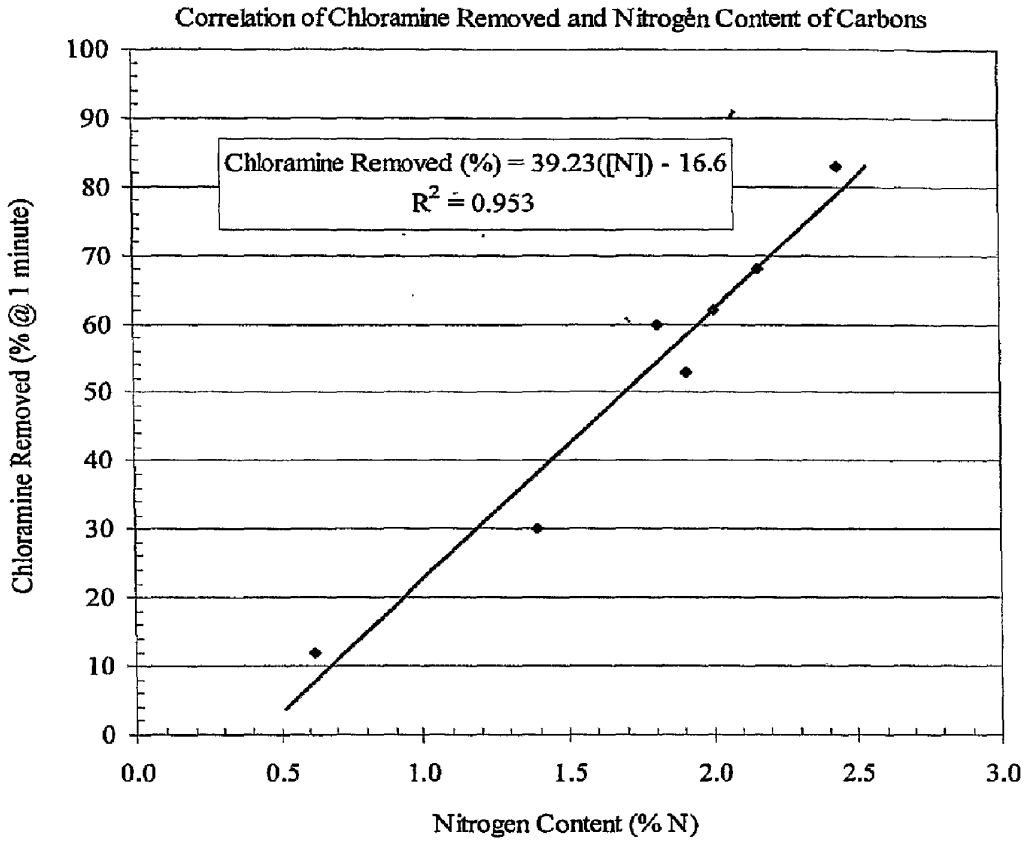


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Figure 6

Influence of Binder on Chloramine Reduction Performance of Invention Carbon and Prior Art Carbon Product

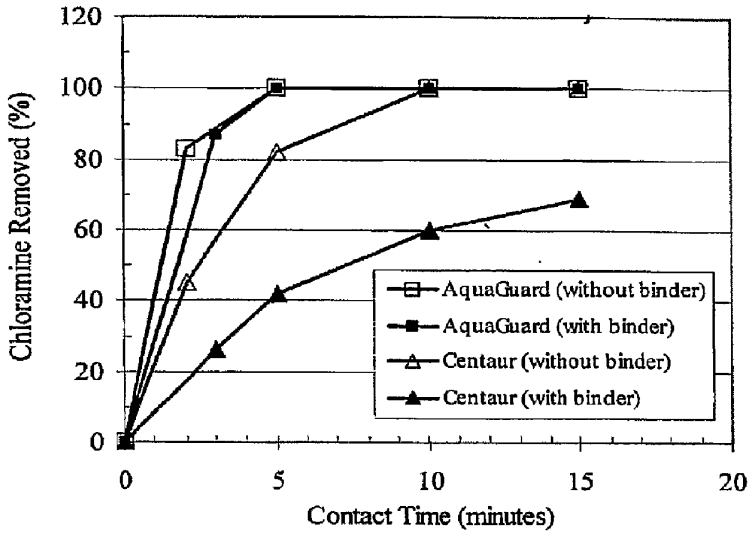


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Espacenet

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Verfahren zur Herstellung eines Aktivkohlekatalysators

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(56) Im Prüfungsverfahren entgegengehaltene Druckschriften nach § 44 PatG:
Z. Fuel, 1984, Vol. 83, S. 1061-1063;

(54) Verfahren zur Herstellung eines Aktivkohlekatalysators

Verfahren zur Herstellung eines Aktivkohlekatalysators, bei dem durch eine Vorbehandlung katalytisch aktive Substanzen auf die Aktivkohle aufgebracht werden, indem eine Aktivkohle/Aktivkoks mit einer wäßrigen Lösung von Ammoniumsulfat, die mit Schwefelsäure versetzt sein kann, getränkt, bei 120° C getrocknet und anschließend auf Temperaturen oberhalb von 350° C in einem Inertgasstrom erhitzt wird. Verwendung des Aktivkohlekatalysators als Reduktions- und/oder Oxidationskatalysator, z. B. für die NO_x-Entfernung mit Ammoniak aus Abgasen.

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Patentansprüche

1. Verfahren zur Herstellung eines Aktivkohlekatalysators, durch Ammoniakbehandlung von Aktivkohle bei hohen Temperaturen, **dadurch gekennzeichnet,** daß Aktivkohle oder Aktivkoks mit einer wäßrigen, gegebenenfalls mit Schwefelsäure versetzten Ammoniumsulfatlösung getränkt, bei 120°C getrocknet und anschließend auf Temperaturen oberhalb von 350°C in einem Inertgasstrom erhitzt wird, bis keine SO_2-Entwicklung mehr stattfindet.

2. Verwendung des nach Anspruch 1 hergestellten Aktivkohlekatalysators für die NO_x-Entfernung mit Ammoniak aus Abgasen.

Beschreibung

Die Erfindung betrifft ein Verfahren zur Herstellung eines Aktivkohlekatalysators gemäß dem Oberbegriff des Anspruchs 1.

Es ist bekannt, die katalytische Aktivität von Aktivkohle durch Behandlung mit Ammoniak bei hohen Temperaturen zu verbessern. So hat H. P. Böhm (Fuel, 1984, Vol 63, Seite 1061—1063) gefunden, daß die Behandlung von Aktivkohle mit Ammoniak oder Blausäure bei Temperaturen oberhalb von 600°C die katalytische Aktivität der Aktivkohle bei Oxidationsreaktionen in der wäßrigen Phase erhöht. Diese Aktivkohlen haben jedoch den Nachteil, daß sie sehr schnell desaktivieren.

Der Erfindung liegt die Aufgabe zugrunde, einen Aktivkohlekatalysator herzustellen, der eine geringe Desaktivierung aufweist.

Diese Aufgabe wird erfindungsgemäß dadurch gelöst, daß eine Aktivkohle oder Aktivkoks mit einer wäßrigen, gegebenenfalls mit Schwefelsäure versetzten Ammoniumsulfatlösung getränkt, bei 120°C getrocknet und anschließend auf Temperaturen oberhalb von 350°C in einem Inertgasstrom erhitzt wird, bis keine SO_2-Entwicklung mehr stattfindet.

Durch eine Wiederholung der beschriebenen Behandlung kann die katalytische Aktivität noch weiter gesteigert werden. Es können alle handelsüblichen Aktivkohlen und auch die nicht aktivierten Aktivkohlevorprodukte (Aktivkokse) eingesetzt werden.

Die so hergestellten Katalysatoren eignen sich vorteilhaft für alle katalytischen Reduktions- und Oxidationsreaktionen, die an Aktivkohlen ablaufen, wie z. B. die Reduktion von Stickoxiden mit NH_3, die Oxidation von H_2S mit Luftsauerstoff zu elementarem Schwefel und die SO_2-Oxidation mit Luftsauerstoff und Wasserdampf zu H_2SO_4.

Besonders vorteilhaft ist die Verwendung der hergestellten Katalysatoren für die Entfernung von Stickoxiden aus Abgasen mit Ammoniak nach folgender Summengleichung:

$$4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$$

Bei dieser Reaktion fungiert der erfindungsgemäß hergestellte Aktivkohlekatalysator sowohl als Reduktions- als auch als Oxidationskatalysator. In einem ersten Schritt erfolgt die Oxidation von NO mit Luftsauerstoff zu NO_2, das dann zusammen mit weiterem NO durch Ammoniak zu Stickstoff und Wasser reduziert wird.

Durch das erfindungsgemäße Herstellungsverfahren ist es gelungen, in die Aktivkohle katalytisch aktiven Stickstoff einzubauen, der selbst durch eine Temperung bei 900°C nicht entfernt werden kann.

Erfolgt der Stickstoffeinbau in die Aktivkohle durch die aus dem Stand der Technik bekannte Behandlung mit Ammoniak, so desaktivieren die Aktivkohlen bei der katalytischen NO_x-Reduktion. Nach etwa 5—7 h Versuchsdauer konnte in einem Vergleichsversuch kein Unterschied zwischen einer mit Ammoniak behandelten Aktivkohle und einer unbehandelten Aktivkohle mehr festgestellt werden.

Beispiel 1

Eine Aktivkohle mit einer spezifischen Oberfläche nach BET (DIN 66 131) von 800 m^2/g wird mit einer gesättigten Ammoniumsulfatlösung, die mit 5 bzw. 15 Gew.-% Schwefelsäure versetzt wurde, bei Raumtemperatur getränkt, über Nacht bei 120°C getrocknet und anschließend bei 420°C im Stickstoffstrom erhitzt. Nach 1,5 h fand keine SO_2-Entwicklung mehr statt.

Beispiel 2

Eine Aktivkohle mit einer spezifischen Oberfläche nach BET (DIN 66 131) von 1350 m^2/g wird mit einer gesättigten Ammoniumsulfatlösung, die mit 10 Gew.-% Schwefelsäure versetzt wurde, bei Raumtemperatur getränkt, über Nacht bei 120°C getrocknet und anschließend 1,5 h bei 420°C im Stickstoffstrom erhitzt.

Beispiel 3

Die Aktivkohle aus Beispiel 1 wird mit einer gesättigten Ammoniumsulfatlösung getränkt, bei 120°C getrocknet und anschließend 1,5 h bei 420°C im Stickstoffstrom erhitzt.

Die Behandlung wird zweimal bzw. viermal durchgeführt.

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Beispiel 4

200 ml der nach den Beispielen 1 bis 3 hergestellten Aktivkohlekatalysatoren und die Ausgangsprodukte werden in einem Reaktor mit einer lichten Weite von 55 mm und einer Höhe von 400 mm auf ihre katalytische Aktivität bezüglich der NO-Reduktion mit Ammoniak getestet. Die Versuchstemperaturen liegen zwischen 100 und 160° C. Die Eingangskonzentrationen an Wasserdampf betragen 10 Vol.-% und an Sauerstoff 5 Vol.-%. Die Kontaktzeit beträgt 6 sec. Die Konzentration an NO beträgt 490 vpm und die NH_3-Konzentration 585 bzw. 835 vpm. Die Ergebnisse sind in der Tabelle zusammengefaßt. Der Umsatz an NO wurde nach 24 h bestimmt. Von dem Katalysator aus Beispiel 1 (15 Gew.-% H_2SO_4-Behandlung) wurde die katalytische Aktivität zusätzlich noch nach 2 Wochen Versuchsdauer bestimmt.

Katalysatoren	Co_{NH_3} (vpm)	T (°C)	U_{NO} (%)	NH_3/NO
Ausgangsaktivkohle aus Beispiel 1	835	100	65	1,2
		120	71	1,2
		160	80	1,3
	585	100	59	–
		120	67	1,3
		160	71	1,2
Katalysator aus Beispiel 1 (5 Gew.-% H_2SO_4)	835	100	87	1,2
		120	93	1,1
		130	95	1,1
	585	100	80	1,2
Katalysator aus Beispiel 1 (15 Gew.-% H_2SO_4)	835	100	88	1,3
		120	95	–
		130	99	1,1
	585	100	81	1,2
		100**	82	1,1
Ausgangsaktivkohle aus Beispiel 2	835	100	41	1,2
Katalysator aus Beispiel 2 (10 Gew.-% H_2SO_4)	835	100	70	1,1
Katalysator aus Beispiel 3 (2 × behandelt)	835	100	79	1,1
		120	84	1,1
		160	92	1,1
Katalysator aus Beispiel 3 (4 × behandelt)	835	100	84	1,3
		120	92	1,1
		150	98	1,1
	585	100	81	1,2

Co_{NH_3} = Eintrittskonzentration an NH_3.
U_{NO} = Umsatz an NO.
NH_3/NO = Verhältnis der umgesetzten Mole NH_3 zu den umgesetzten Molen NO.
** = Ergebnis Dauerversuch 2 Wochen.

Aus den Versuchsergebnissen ist ersichtlich, daß durch die erfindungsgemäße Vorbehandlung eine Steigerung der katalytischen Aktivität eintritt. So wird der Umsatz an NO der Ausgangsaktivkohle aus Beispiel 1 bei z. B. der Reaktionstemperatur von 100° C von 65 (835 vpm NH_3) bzw. 59% (585 vpm NH_3) auf 87% bzw. 80% erhöht.

Bei der hochaktivierten Aktivkohle aus Beispiel 2 erhöht sich der Umsatz an NO bei gleichen Versuchsbedingungen von 41% auf 70%. Durch eine Wiederholung der Vorbehandlung ist eine weitere Steigerung des Umsatzes an NO auf z. B. 79% bzw. 84% möglich (Katalysator aus Beispiel 3). Die Aktivkohlekatalysatoren zeigten auch nach zwei Wochen Versuchsdauer keine Desaktivierung.

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(54) **Removal of mercury from liquid hydrocarbons.**

(57) Impregnated carbon adsorbents for the removal of mercury from liquid hydrocarbons are used in a variety of applications. The activated carbon impregnated adsorbents in the present invention remain effective in removing mercury. Generally, these activated carbons are comprised of an activated carbon adsorbent impregnated with a composition containing metal halide or other reducing halide, supplemented according to the desired characteristics with other elements. The formulation of the impregnants in the present invention can be varied to adjust the performance characteristics so as to meet the desired mercury removal performance criteria, to achieve enhanced removal of organic bound mercury from liquid hydrocarbon, and to have other advantages useful in a variety of applications. These impregnated carbon adsorbents possess desirable qualities regarding their ability to remove even trace levels of mercury from liquid hydrocarbon without a leaching effect of the impregnants used.

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NOVEL PRODUCT/PROCESS/APPLICATION FOR REMOVAL OF MERCURY FROM LIQUID HYDROCARBON

FIELD OF THE INVENTION

The present invention relates to impregnated carbon adsorbents for removal of mercury from liquid hydrocarbon.

BACKGROUND OF THE INVENTION

Activated carbon has long been used to remove mercury from a stream of liquid and/or gas hydrocarbon. These carbons are useful in a variety of industrial applications and often involve the use of special impregnants to remove mercury that would not otherwise be removed through the use of base carbons. Impregnated activated carbons, as well as formulations of silica, aluminumna and other materials, have been known and used for many years largely for removal of elemental mercury in gas phase and aqueous applications. However, due to the chemical state of the mercury present in liquid hydrocarbons, these formulations have limited effectiveness in removing mercury in non-aqueous liquid applications.

U.S. Patent No. 4,709,118 (Mobil Oil Corp.) teaches mercury removal from liquid hydrocarbon by incorporating elemental Bismuth or Tin or a mixture of these into a Silica, Alumina, or other non-reactive substrate including activated carbon. U.S. Patent No. 4474896 to C. C. Chao relates to polysulfide containing adsorbent compositions for removal of elemental mercury from gas or liquid streams.

U.S. Patents 4338288 to Rollman, French Patent No. 2529802 to Pelosi, et al. and U.S. Patent No. 4094777 to La Villa et al. involve the removal of mercury and/or heavy metals from gas and liquid medium using a variety of sulfur containing sorbents to include manganese nodule particles containing occluded sulfur, alumina and silicate type support media containing elemental sulfur or copper sulfide.

Japanese Patent No. 51003386 describes the use of activated carbon containing a hydrogen halide salt of a compound having one or more functional groups, while U.S. Patent No. 4654322 involves the use of a cysteine residue fixed to any insoluble carrier. Other references disclose removal of mercury by amalgamation, including U.S. Patent No. 3374608 to Manes, U.S. Patent No. 4353741 to Capuano, et al., Japanese Patent No. 62155926 to Miyoshi and French Patent No. 2310795 to Inst. Francais du Petrole.

The greatest number of references relating to the removal of mercury vapor specifically from gas streams involved the use of halogens. Japanese Patents No. 49066592 to Sumitomo Chemical Co. discloses an activated carbon carrying one or more chlorides of Li, Na, K, Mg, Ba, Zn, Al, Sn, Mn, Fe, Co, Ni, and NH^4. Similarly, Swiss Patent No. 1163982 to Belozerov, et al. describes a process for removal of mercury vapor from air containing dusts and aerosols by passage through activated carbon followed by treatment with activated carbon impregnated with monochloroiodide.

Japanese Patent Nos. 49053590, 49053593, 49053592 and 49053591 to Nippon Soda Co. LTD. claim the use of activated carbons containing halides for removal of mercury from gases. In Patent No. 49053590, the use of activated carbons containing halides of Group III-VIII metals provides excellent adsorptive capacity for Hg. Patent No. 49053593 specifies the use of chlorides of Group I metals impregnated on activated carbons and Patent Nos. 49053592 and 49053591 specify similar iodide and bromide compounds, respectively. Other patents describe the use of hydrogen halide and ferric chloride, respectively, impregnated on activated carbon for removal of mercury vapor from gas streams, while references describe the use of metal salts, metals in combination with sulfur or silver and mineral acids.

U.S. Patent No. 4708853 to Calgon Carbon describes the use of sulfur impregnated molecular sieve activated carbon for removal of mercury from natural gas. An independent study on gas separation purification (Henning et al.) evaluated the mercury removal performance of impregnated activated carbons. The carbons studied include the following impregnates: Potassium Iodide, Sulfuric Acid, Sulfuric acid/Potassium Iodide, Sulphur, and Sulphur/Potassium Iodide. The sulphur impregnations were found to be most effective for mercury removal from gas streams.

U.S. Patent 4094098 relates to the removal of mercury vapor via a process which involves the addition of hydrogen sulfide gas and amines into the natural gas stream effecting precipitation of mercury as the sulfide while the amines absorb the excess hydrogen sulfide.

Other references disclose mercury removal from aqueous systems, by chemical addition and by physical separation. Other references involving technology not related to mercury removal applications include the use of mercury or mercury compounds in manufacturing processes, safe handling and disposal

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of mercury removal adsorbent materials and decontamination of equipment, elimination of interferences due to mercury or mercury compounds present in industrial processes and analytical techniques utilizing and evaluating mercury containing compounds.

It is an objective of the present invention to provide an adsorbent which is effective in removing mercury from liquid hydrocarbons, and, in particular, effective in removing even trace levels of mercury through the impregnation of the activated carbon adsorbent with reactant/reducing agents. It is a further objective of the invention to provide a carbon adsorbent for use in a variety of non-aqueous industrial and other mercury removal applications.

SUMMARY OF THE INVENTION

The present invention embodies an impregnated carbon adsorbent that removes mercury from liquid hydrocarbons by conversion of organo-mercury compounds to inorganic mercury halides and/or the reduction of non-elemental mercury compounds to elemental mercury. Once converted to a more adsorbable form, physical adsorption and/or chemisorption, to include further reaction with amalgamating impregnants may occur.

In one embodiment, enhanced mercury removal capability is achieved by the impregnation of activated carbon with at least one metal halide consisting of the halides of I, Br and Cl. The metal I, Br and Cl halides in this embodiment of the present invention facilitate the mercury conversion and removal process; as such, although the metals from Groups I and II of the periodic table are preferred, any metal from the periodic table of the elements can serve as the "vehicle" for the depositing and/or maintaining the I, Br and Cl halides on the carbon surface.

The use of one or more of these impregnants on activated carbon efficiently converts organo-mercury and weakly adsorbable compounds present in liquid hydrocarbon to the desired inorganic mercury halides, after which adsorption of that mercury can efficiently occur.

Generally, the present invention comprises an activated carbon adsorbent impregnated to contain, depending on the particular characteristics desired, a final composition by weight of containing a mixture from .5% to 25% metal halide. Poor mercury removal efficiency (shown in Table 1) is most likely due to the nature of the mercury species present in the liquid hydrocarbon. (Mercury in an organic form is difficult to adsorb.)

Activated carbon can also be usefully impregnated with reducing agents comprising at least one impregnant of the metal cations of Sn^{+2}, Ti^{+2} and/or Cu, each of which will act to efficiently convert organic mercury and organic mercury salts to elemental mercury for physical adsorption, in that each of these cations have sufficient reduction capability so as to facilitate this conversion. Chemisorption of the mercury with amalgamating impregnants such as Ag, Sn, Zn, Al, Au, Cu and alkali elements from the periodic table of elements is also useful in that these known amalgamating elements in the context of the present invention "fix" the mercury to the surface of the carbon enhancing the strength of adsorption and is not dependent on equilibrium forces.

Specific embodiments of the present invention comprise an activated carbon adsorbent impregnated so as to result in a composition comprising by weight from 1% to 25% of Sn^{+2}. As set forth above, these activated carbons may also optionally be comprised of by weight from 1% to 15% Ag, Sn, Zn, Al, Au, Cu and/or alkali elements, which function as amalgamating or reactive agents.

Uses for the present invention include the treatment of liquid hydrocarbon prior to olefin production, liquid propane gas and liquid natural gas processing, or similar operations. Other applications include the prevention of mercury poisoning of precious metal catalysts and the prevention of metal embrittlement damage to piping and equipment, as well as any other situation in which high and in particular, low-level concentrations of mercury are to be removed from liquid hydrocarbon.

The advantages of the present invention over other ways of removing mercury include that it permits mercury removal from hydrocarbon via the novel concept of the impregnating compounds in activated carbon so that the impregnants perform as reactant or reducing agents. In this sense the activated carbon may selectively adsorb efficient levels of mercury that would otherwise escape less effective mercury removal systems. As a result of the reactant-impregnated carbon's ability in the present invention to convert mercury to more readily adsorbable forms, these carbons perform their mercury removal function in a manner not previously contemplated, and in a manner that significantly increases the capacity of filters using these carbons in removing trace levels of mercury that is not possible through the use of other activated carbons.

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PRESENTLY PREFERRED EMBODIMENTS

Initial Carbon Screening Tests:

A variety of impregnated and non-impregnated carbons have been tested to determine their effectiveness for removing mercury from liquid hydrocarbon. The carbons differed in types of impregnants, pore structure and activity as well as source of raw material. The carbons tested included coconut based carbon (PCB), high activity coal-based carbon (BPL and Filtrasorb 400), medium activity coal-based carbon (CWS), BPL carbon impregnated with (by weight) 1% Ag, CWS carbon impregnated with 4% Ag, as well as a coal based surface modified carbon having a highly reactive surface (CAT). Additional impregnated carbons currently used in a variety of applications included other impregnated coal-based carbon formulations. The results of the initial tests presented in Table I reveal the poor mercury adsorptive capacity of these carbons in comparison to the impregnated carbons tested in the Tables that follow.

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TABLE I

INITIAL ISOTHERM TEST RESULTS FOR REMOVAL OF MERCURY FROM LIQUID HYDROCARBON					
CARBON I.D.	CLASSIFICATION/IMPREGNANT	CARBON DOSE (wt%)	*RESIDUAL Hg CONC. (ug/kg)	Hg LOADING (ug/g)	%Hg REMOVAL
BPL 12x30	CB/NI	1.0	8	3.22	80.0
		5.0	5	0.70	87.5
		10.0	4	0.36	90.0
PCB 12x30	CNB/NI	1.0	22	1.85	45.0
		5.0	8	0.64	80.0
		10.0	14	0.25	65.0
CWS 12x30	CB/NI	1.0	5	3.58	87.5
		5.0	8	0.64	80.0
		10.0	<3	>0.37	>92.5
BPL 12x30	CB/1% SILVER	1.0	14	2.62	65.0
		5.0	4	0.73	90.0
		10.0	8	0.32	80.0
CWS 12x30	CB/4% SILVER	1.0	8	6.53	80.0
		5.0	15	2.47	62.5
		10.0	3	0.75	92.5
CAT (12x30)	CB/NI- SURFACE MODIFIED HIGH REACTIVITY	0.5	7.3	3.64	71.4
		1.0	<3	>2.25	>88.2
		5.0	<3	>0.45	>88.2
FILTRASORB 400 12x30	CB/NI	5.0	7	0.32	69.6
		5.0	3	0.40	87.0
HGR 4x8	CB/15% SULFUR	5.0	15	0.16	34.8
		5.0	16	0.14	30.4
FCB 12x30	CB/7% CuO	5.0	15	0.16	34.8
		5.0	17	0.12	26.1
FCA 12x30	CB/7% CuO + 2% CrO^3	5.0	9	0.28	60.9
		5.0	10	0.26	56.5
ASC (12x30)	CB/7% CuO + 2% CrO^3 + .05% SILVER	5.0	6	0.34	73.9
		5.0	15	0.16	65.2

* Minimum Mercury detection limit = 3 ug/kg
CB = Coal based activated carbon
CNB = Coconut based activated carbon
NI = Non-impregnated

Impregnated Carbon Test Preparations and Procedures:

In the preparation process, the activated carbons tested were first pulverized and oven dried. Carbon dosages in the procedure ranged from .0003 to 5 grams per 100 grams of C5-C7 industrial grade natural gas condensate. The carbon/hydrocarbon mixture was placed in an air tight vessel with no head space and allowed to equilibrate with stirring for 24 hours. The carbon was removed from the samples by filtration prior to analysis for residual mercury concentration. The test samples were analysed by hydrobromic acid extraction followed by ICP/Mass Spectrometry quantifying the two major mercury isotopes.

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Mercury liberation tests subsequently performed on liquid hydrocarbon indicated the liberation of elemental mercury vapor upon addition of aqueous stannous chloride. Mercury vapor was not liberated from the liquid hydrocarbon in the absence of reducing agent stannous chloride. As a result of these tests, it was determined that the mercury content of the liquid hydrocarbon was most likely not in an elemental state. It was discovered that the presence of stannous chloride acted as a reducing agent and potassium iodide acted as a reactant, thereby significantly enhancing adsorption of mercury on activated carbon by converting what appears to be organic-bound mercury into a more readily adsorbable form of mercury. The stannous cation reduces the mercury to its elemental state, whereas the potassium iodide reacts so as to form a mercury halide salt.

The concept of converting organic mercury to a more adsorbable form was first tested with equilibrium isotherm studies using a 1% Ag impregnated coal based carbon (BPL), and a non-impregnated coal based carbon (CWS) to which an aqueous $SnCl_2$ solution was added. A 2% KI impregnated pelleted wood based carbon was included to evaluate the halogen reaction concept. Table II sets forth the results of these studies and demonstrates the fundamental effectiveness of the impregnated carbons in reducing concentrations of mercury. These tests dramatically demonstrate the potential of certain carbon formulation concepts and the particularly remarkable results that these concepts (such as with the wood based pellet carbon impregnated with 2% KI) were capable of attaining.

It is important to note that in all Tables describing all isotherm and column tests, the minimum reliable mercury detection limit was determined to be 3 ug/kg; as such, due to the analytical limitations of the method used to evaluate the amount of residual mercury present, the Tables use "<3 ug/kg" as the lowest residual mercury figure. In the case of the impregnated carbons of the present invention, readings well below the reliable detection limit of 3 ug/kg were often obtained, indicating that even more efficient mercury removal may actually be obtained by practicing the present invention than indicated in the Tables by the minimum reliable figure. Further, the base figure of <3ug/kg artificially holds the mercury removal percentages below the levels they would otherwise be if a more accurate residual mercury measurement were possible.

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TABLE II

ISOTHERM TEST RESULTS FOR REMOVAL OF MERCURY FROM LIQUID HYDROCARBON					
CARBON I.D.	CLASSIFICATION/IMPREGNANT	CARBON DOSE (wt%)	*RESIDUAL Hg CONC. (ug/kg)	Hg LOADING (ug/g)	%Hg REMOVAL
BPL 12x30	CB/1% SILVE-R- + TFR ID = 11.-012>**- AQ. $SnCl_2$	0.1	<3	>22.5	>88.2
		0.5	<3	>4.5	>88.2
		1.0	<3	>2.25	>88.2
		5.0	<3	>0.45	>88.2
CWS 12x30	CB/NI + TFR ID = 11.-012>**- AQ. $SnCl_2$	0.1	<3	>22.5	>88.2
		0.5	<3	>4.5	>88.2
		1.0	<3	>2.25	>88.2
		5.0	<3	>0.45	>88.2
4mm PELLET	WB/2% KI	0.5	<3	>4.5	>88.2
		1.0	<3	>2.25	>88.2
		5.0	<3	>0.45	>88.2

* Minimum Mercury detection limit = 3 ug/kg
** 10% Aqueous $SnCl_2$ solution added to hydrocarbon-carbon slurry
CB = Coal based activated carbon
CNB = Coconut based activated carbon
WB = wood based activated carbon
NI = Non-impregnated

Follow-up studies were conducted using impregnations of coal based activated carbons with 2% Sn^{+2} as $SnCl_2$, and coal based activated carbon with 2% Ag + 2% Sn^{+2} as $SnCl_2$. A wood based 2% KI impregnated activated carbon, a high activity coconut carbon impregnated with 2% KI (GRC-11); a control sample of the non-impregnated coal based carbon (CWS) was also included in the study. Due to the expected enhanced capability of these impregnated carbons for mercury removal, carbon dosages were lowered significantly to provide data distinguishing each carbon's level of performance. The results of these studies demonstrates the effectiveness of impregnated carbons in reducing high- as well as low-level concentrations of mercury. Table III sets forth the results of these selected carbon isotherm test. The impregnated carbons tested in this initial phase clearly demonstrate greatly enhanced mercury removal performance over the performance characteristics of the non-impregnated base carbons.

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PHASE I ISOTHERM TEST RESULTS FOR REMOVAL OF MERCURY FROM LIQUID HYDROCARBON

CARBON I.D.	CLASSIFICATION/IMPREGNANT	CARBON DOSE (wt%)	*RESIDUAL Hg CONC. (ug/kg)	Hg LOADING (ug/g)	%Hg REMOVAL
4mm PELLET	WB/2% KI	0.003	9.1	1029.4	76.1
		0.01	<3	>350.0	>92.1
		1.0	<3	>35.0	>92.1
		0.56	<3	>6.25	>92.1
GRC-11 12x30	CNB/2% KI	0.0014	16.1	228.6	10.6
		0.003	15.1	142.2	16.1
		0.011	16.9	21.0	6.1
		0.11	3.1	14.5	82.8
CWS 12x30	CB/2% $SnCl_2$	0.003	38.0	0	0
		0.1	<3	>35.0	>92.1
CWS 12x30	CB/2% $SnCl_2$ + 2% SILVER	0.003	35.0	102.8	7.9
		0.01	16.0	189.6	57.9
		0.1	<3	>35.0	>92.1
CWS 12x30	CB/NI	0.003	38.0	0	0
		0.01	37.0	8.9	2.6
		0.1	30.0	7.1	21.1
		0.56	6.6	5.6	82.6

* Minimum Mercury detection limit = 3 ug/kg
CB = Coal based activated carbon
CNB = Coconut based activated carbon
WB = wood based activated carbon
NI = Non-impregnated

Both the Table II and Table III preliminary tests both illustrate the superior performance of these impregnated carbons for mercury removal over the carbons as tested in Table I. The Table II and III tests results establish the effectiveness of reactant/reducing agent impregnated carbons in removing mercury from liquid hydrocarbon. The Table II and III studies also show that well-balanced performance in all critical areas is attained with the present invention composition containing either metal halides. Theoretically, Sn^{+2}, Sn^{+3}, Ti^{+2}, Ti^{+3}, and Cu have the requisite structure to act as reactant/reducing agents. The Table I and II compositions show that these impregnated carbons perform extremely well in removing even trace levels of mercury from a liquid hydrocarbon media. Good performance is also attained in all critical areas with the present invention using specialized compositions containing Ag, Sn, Zn, Al, Au, Cu and alkali elements. Other agents may also be added, depending on the desired performance characteristics; The compositions used can be tailored to meet specific desired performance characteristics for any number of industrial or other needs.

The second phase of carbon isotherm testing included evaluation of alternative metal halide impregnants in facilitating mercury removal from liquid hydrocarbon. Metal halide impregnated carbons were prepared in the laboratory including KCl, KBr, $CaCl_2$, $CuCl_2$, $FeCl_3$, and $ZnCl_2$ on 1mm wood based pellets. The data set forth in Table IV clearly indicates the chloride, iodide, and bromide halides in conjunction with a wide variety of metals also exhibit enhanced mercury removal capacity compared to the materials in Table I.

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TABLE IV

PHASE II ISOTHERM TEST RESULTS FOR REMOVAL OF MERCURY FROM LIQUID HYDROCARBON					
CARBON I.D.	CLASSIFICATION/IMPREGNANT	CARBON DOSE (wt%)	*RESIDUAL Hg CONC. (ug/kg)	Hg LOADING (ug/g)	%Hg REMOVAL
4mm PELLET	WB/2% KI	0.0013	4	1049.5	77.7
		0.0044	4	317.8	77.7
		0.106	<3	>14.1	>83.3
1mm PELLET	WB/2% KI	0.0014	<3	>1071.4	>83.3
		0.0043	4	324.3	77.7
		0.105	<3	>14.3	>83.3
1m PELLET	WB/2% KCl	0.0015	4	956.6	77.7
		0.0043	3	349.5	83.3
		0.107	5	12.1	72.2
1mm PELLET	WB/2% KBr	0.0013	3	1126.6	83.3
		0.0043	4	328.3	77.7
		0.104	4	13.5	77.7
1mm PELLET	WB/2% $CaCl_2$	0.0016	6	770.8	66.7
		0.054	9	16.6	50.0
1mm PELLET	WB/2% $CuCl_2$	0.0014	8	711.5	55.5
		0.052	5	25.2	72.2
1mm PELLET	WB/2% $ZnCl_2$	0.0015	9	592.5	50.0
		0.052	10	15.3	44.4
1mm PELLET	WB/2% $FeCl_3$	0.053	10	15.2	44.4

* Minimum Mercury detection limit = 3 ug/kg
CB = Coal based activated carbon
CNB = Coconut based activated carbon
WB = wood based activated carbon
NI = Non-impregnated

A third phase of isotherm testing was performed on laboratory prepared impregnated carbons to evaluate the effects on mercury removal capacity versus impregnant loading. The 1mm pelleted wood based activated carbon was impregnated to contain levels ranging from 2 wt.% to 25 wt% KI. Similar impregnations were prepared using $SnCl_2$ and silver. The test results set forth in Table V indicate excellent mercury removal performance at all impregnant loadings tested. The combination of excellent carbon capacity and low mercury content of the hydrocarbons makes it extremely difficult to evaluate impregnant loading mercury capacity relationships.

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TABLE V

ISOTHERM TEST RESULTS FOR REMOVAL OF MERCURY FROM LIQUID HYDROCARBON					
CARBON I.D.	CLASSIFICATION/IMPREGNANT	CARBON DOSE (wt%)	*RESIDUAL Hg CONC. (ug/kg)	Hg LOADING (ug/g)	%Hg REMOVAL
1mm PELLET	WB/2% KI LP	0.0015 0.003 0.01 0.1	16.4 15.7 9.4 3.0	187.7 123.3 88.8 15.0	8.9 12.8 47.8 83.3
1mm PELLET	WB/4% KI LP	0.0015 0.003 0.01 0.1	12.9 10.8 4.3 <3	405.7 287.8 129.5 >15.0	28.3 40.0 76.1 >83.3
1m PELLET	WB/8% KI LP	0.0015 0.003 0.01 0.1	8.0 10.4 8.7 <3	751.5 290.1 93.9 >15.0	55.6 42.2 51.7 >83.3
1mm PELLET	WB/12% KI LP	0.0015 0.003 0.01 0.1	7.7 <3 3.3 <3	821.3 >500.0 139.4 >15.0	57.2 >83.3 81.7 >83.3
1mm PELLET	WB/18% KI LP	0.0013 0.0045 0.1	5 6 <3	967.3 259.0 >15.0	72.2 66.6 >83.3
1mm PELLET	WB/25% KI LP	0.0013 0.0045 0.1	6 7 <3	924.7 262.4 >15.0	66.7 61.1 >83.3
1mm PELLET	WB/0.5% $SNCl^{2+}$ 0.5% SILVER LP	0.0013 0.0045	8 9	706.7 208.0	55.6 50.0
1mm PELLET	WB/5% $SNCl^{2+}$ 10% SILVER LP	0.0013 0.0045	9 12	616.5 120.2	50.0 33.3

* Minimum Mercury detection limit = 3 ug/kg
CB = Coal based activated carbon
CNB = Coconut based activated carbon
WB = wood based activated carbon
NI = Non-impregnated
LP = Carbon prepared in laboratory

Column Tests

Column testing of impregnated carbons was also conducted so as to evaluate mercury removal performance in a column treatment system. Column beds containing non-impregnated and 2% KI impregnated activated carbon pellets were used to treat an industrial hydrocarbon containing 38 ug/kg mercury. The tests were conducted under identical operating conditions, allowing a 30 minute contact time. The test results set forth in Table VI clearly show the mercury removal advantage attained with the impregnated product over the non- impregnated base carbon.

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TABLE VI

MERCURY REMOVAL PERFORMANCE COLUMN TEST RESULTS NON-IMPREGNATED VS. IMPREGNATED				
Non-impregnated 4mm Pellets: Column Effluent Data				
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	Effluent Hg Conc. (ug/kg)	% Mercury Removal
60	0.008	19108	4.6	87.9
175	0.23	665	11.0	71.1
325	0.43	356	13.0	65.8
2% KI Impregnated 4mm Pellets: Column Effluent Data				
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	Effluent Hg Conc. (ug/kg)	% Mercury Removal
60	0.008	19108	<3	>92.1
175	0.23	665	<3	>92.1
325	0.43	356	<3	>92.1
Column Conditions:				
5cc/min Flow Rate 30 Minute EBCT 1 Ft. Bed Depth Ambient Temperature and Pressure				

An additional column study was conducted on a 1mm wood based pellet impregnated to contain 2% KI. The study was designed to define the bed depth required to achieve mercury removal to below detectable limits when treating liquid hydrocarbon at an arbitrarily selected 4 GPM/Sq.Ft. loading rate. The segmented column design allowed the extraction of treated hydrocarbon at various bed depths during the treatment process. An industrial grade liquid hydrocarbon containing 18 ug/kg mercury was used in the laboratory study. The data set forth in Table VII indicates a 50% reduction in mercury concentration is achieved within the first 12 inches of the carbon column. Complete removal of mercury to below the minimum mercury detection limit of 3 ug/kg is demonstrated within 6.75 ft. of the carbon bed.

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TABLE VII

COLUMN TEST RESULTS USING PELLETS CONTAINING 2% KI. TREATING INDUSTRIAL GRADE NAPHTHA AT 4 GPM/Sq. Ft.				
1 ft. Column Effluent Data (Influent Hg = 18 ug/kg):				
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	Effluent Hg Conc. (ug/kg)	% Mercury Removal
65	1.54	103.3	9.1	49.4
545	12.96	12.3	9.3	48.3
2.75 ft. Column Effluent Data:				
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	Effluent Hg Conc. (ug/kg)	% Mercury Removal
246	5.85	74.8	8.3	42.7
366	8.7	50.3	7.1	60.6
426	10.1	43.2	5.9	67.2
486	11.6	37.8	7.1	60.6
4.5 ft. Column Effluent Data:				
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	Effluent Hg Conc. (ug/kg)	% Mercury Removal
367	8.7	82.0	5.2	71.1
427	10.2	70.5	4.5	75.0
487	11.6	61.8	4.9	72.8
547	13.0	55.1	5.1	71.7
577	13.7	52.3	<3	>83.3
6.75 ft. Column Effluent Data:				
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	Effluent Hg Conc. (ug/kg)	% Mercury Removal
548	13.0	82.6	<3	>83.3

Isotherm and Column Test Conclusions:

The precise reaction that occurs to create the observed effectiveness of the impregnated carbons as tested is not readily apparent. Determining the actual identification and concentrations of the various mercury compounds present would be extremely difficult due to the varying characteristics and very low concentrations of individual components that may or may not be present in a particular sample. Based on well known organo-mercury chemistry, the organo-mercury compounds may be present in a variety of forms to include mercaptides with or without halides, dialkylmercury compounds, and organo-mercury salt compounds.

The reactions of each type of organic mercury compound is consistent with the probable removal mechanism whereby metal halides or reducing agents as impregnants convert mercury to an inorganic mercury halide salt or to elemental mercury during the removal process.

The essential ingredient in the impregnant metal halides in the present invention for facilitating mercury conversion and removal are the I, Br and Cl halides. As such, in addition to the representative metals tested in the Tables above, any metal from the periodic table of the elements can serve as the "vehicle" for the depositing and/or maintaining the I, Br and Cl halides on the carbon surface.

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Further, the percentage of reactant metal halide by weight of carbon adsorbent is not critical; when the metal halidecomprises as little as 0.5% metal halide the positive effects of the present invention will result. As much as 25% or more metal halide by weight of carbon adsorbent may be desired, depending on the desired performance characteristics of the of said impregated carbon adsorbent.

Similarly, when a Sn^{+2}, Ti^{+2} and/or Cu reducing agent is used to reduce organic mercury to its elemental state, depending on the application to be made, from about 0.5% to 25% reducing agent by weight of carbon adsorbent may be desired. When an Ag, Sn, Zn, Al, Au, Cu and/or alkali element amalgamating agent is additionally impregnated on the carbon adsorbent, the amalgamating agent may usefully comprise from about 0.5% to 15% of amalgamating agent by weight of impregated carbon adsorbent.

In short, the isotherm and column tests conducted using the carbons of the present invention yielded outstanding mercury adsorptive results that had previously been thought impossible to obtain.

Carbon Impregnant Leach Testing:

Leach tests were run to determine if any of the impregnants used resulted in undesirable leaching of the impregnants. The data set forth in Tables VIII and IX indicates that significant levels of the impregnants and ash constituents do not leach from the carbon during treatment in either a column or in equilibrium (batch) form.

Batch equilibrium leach studies were conducted similar to the isotherm adsorption studies. Pulverised 10 g doses of non-impregnated base and the 2% KI impregnated pellet carbons were contacted with approximately 150 g of hydrocarbon and allowed to equilibrate with mixing for 36 hours. The liquor was then pressure filtered through 0.45 µm nylon pads for removal of carbon and submitted for analysis. A blank, untreated aliquot of the hydrocarbon was also filtered and submitted.

The column leach studies were performed with the 4 mm nonimpregnated and impregnated carbons loaded into 1" diameter columns to 1 foot bed depths (approximately 67 g). Liquid hydrocarbon was introduced upflow into the dry carbon bed simulating the worst case scenario for impregnant leaching, that being the initial wet down/degassing process. The first bed volume of treated liquor was collected, filtered through 0.45 µm nylon pads for removal of fines, and submitted for analysis. A 5 cc/min flow rate was used allowing for a 30 minute EBCT. A significant increase in temperature was observed during the initial wet down process, which quickly dissipated as the liquid level progressed up the bed. Approximately 10 bed volumes of hydrocarbons (1500 cc) were treated with each carbon column prior to termination of the studies. Additional samples were collected after 1, 5 and 10 bed volumes for mercury analysis presented previously in Table VI.

The data set forth in Table VIII indicates that significant levels of the impregnants and ash constituents do not leach from the carbon during treatment. The 43.6 ug/kg potassium concentration found in the impregnated carbon treated liquor represents 0.0015% of the total potassium available on the carbon surface and is only twice the concentration of potassium in the original untreated hydrocarbon.

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TABLE VIII

PRELIMINARY IMPREGNANT/ASH LEACH TEST RESULTS								
BATCH EQUILIBRIUM TESTS*								
CARBON I.D.	CLASSIFICATION/IMPREGNANT	K (ppb)	I (ppb)	Al (ppb)	Cu (ppb)	Fe (ppb)	Mg (ppb)	Si (ppb)
CONTROL	UNTREATED	21	<100	<10	3	13	150	40
4mm PELLET	WB/NI	24.5	200	<10	<1	6	113	<10
4mm PELLET	WB/2% KI	<1	<100	<10	<1	<2	<1	<10
COLUMN TESTS**								
CARBON I.D.	CLASSIFICATION/IMPREGNANT	K (ppb)	I (ppb)	Al (ppb)	Cu (ppb)	Fe (ppb)	Mg (ppb)	Si (ppb)
4mm PELLET	WB/NI	3.5	<100	<10	2	14.9	13	<10
4mm PELLET	WB/2% KI	43.6	100	500	<2	156	64	13

* = 6 grams carbon/100 grams of hydrocarbon.
Equilibrated for 36 hours, followed by pressure filtration.
** = 30 Min. EBCT. Sample represents initial column effluent liquor.
WB = Wood based activated carbon.
NI = Nonimpregnated
WI = Potassium Iodide

The previously discussed mercury removal performance testing also provided valuable tools for the evaluation of impregnant leachability during normal treatment processes. The additional leach tests conducted also suggest that the impregnants do not leach from the activated carbon upon exposure to liquid hydrocarbon. The data set forth in Table IX indicates an actual reduction in potassium and iron upon treatment and the iodide level remained below the analytical detection limits.

TABLE IX

COLUMN TEST RESULTS USING 1mm PELLETS CONTAINING 2% KI TREATING INDUSTRIAL GRADE NAPHTHA AT 4 GPM/Sq. Ft. IMPREGNANT LEACH DATA					
Run Time (Mins)	Volume Treated (Gals.)	Carbon Use Rate (Lbs/1000 Gals)	I (ppm)	K (ppm)	Fe (ppm)
Influent	--	--	<.4	0.6	2.43
66	1.57	1332.8	<.4	0.12	0.08
246	5.85	357.7	<.2	0.03	0.49
546	12.98	161.2	<.05	0.12	0.98
Notes: EBCT = 23 Mins Ambient temperature and pressure					

In short, the impregnated carbons of the present invention do not appear to result in undesired leeching of the impregnants.

Claims

1. An activated carbon adsorbent for the removal of mercury from liquid hydrocarbon, said carbon adsorbent being impregnated with a reactant metal halide wherein said metal is selected from the group

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consisting of metals on the periodic table of elements and said halide being selected from the group consisting of I, Br and Cl, said metal halide comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

2. An activated carbon adsorbent for the removal of mercury from liquid hydrocarbon as set forth in Claim 1 wherein said metal in the reactant metal halide is comprised of a metal selected from the group consisting of the metals from Group I and Group II of the periodic table of elements.

3. An activated carbon adsorbent for the removal of mercury from liquid hydrocarbon as set forth in Claim 1 wherein said metal in the reactant metal halide is comprised of a metal selected from the group consisting of K, Cu, Ca, Fe and Zn.

4. An activated carbon adsorbent for the removal of mercury from liquid hydrocarbon, said carbon adsorbent being impregnated with a reducing agent, wherein said reducing agent is selected from the group consisting of Sn^{+2}, Ti^{+2} and Cu, said reducing agent comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

5. An activated carbon adsorbent for the removal of mercury from liquid hydrocarbon as set forth in Claim 4 wherein said carbon adsorbent is additionally impregnated with an amalgamating agent selected from the group consisting of Ag, Sn, Zn, Al, Au, Cu and alkali elements from the periodic table of elements, said amalgamating agent comprising from about 0.5% to 15% by weight of said impregated carbon adsorbent.

6. A process for removing mercury from liquid hydrocarbon whereby organic bound mercury in said liquid hydrocarbon is adsorbed by an activated carbon, said activated carbon being impregnated with a reactant metal halide wherein said metal is selected from the group consisting of metals on the periodic table of elements and said halide being selected from the group consisting of I, Br and Cl, said metal halide comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

7. A process for removing mercury from liquid hydrocarbon as set forth in Claim 6, wherein said activated carbon wherein said metal in the reactant metal halide is comprised of a metal selected from the group consisting of the metals from Group I and Group II of the periodic table of elements.

8. A process for removing mercury from liquid hydrocarbon as set forth in Claim 6, wherein said metal in the reactant metal halide is comprised of a metal selected from the group consisting of K, Cu, Ca, Fe and Zn.

9. A process of removing mercury from liquid hydrocarbon whereby organic bound mercury in the hydrocarbon is reduced to an elemental state by contact with a reducing agent impregnated on a carbon adsorbent, said reducing agent being selected from the group consisting of Sn^{+2}, Ti^{+2} and Cu is impregated in said carbon adsorbent to convert said organic bound mercury to said elemental state, said reducing agent comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

10. A process of removing mercury from liquid hydrocarbon as set forth in Claim 9, wherein the process also includes reacting the mercury after reduction to said elemental state with an amalgamating agent, wherein said amalgamating agent is selected from the group consisting of Ag, Sn, Zn, Al, Au, Cu and alkali elements from the periodic table of elements, said reducing agent comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

11. A method of treating liquid hydrocarbon whereby organic bound mercury in the hydrocarbon is removed by contacting the liquid hydrocarbon with a carbon adsorbent, said carbon adsorbent being impregnated with a reactant metal halide wherein said metal is selected from the group consisting of metals on the periodic table of elements and said halide being selected from the group consisting of I, Br and Cl, said metal halide comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

12. A method of treating liquid hydrocarbon as set forth in Claim 11 wherein said metal in the reactant metal halide is comprised of a metal selected from the group consisting of the metals from Group I and Group II of the periodic table of elements.

13. A method of treating liquid hydrocarbon as set forth in Claim 11 wherein said metal in the reactant metal halide is comprised of a metal selected from the group consisting of K, Cu, Ca, Fe and Zn.

14. A method of treating liquid hydrocarbon whereby organic bound mercury in the hydrocarbon is converted to an elemental state and removed by contacting the liquid hydrocarbon with a reducing agent impregnated on a carbon adsorbent, said reducing agent being selected from the group consisting of Sn^{+2}, Ti^{+2} and Cu, said reducing agent comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

15. A method of treating liquid hydrocarbon as set forth in Claim 14 whereby the treatment also includes reacting the mercury after reduction to said elemental state with an amalgamating agent, wherein said amalgamating agent is selected from the group consisting of Ag, Sn, Zn, Al, Au, Cu and alkali elements from the periodic table of elements, said reducing agent comprising from about 0.5% to 25% by weight of said impregated carbon adsorbent.

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Application Number

EP 90 12 2092

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 325 486 (MITSUI PETROCHEMICAL IND.) * Claims 1,2,4; table 4 *	1-4,6-9, 11-14	C 10 G 25/00
A	EP-A-0 342 898 (MITSUI PETROCHEMICAL IND.) * Claims 1,2,3 *	1-4,6-9, 11-14	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

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Place of search	Date of completion of search	Examiner
The Hague	11 March 91	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

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(54) Adsorbent sheet material for parallel flow passage contacting devices

(57) An adsorbent material fabricated into a reinforcement-free, self-supported coherent thin sheet and configured for use as a parallel passage contactor element in adsorption / separation applications with gases and liquids is disclosed. The adsorbent sheet material is obtained by enmeshing fine adsorbent particulates in a polymer binder. Particulates include but are not limited to carbon particles, inorganic oxides particles, or ceramic particles, or synthetic polymer resin particles, where the characteristic length of particles is in the range from 0.01 μm to 100 μm. Particles of nano scale and mixtures of particle sizes may be advantageously incorporated. The adsorbent sheet advantageously contains a large volume percentage of active adsorbent particles. The parallel passage contactor device fabricated from the adsorbent sheet material is characterized by minimal mass transfer resistance and better separation efficiency expressed as height equivalent to a theoretical plate, while it maintains most of the adsorptive properties of the starting particulates, and can be used in gas separation applications with short adsorption cycles, such as rapid pressure swing adsorption, rotary concentrators, rapid electric swing adsorption.

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Description

BACKGROUND OF THE INVENTION

Field of Invention

[0001] This invention discloses an adsorbent material fabricated into a self-supported coherent sheet and configured for use as a parallel passage contactor.

Prior Art

[0002] Traditional mass transfer devices for adsorption process include monoliths (e.g. honey combs), cloth (e.g. activated carbon fiber cloth) and packed bed of adsorbent particles. The packed bed is cheap and versatile, but quite inefficient in operation at high flow rate regimes due to the high costs associated to the large internal pressure drop. Calculations by Ruthven and Thaeron (in Gas. Sep. Purif. vol. 10, (1996) p. 63) have shown that a significant improvement in the mass transfer / pressure drop characteristics over the packed bed configuration could be achieved with parallel passage contactors. These are mass transfer devices in which the gas passes in laminar flow through straight channels between equally spaced parallel sheets of adsorbent. Rapid mass transfer enables rapid cycling and smaller devices. One application of parallel passage contactors is Pressure Swing Adsorption (PSA).

[0003] PSA has become of interest for small-scale gas separation applications because of its potential for high separation performance (product purity and recovery) compared with other gas separation technologies. Depending on the actual mechanism, PSA separations could be categorized as equilibrium or kinetically (diffusion) controlled. An example for the first category is separation of air on zeolite 5 Å into almost pure nitrogen and oxygen streams based on differences in equilibrium adsorption isotherms between nitrogen and oxygen. An example for the second group is the same separation carried out on zeolite 4 Å, where the mechanism is based on the differences in diffusion rates between nitrogen and oxygen, which have different effective kinetic diameters (3.46 Å and 3.64 Å, respectively). While the equilibrium based PSA separation has been relatively well established theoretically and already commercialized for some applications, the diffusion-induced PSA still needs theoretical development and is not fully commercialized. The reader is referred to several recent publications such as by Shin and Knaebel, in AIChE Journal, vol. 33, p. 654 (1987), and vol. 34, p. 1409 (1988); by Chung and others, in Computers Chem. Engn. Vol. 22, Suppl., p. S637 (1998); and to the "Pressure Swing Adsorption" monograph book by Ruthven, Farooq and Knaebel, VCH Publisher, 1994.

[0004] Another way for optimization of PSA in terms of enhancing the adsorbent productivity at equal recovery and product purity parameters is through shortening the cycle times. Enhanced adsorbent productivity results in reducing the cost and foot print size of PSA beds. When the intra particle diffusion limits the rate of mass transfer in PSA, one way to shorten the cycle times is by using adsorbent with very small particle sizes. This was demonstrated first in US Patent 4,192,892, where relatively small particles of adsorbent were used in a packed bed configuration at cycle times of less than 30 seconds, with substantially higher product recovery than in previous art. US Patent 4,354,858 demonstrated a further increase in productivity by executing rapid cycle PSA with two pistons operating out-of-phase at the ends of the adsorption column.

[0005] However, the gas separation efficiency in rapid cycle PSA, as described by US Patents 4,192,892 and 4,354,858, is limited by the pressure drop in the randomly packed bed column. To circumvent this, Farooq, Thaeron and Ruthven (Sep. Pur. Tech., vol. 13 (1998) p. 181-193) suggested combining piston-driven rapid cycle PSA with parallel passage contactors, thus providing an economical solution to older separation technologies such as air drying, air separation, and VOC removal. Based on numerical simulation models developed by Ruthven and Thaeron (Gas Sep. Purif. vol. 10 (1996) 63-73), for example, a parallel passage contactor with sheet thickness of about 500 to 800 μm and sheet spacing of about 100 μm should be well suited to rapid cycle adsorption processes for CO_2 / N_2 separation. The adsorbent described by Ruthven and Thaeron was activated carbon fiber (ACF) sheet with fiber diameters of 10 - 15 μm. For this adsorbent characteristic length, the optimal cycle frequency was 10 - 20 rpm, the rate being limited by the inter particle, macro pore diffusion. However, it became evident for those who tried to use carbon fiber adsorbent in woven or non-woven form in rapid cycle PSA systems that a great disadvantage of these materials is that they are not dimensionally stable.

[0006] Further increase in cycle frequency and thus more performance improvement of the separation process is possible in principle by using even smaller adsorbent particles (about 10 μm in size). Problems with small particles in packed beds subjected to high flow velocities include particle break up, particle attrition from the bed, and particle fluidization. US Patent 6,176,897 teaches a high frequency pressure swing adsorption system in which granular adsorbent beds are replaced by a high surface area adsorbent monolith or layered support, with adsorbent elements formed of layered or laminated sheet materials using fibrous reinforcements (such as glass, carbon or kevlar fibers) which support zeolite loaded composites in adsorbent sheets. However, the availability of materials that could be suc-

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cessfully used for fabrication of such adsorbent structures is limited. Also, the use of reinforcement materials limits the adsorption capacity per volume of adsorption bed, because a relatively large fraction of the adsorbent bed volume, associated with the reinforcement structures, is not effectively used for adsorption.

[0007] It was demonstrated that inorganic adsorbent particles with sizes in the range of tens to hundreds of nanometers (also called adsorbent nanoparticles) have enhanced adsorption and chemical surface reactivity due to the very high ratio of surface atoms to bulk atoms. For more information, the reader is directed to the recently published book entitled "Nanoscale Materials in Chemistry" (Wiley, 2001) by Klabunde. However, integrating adsorbent nanoparticles into usable sorptive materials has been a challenge so far. Efficient means for binding, stabilizing or incorporating adsorbent particles with sizes in the nanometer range in structures that can be used for adsorption and separation applications are deemed necessary.

[0008] Recently, sorptive materials based on polytetrafluoroethylene (PTFE) matrix have been described in the patent literature. US Patents 4,810,381 and 4,906,378 describe a chromatographic sorptive material composed of PTFE fibril matrix and non-swellable adsorbent particles enmeshed in the matrix. US Patents 4,153,661 and 5,071,610 disclose manufacturing methods and uses of composite sheet materials comprised of fine, non-swellable adsorbent particles held by a fibrillated polymer matrix, and methods for the control of internal porosity. The resulting sheet is extremely pliable and it is said to be useful as an electronic insulator or semi permeable membrane. US Patent 4,373,519 discloses a composite wound dressing comprising hydrophilic absorptive particles enmeshed in a PTFE matrix. US Patents 4,565,663 and 4,460,642 disclose water swellable composite sheets having a PTFE matrix in which are enmeshed swellable hydrophilic sorptive particles. However, sorptive materials obtained by enmeshing particulate sorbents, , in a fibrillated PTFE matrix with specification for use as a parallel passage contactor have not been disclosed.

[0009] Self-supported porous membranes obtained by compacting micron-size carbon particles and fibrillated PTFE could also be used as porous electrodes in electrochemical applications. The US Patent 4,585,711 teaches a hydrogen electrode for a fuel cell obtained by roll compaction of granular PTFE and platinum-covered carbon black particles. The US Patent 4,379,772 disclosed a method for forming an active layer electrode for fuel cells in which granules of active carbon are mixed with fibrillated PTFE and rolled into a self-supported, coherent sheet form. US Patent 4,468,362 discloses a method for preparing a self-sustained electrode-backing layer with excellent electrical conductivity through dispersing PTFE particles and finely divided carbon black particles (50 to 3000 A). US Patent 4,500,647 teaches the preparation of three-layer matrix electrodes for fuel cell or other electrochemical applications in which active carbon particles are present within an unsintered carbon black—fibrillated PTFE material. US Patent 5,636,437 discloses a fabrication method of solid carbon porous electrodes from various carbon powders and thermoset resin binders. These un-reinforced, self-supporting sheets have not been specified for use as a parallel passage contactor. The prior art is limited to adsorbent cloths or reinforced sheets for parallel passage applications.

BRIEF SUMMARY OF THE INVENTION

[0010] This invention discloses an adsorbent material fabricated into a reinforcement-free, self-supported coherent sheet, and configured for use as a parallel passage contactor. The adsorbent material is obtained by enmeshing fine adsorbent particulates, including but not limited to carbon particles, inorganic oxide particles, or ceramic particles, or synthetic polymer resins. For the purpose of the present invention, the characteristic length of these particles is in the range from 0.01 μm to 100 μm. The sheet material is a high surface-to-volume composite, characterized by sheet surface area to total sheet volume ratio in the range of 200 to 2500 m^2/cm^3 and the sheet micro pore volume to total sheet volume ratio is in the range of 0.1 to 0.9. For use as a parallel passage contactor, the sheet material is configured in the form of flat parallel layers with gaps between adjacent sheets, or is corrugated, or is embossed, or is spiral wound, or is in any other form that allows the gas to flow parallel to the sheet surface. The material configured as parallel passage contactor can be used in many gas separation applications, or liquid applications, where fast adsorption, low pressure drop, and minimal mass transfer resistance are essential, such as in rapid cycle pressure swing adsorption. Examples of preferred uses of parallel passage contactor devices manufactured with the material disclosed in the present invention include but are not limited to hydrogen purification and air separation by rapid cycle pressure swing adsorption, air desiccation and VOC abatement by HVAC rotary wheel technology, rapid gas capture and controlled release for adsorbed natural gas fueled vehicles or analytical sampling purposes.

Object and Advantages

[0011] When parallel passage contactor elements are built, they must combine thin adsorbent sheets of high micropore volume capacity with a porous, low pressure drop separator (or no separator at all). The first requirement is introduced by the need to maximize the adsorption capacity of the sheet adsorbent; the second ensures that a low pressure drop device is being obtained. For fast cycle PSA application, the intra-particle diffusion must be minimized, which can be realized by using very small adsorbent particles, preferably in sub-micron size. Based on all these con-

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siderations, a means for manufacturing thin sheets of adsorbent materials, which hold very small adsorbent particulates, was deemed highly necessary for further improving the efficiency of PSA systems through rapid cycle technology. Calculations showed that to be useful, the adsorbent sheet must have a sheet thickness less than about 0.8 mm, a void volume fraction in the range of about 0.3 to 0.9, particle sizes smaller than about 0.7 μm, and an linear driving force mass transfer coefficient larger than about 1 sec^{-1}. The contactor must withstand the high velocity flow associated with rapid cycling PSA, in conditions wherepelletized powders fluidize and suffer from attrition, and woven cloths do not have sufficient stability or structural integrity.

[0012] It is therefore an object of this invention to provide an adsorbent material, which immobilizes and incorporates a multitude of fine adsorbent particulates, with characteristic dimensions in the nanometer or micrometer range, which otherwise are too small to be used alone for adsorption applications.

[0013] Another object of this invention is to provide an adsorbent material that maintains much of the adsorptive properties of the starting adsorbent particles, thus that one can take full advantage of the high reactivity and fast adsorption or reaction rates associated to small adsorbent particles in the nanometer and micrometer range.

[0014] Yet another object of this invention is to provide an adsorbent material configured as a reinforcement-free, self-supported, flexible thin sheet layer or membrane.

[0015] Yet one more object of this invention is to teach the use of the above said thin sheet reinforcement-free adsorbent material as an element of parallel passage contactors for adsorption or separation applications in gas or liquid phase.

[0016] In this application, "reinforcement" means an essentially freestanding, sizable structure that adds integrity and mechanical stability to a manufactured object, does not necessarily have adsorption properties, and on which one can support with appropriate binders a variety of adsorbent particulates.

[0017] In this application, "binder" means a component that, when added in a small amount to a manufactured object, provides structural integrity by gluing together a multitude of component particles, but which does not possess structural integrity by itself, e.g. without the presence of a multitude of particles.

[0018] In this application, "self-supporting" means that no rigid backing support is needed for the manufactured object.

[0019] In this application, "particles" or "particulates" means solid shapes (not including PTFE) with a diameter from about 0.010 μm to about 100 μm.

[0020] One advantage of this invention over prior art consists in the effective immobilization of nanosized adsorbent particulates, in general starting from about 10 nm, for more efficient use in adsorption and separation applications. Also, this invention teaches the manufacturing of a reinforcement-free, self-supported, coherent, and dimensionally stable adsorbent material which can be configured as an element of a parallel passage contactor. An obvious advantage of this material, which comes from the lack of any structural reinforcement, is that its apparent volume is essentially filled with adsorbent particles, thus maximizing the adsorption capacity per volume of adsorbent sheet. Yet, the parallel passage contactors made from the said material, when used for adsorption or separation applications, combine good mass phase transfer properties with low pressure drop. Another advantage of this invention comes from the fact that the said adsorbent material can be obtained as a thin and flexible sheet, which makes it useable in many forms, such as parallel sheets, corrugated sheets, embossed sheets, spiral wound or in a honeycomb configuration, as elements of a parallel passage contactor. Yet a more distinct advantage of this invention is that it provides a means for using small adsorbent particulates, with sizes in the nanometer or micrometer range, in a freestanding, reinforcement-free, dimensionally stable material which becomes suitable for manufacturing parallel passage contactors to be used in rapid cycles pressure swing adsorption.

[0021] Further objectives and advantages of this invention will become apparent from a consideration of the following full description of embodiments.

Figures

[0022] Figure 1 is a scanning electron microscope picture of the adsorbent sheet material obtained according to the procedure outlined in Example 1. The primary carbon nanoparticles of less than 20 nm are randomly distributed and enmeshed by the polymer fibrils (not seen in the picture). The scale bar length is 100 nm.

[0023] Figure 2 is another scanning electron microscope picture of the adsorbent sheet materials obtained according to the procedure outlined in Example 1. It shows that carbon nanoparticles form an open structure, with very little attachments and contact points to polymer fibrils. A polymer binder fibril about 1000 nm long and less than 40 nm in diameter is also seen. The scale bare length is 200 nm.

[0024] Figure 3 is a scanning electron microscope picture of the adsorbent sheet material obtained according to the procedure outlined in Example 2. It shows a mixture of activated carbon particles of various sizes, forming a reinforcement-free open structure held together by polymer fibrils (not seen in the picture). The scale bar length is 2 μm.

[0025] Figure 4 is a schematic drawing showing a parallel passage contactor element configured as a multitude of flat adsorbent sheets **1** in a parallel arrangement. Air inlet **2** and air outlet **3** are arranged such that the direction of

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airflow is parallel with the surface of flat sheets.

[0026] Figure 5 is a schematic drawing showing a parallel passage contactor element configured as a spiral structure made from an adsorbent sheet **1**. Air inlet **2** and air outlet **3** are arranged such that the direction of airflow is parallel with the surface of adsorbent sheet.

[0027] Figure 6 is a schematic drawing showing a parallel passage contactor element configured as a honeycomb structure consisting of alternating flat sheets 1 and corrugated sheets **2**. Air inlet **3** and air outlet **4** are arranged such that the direction of airflow is parallel with the surface of corrugated and flat sheets.

[0028] Figure 7 compares results on CO_2 breakthrough from a packed bed of 1 mm granular carbon and a parallel passage contactor element made from a carbon adsorbent sheet manufactured according to Example 2, and configured as a spiral structure according to Example 7.

[0029] Figure 8 shows thermogravimetric data on raw Na-X zeolite powder and two samples of zeolite powder processed in sheet form according to the procedure outlined in Example 10. It shows that domains of thermal stability for zeolite sheet samples are between 300 and 400 C.

[0030] Figure 9 shows results on drying at 350 C followed by N_2 adsorption / desorption cycles at 45 C on raw Na-X zeolite powder.

[0031] Figure 10 shows results on drying at 350 C followed by N_2 adsorption / desorption cycles at 45 C of zeolite processed in sheet form according to the procedure outlined in Example 11.

[0032] Figure 11 shows results on drying at 350 C followed by N_2 adsorption / desorption cycles at 45 C of zeolite processed in sheet form according to the procedure outlined in Example 11.

DETAILED DESCRIPTION OF THE INVENTION

[0033] By employing a process like the one disclosed by US Patents 4,153,661 and 5,071,610, a sheet material is obtained, containing a first type of adsorbent particulates, either alone or admixed with a second type of adsorbent particulates, or the second type of adsorbent particulates alone, and a polymer binder.

[0034] The first type of adsorbent particulates includes but is not limited to carbon nanoparticles and inorganic oxides nanoparticles and is characterized by particle sizes in the range of about 10 to about 200 nm. Examples of carbon nanoparticles include but are not limited to carbon black particles and multiwalled carbon nanotubes. Examples of inorganic oxide nanoparticles include but are not limited to silica, alumina, aluminosilicates (e.g. zeolites), magnesia, zirconia, titania, ceria.

[0035] The second type of adsorbent particulates is comprised of activated carbon, inorganic oxides, ceramic materials, or synthetic polymeric resins with particle sizes in the range from about 0.2 to about 100 μm.

[0036] The adsorbent particulates from the first and second group are characterized, in general, by adsorptive properties that make them suitable for use as adsorbents in the parallel passage contactor after incorporation in the sheet form. Although the nature of these adsorbent particulates may vary within quite large limits, the adsorptive properties are expected to correlate with their specific surface area and micropore volume, as measured by nitrogen adsorption. The acceptable limits for specific surface area are between 200 and 2500 m^2/g and the acceptable limits for the micropore volume are between 0.2 and 1 cm^3/g. For practical applications were the device footprint or the device volume should be minimized, a more convenient measure of the adsorptive properties is based on the apparent or bulk volume of the adsorbent, which can be contained in the working volume of the adsorption device. Thus, when the bulk density of obtained sheet materials is properly accounted for, the adsorption capacity could also be expressed as the total BET surface area or total micropore volume of the adsorbent material per apparent unit volume of the adsorbent material. The corresponding range for sheet surface area to total sheet volume ratio is 200 to 2500 m^2/cm^3 and the range for the sheet micropore volume to total sheet volume ratio is of 0.1 to 0.9.

[0037] Examples of polymer binder include but are not limited to polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyamide, cellulose acetate, polyvinyldifluoride (PVDF) or any other natural or synthetic polymer that is capable of suspending other particles in a random manner.

[0038] The optimal ratio of adsorbent particulates to polymer fibril binder can be varied, but should be kept, in general, in the range from 98:2 to 60:40 by weight. Under these conditions, the composite sheet is obtained with porosity in the range of 30 to 95 % void volume, and the mean pore size in the range of 0.002 to 2 μm. Fugitive pore formers such as salts, or excess solvents, or polymers may be added to increase the pore size and porosity.

[0039] The obtained sheet material can be formed with sheet thickness in the range from 50 to 1000 μm, but it is convenient for the purpose of the present invention to manufacture it in very thin sheets. When the particulate adsorbent particles are preponderantly in the form of nanoparticles with large surface area to volume ratio it is preferable to manufacture the composite sheet material with small thickness in order to take advantage of the properties of individual nanoparticles.

[0040] One important advantage offered by thin sheet nanocomposite is the ability to freely access the particle and interparticle surfaces, which thus can efficiently be used for gas or vapor adsorption, pathogen annihilation, surface

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chemical reactions, or electrochemical energy storage, to name a few.

EXAMPLE 1

[0041] This example demonstrates that processing the nanoparticulate carbon black in a sheet form does not substantially reduce the surface area and mesopore volume of the starting carbon black material. According to one of preferred embodiments, a nanoparticulate carbon sheet containing 85% furnace carbon black (such as Black Pearls 2000 available from Cabot Corporation) and 15% PTFE (available commercially as Teflon 30 or Teflon 601 A) was obtained by blending the particulate adsorbent material with PTFE in the presence of water, followed by intensive mixing to cause PTFE fibrillation, biaxial calendaring to form the sheet, and drying. A carbon sheet with thickness of 250 μm was obtained. Figure 1 shows a SEM (scanning electron microscopy) image of the obtained material; carbon black nanoparticles with sizes in the 20 - 50 nm range are visible. A polymer fibril about 1000 nm long and 20 nm in diameter is seen in Figure 2. The carbon nanoparticles bound around and between polymer fibrils form an open, essentially reinforcement-free structure. The carbon black used in this example had a surface area of 1500 m^2/g, and a total pore volume of 1.65 cm^3/g distributed mostly (54 %) in the mesopores (2 - 50 nm), see Table 1. The resulted nanoparticulate carbon black sheet had a total surface area of 1200 m^2/g and a total pore volume of 1.55 cm^3/g, from which more than 70 % is distributed in the mesopores, (see Table 1). The BET surface area was calculated from nitrogen adsorption data at liquid nitrogen temperature, and the pore volume distribution was calculated using the DFT method (as developed by Micromeritics) and nitrogen adsorption data. While the average particle size of the starting carbon black was approximately 12 - 15 nm, it is estimated that pore sizes of greater than 50 - 100 nm exist in the obtained carbon sheet, as pores between complex strands and agglomerates of particles (see Figure 1). The material was tested for static VOC adsorption capacity (see Example 3).

Table 1

Surface area and pore volume distribution of starting particulate materials and sheet processed carbon materials				
	Carbon black (BP 2000)	Carbon black sheet	Activated carbon (MSP 20)	Activated carbon sheet
BET surface area (m^2/g)	1500	1200	2400	1900
Total pore volume (< 120 nm) (cm^3/g)	1.65	1.55	0.88	0.83
Ultra micropores (<1.18 nm) (cm^3/g)	0.19	0.15	0.45	0.33
Super micropores (1.18 - 2 nm) (cm^3/g)	0.13	0.14	0.33	0.26
Total micropores (< 2 nm) (cm^3/g)	0.32	0.29	0.78	0.59
Micropores fraction (%)	19.39	18.71	88.64	71.08
Mesopores (2 - 50 nm) (cm^3/g)	0.89	1.11	0.07	0.12
Mesopore fraction (%)	53.94	71.61	7.95	14.46

EXAMPLE 2

[0042] This example demonstrates that processing high surface area activated carbon particles in a sheet form does not substantially reduce the surface area and micropore volume of the starting activated carbon material. According to another embodiment, a carbon sheet containing 80 % activated carbon particles (such as MSP20 activated carbon available from Kansai Coke & Chemical Company), 10 % carbon black (such as Black Pearls 2000 available from Cabot Corporation) and 10 % PTFE (available commercially as Teflon 30 or Teflon 601A) was prepared according to the procedure from Example 1. A carbon sheet with thickness of 200 μm was obtained. Figure 3 shows a SEM (scanning

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electron microscopy) image of the obtained material; carbon particles of various sizes and irregular shape form an open, reinforcement-free structure. The BET surface area and the pore volume distribution were calculated as explained in Example 1. The initial activated carbon was characterized by a BET surface area of 2400 m^2/g and a total pore volume of 0.88 cm^3/g, of which 88 % was comprised in micropores (below 2 nm), see Table 1. The resulted activated carbon sheet material was
characterized by a surface area of 1900 m^2/g and a total pore volume of 0.83 cm^3/g, of which 71 % was comprised in micropores (below 2 nm) and 15 % in mesopores (2 - 50 nm), see Table 1. The material was tested for static VOC adsorption capacity (see Example 4) and CO_2 adsorption capacity and kinetics (see Example 5).

EXAMPLE 3

[0043] This example demonstrates that processing carbon black material in sheet form does not significantly reduce the static VOC adsorption capacity of starting carbon black. Static adsorption of volatile organic compounds (VOC) was measured on the starting carbon black material (Black Pearls 2000) and on the derived carbon sheet material from Example 1. The samples (0.3 - 0.5 g) were dried at 180 C and accurately weighed in capped glass bottles. The capped bottles were placed in desiccators containing a beaker with a few milliliters of liquid VOC (either one of toluene, carbon tetrachloride, and trimethylpentane). The lids of the desiccators were tightly closed and the bottles were uncapped. The adsorbent samples were allowed to equilibrate with the respective VOC vapors for 3 hours at room temperature. After 3 hours, the bottles were capped, removed from desiccators and accurately weighed. The weight gain represents the amount of VOC adsorbed plus the weight of saturated vapors trapped inside the capped bottles. In order to correct for the weight of saturated vapors, the adsorbent samples were replaced in the desiccators, uncapped, and the desiccator's lids were partially open to the ambient. After one more hour, the bottles were re-capped, removed from the desiccators and weighed. The weight gain versus the initial weight of dried samples represents the capacity for static VOC adsorption at the pressure of saturated vapors of respective VOC, at room temperature. The results are shown in Table 2. It is seen that the static VOC capacity of carbon sheet materials derived from carbon black are within 80 - 95 % if the VOC capacity of the starting carbon black material.

Table 2:

Static VOC adsorption data on carbon black and carbon black derived sheet materials						
	Toluene		Carbon tetrachloride		Trimethylpentane	
	Carbon black BP2000	Adsorbent Carbon Sheet	Carbon black BP2000	Adsorbent Carbon Sheet	Carbon black BP2000	Adsorbent Carbon Sheet
Weight of initial sample (g)	0.3914	0.4241	0.3704	0.4650	0.3733	0.3868
Weight of dried sample (g)	0.3823	0.4117	0.3616	0.4541	0.3642	0.3753
Weight of sample after adsorption (g)	0.7614	0.8058	0.7362	0.8527	0.6198	0.5839
Amount adsorbed (%)	99.16	95.73	103.60	87.78	70.18	55.58

EXAMPLE 4

[0044] This example demonstrates that processing the material in sheet form does not significantly reduce the static VOC adsorption capacity of activated carbon material. Static adsorption of volatile organic compounds (VOC) was measured on the starting activated carbon material (MSP 20) and on the derived activated carbon sheet material from Example 2. The procedure was similar to that from Example 3. The results are shown in Table 3. It is seen that the static VOC capacity of activated carbon sheet materials derived from activated carbon materials are within 85 - 90 %

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if the VOC capacity of the starting activated carbon material.

Table 3:

Static VOC adsorption data on activated carbon and activated carbon derived sheet materials						
	Toluene		Carbon tetrachloride		Trimethylpentane	
	Activated Carbon MSP 25	MSP-20 Adsorbent Carbon Sheet	Activated Carbon MSP 25	MSP-20 Adsorbent Carbon Sheet	Activated Carbon MSP 25	MSP-20 Adsorbent Carbon Sheet
Weight of initial sample (g)	0.3911	0.5698	0.3911	0.5698	0.3375	0.5699
Weight of dried sample (g)	0.2413	0.5350	0.3905	0.5515	0.3371	0.5514
Weight of sample after adsorption (g)	0.4227	0.8907	0.9050	1.1630	0.5356	0.8299
Amount adsorbed (%)	75.18	66.49	131.75	110.88	58.88	50.51

EXAMPLE 5

[0045] This example demonstrates that the activated carbon sheet material is characterized by faster adsorption kinetics and higher adsorption capacity for CO_2 adsorption in comparison with granular activated carbon and activated carbon fibers. A carbon sheet material was obtained as shown in Example 2. The adsorption of CO_2 at room temperature was measured by the volumetric method, in which the adsorption is monitored through pressure variations following successive gas dose introductions in a close, calibrated volume. The activated carbon sheet material of Example 2 was tested against a 12 x 30 mesh granular activated carbon (GAC) sample obtained from coconut shell (bulk density 0.4 g/cm^3) and an activated carbon fiber (ACF) cloth (bulk density 0.2 g/cm^3). The results are shown in Table 4. It is seen that the activated carbon sheet obtained according to Example 2 is characterized by a substantially higher isothermal adsorption capacity for CO_2, on a weigh basis and on a volumetric basis, as well as by a faster mass transfer coefficient. The increased capacity, coupled with the faster mass transfer coefficient, demonstrate the advantage of using activated carbon sheet materials as components of parallel passage contactors for rapid cycle pressure swing adsorption systems. The improvement over GAC and ACF cloth comes from the open access of gas to sub-micrometer sized carbon particles immobilized in the sheet form, according to the present invention disclosure.

Table 4

Isothermal capacity and kinetic constant of CO_2 adsorption on activated carbon adsorbent sheet and other forms of adsorbent carbon for reference			
	MSP-20 Adsorbent Carbon Sheet	Coconut Shell Granular Carbon (12x30 mesh)	Activated Carbon Fiber Cloth
Isothermal CO_2 working capacity@ 30 C (0.5 to 5 atm) (mmole/g)	5.9	4.1	4.7
Isothermal CO_2 volumetric capacity@ 30 C (0.5 to 5 atm) (mmole/cm^3)	2.54	1.64	0.94
Mass transfer coefficient of CO_2 uptake (sec^{-1})	1.4	0.7	1.4

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EXAMPLE 6

[0046] This example shows the making of a parallel passage contactor with flat sheets configuration. Reference is made to Figure 4. The adsorbent material obtained as disclosed in this invention was manufactured as a multitude of flat sheets 1 stacked together with gaps between adjacent sheets to allow the flow of gas parallel to the sheet surface from the direction of gas inlet **2** to gas outlet **3**. A separator material was used between adjacent layers of carbon sheet. In this example the separator was a 230 μm thick polypropylene mesh.

EXAMPLE 7

[0047] This example shows the making of a parallel passage contactor with spiral configuration. Reference is made to Figure 5. The adsorbent material obtained as disclosed in Example 2 of this invention was manufactured as a long and continuous sheet **1** which was then rolled into a spiral with gaps between adjacent layers. The gas was allowed to flow parallel to the sheet surface from the direction of gas inlet **2** to gas outlet **3**. A separator material was used between adjacent layers of carbon sheets. In this example the separator was a 230 μm thick polypropylene mesh. The parallel passage contactor was tested for CO_2 / N_2 separation (see Example 9).

EXAMPLE 8

[0048] This example shows the making of a parallel passage contactor with honeycomb configuration. Reference is made to Figure 6. The adsorbent material obtained as disclosed in this invention was manufactured as a multitude of corrugated sheets **1** and flat sheets **2**. A multitude of alternating corrugated and flat sheets was assembled as shown in Figure 6. The gas would be allowed to flow parallel to the sheet surface from the direction of gas inlet **3** to gas outlet **4**.

EXAMPLE 9

[0049] This example demonstrates the performance of adsorbent materials manufactured according to the methods disclosed in Examples 1 and 2 when assembled as parallel passage contactors. Various activated carbon powders (such as MSP 20 from Kansai Coke & Chemicals Company; WPH from Calgon Carbon Corporation; and Picactif PCO from Pica USA), together with carbon black nanoparticles (Black Pearls 2000 from Cabott Corporation), were selected as raw materials for manufacturing adsorbent sheet materials according to the general procedures described in Examples 1 and 2. The properties of the obtained adsorbent sheet materials are outlined in Table 5. The manufactured materials were spiral wound around a central rod (0.63 cm diameter) to form parallel passage contactors as described in Example 7. The separator between adjacent adsorbent layers was a 230 μm thick polypropylene mesh. The typical length of the spiral wound rolls was 10.2 cm and the outer diameter was 2.22 cm. The resulted rolls were inserted in cylindrical canisters, which were connected to the gas line. In this configuration, the gas flow direction is parallel to the carbon adsorbent surface, as shown schematically in Figure 5.

Table 5

Properties of adsorbent carbon sheet materials made with carbon particulates from various sources							
Activated carbon source	Carbon precursor	Thickness (mm)	Bulk density (g/cm^3)	Areal weight (m^2/g)	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)
Cabott Corp. BP2000	Furnace carbon black	0.29	0.369	107	1200	0.257	1.60
Kansai Coke Maxsorb MSP20	Phenolic resin	0.20	0.525	105	1870	0.687	1.03
Calgon Carbon WPH	Bituminous coal	0.22	0.673	145	685	0.289	0.683
Picactif PCO	Coconut shell	0.33	0.596	197	907	0.404	0.606

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[0050] Pressure drop tests were performed for each cartridge using nitrogen, with the outlet at atmospheric pressure. The flow rate was increased to a maximum of 4.5 Umin and the pressure drop across the canisters was measured using a differential pressure transducer. The permeability of canisters was calculated from the following equation:

$$\beta = \frac{\mu Q l}{A \Delta P}$$

[0051] where Q (cm^3/min) is the flow rate, l (cm) is the length, and A (cm^2) is the cross section of parallel passage contactors, ΔP (Torr) is the pressure drop, and μ = 1.83 x 10^{-5} Pa.s is the gas viscosity. The permeability values expressed in Darcy units (1 Darcy = 0.987 x ^{10}-10 Pa.s) are given in Table 6. The higher the permeability, the lower the pressure drop across canister at equal volume flow rates.

[0052] Breakthrough tests were measured with 1 % CO_2 in nitrogen, at atmospheric pressure and room temperature. The canisters were purged several hours with pure nitrogen before each test. The tests consisted in injecting a step of 1 % CO_2 concentration in the nitrogen feed, and recording the gas composition at the outlet of the contactor. The gas composition in the feed was adjusted by varying the volume flow of nitrogen (between 1500 and 4500 Ncm^3/min) and carbon dioxide (between 5 and 60 Ncm^3/min). The gas composition downstream the contactor was analyzed using a Stanford Research Systems residual gas analyzer model RGA-100. The gas was continuously sampled from the discharge flow and directed into the analyzer via a 0.76 mm capillary and a differential pumping system. The sampling rate of the mass spectrometer was 2 seconds. The breakthrough profiles were analyzed according to the model developed by Yoon and Nelson (Am. Ind. Hygiene Assoc. J., 45 (8), 509, 517 (1984)) based on gas adsorption kinetics in a bed of solid sorbent. The main equation of the Yoon - Nelson model is:

$$\frac{C_{out}}{C_{in}} = \{1 + \exp[-k'(t - \tau)]\}^{-1}$$

[0053] It relates the concentration of contaminant that enters (C_{in}) or escapes (C_{out}) the contactor with τ, the time at 50 % breakthrough, and k', an apparent kinetic constant that indicates the slope of the breakthrough curves. With τ and k' measured from experimental data, an intrinsic kinetic constant k (independent on flow rate and concentration conditions) and an equilibrium adsorption capacity W_e (at the corresponding gas concentration) can be calculated:

$$k' = k\frac{C_{in}Q}{W_e} = \frac{k}{\tau}$$

[0054] The calculated values are given in Table 6. Large k values indicate fast mass transfer kinetics.

[0055] The separation efficiency of each contactor was evaluated from the number of theoretical plates, N, calculated as the ratio of the total column length to the height equivalent to a theoretical plate (L_{HETP}). The L_{HETP} values were calculated following the theoretical analysis of Ruthven and Thaeron (Gas. Sep. Purif. 10, 63 (1996)) from the first and second moments of the experimental breakthrough curves:

$$L_{HETP} = \frac{\sigma^2}{\mu^2}$$

[0056] where μ and σ are defined as follows in case of a step concentration variation:

$$\mu = \tau = \int_0^\infty \left(1 - \frac{C_{out}}{C_{in}}\right) dt$$

$$\sigma^2 = \int_0^\infty 2\left(1 - \frac{C_{out}}{C_{in}}\right) t\,dt - \mu^2$$

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[0057] Examples of calculated values are given in Table 6. The smaller the L_{HETP} value, the higher the separation efficiency of the parallel passage contactor.

[0058] The energy efficiency of the contactors was calculated in terms of pressure drop per theoretical stage, $\Delta P_{HETP}/L_{HETP}$, as suggested in the above cited reference by Ruthven and Thaeron. For this calculation we used the experimental permeability values (β) of each canister:

$$\frac{\Delta P_{HETP}}{L_{HETP}} = \frac{v}{\beta}$$

[0059] where v is the linear velocity. Examples of calculated values are given in Table 6. The smaller the ($\Delta P_{HETP}/L_{HETP}$) value, the lower is the energy penalty for circulating the gas through the parallel passage contactor.

Table 6

Performance of various adsorbent sheet materials when assembled in parallel passage contactors for CO_2/N_2 separation

Example	Activated carbon source	Carbon packing density (g carbon / cm^3)	Contactor permeability (Darcy)	Intrinsic kinetic constant	Capacity @ 7.6 Torr CO_2 (mmol/cm^3)	L_{HETP} @ 4.5 L/min (cm)	$\Delta P_{HETP}/L_{HETP}$ (mTorr/cm)
9	Granular 1 mm activated carbon	0.56	1645	2.82	0.038	3.71	1.6
9	Cabott Corp. BP2000	0.22	234	10.07	0.016	2.95	12.5
9	Kansai Coke Maxsorb MSP20	0.35	160	8.39	0.030	1.68	18.3
9	Calgon Carbon WPH	0.41	213	11.33	0.029	1.57	13.8
9	Picactif PCO	0.42	211	11.81	0.037	1.37	13.9
10	Kansai Coke Maxsorb MSP20 (no spacer)	0.32	794	7.67	0.028	1.63	3.9

[0060] The results in Table 6 show that, with one exception, all canisters have almost constant adsorption capacity for CO_2 at 7.6 Torr CO_2 in gas phase. This is a consequence of the intrinsic adsorption properties of various carbon materials and of the packing densities that can be achieved with them.

[0061] A comparison of CO_2 breakthrough curves from 1 vol % and 2 vol % CO_2 in N_2 at several flow conditions is shown in Figure 7 for equal volume canisters containing a bed a 1 mm granular activated carbon and a parallel passage contactor structure made from Kansai Coke Maxsorb MSP 20 activated carbon, according to this Example. Both canisters have almost equal capacity for CO_2, but the breakthrough profile is much sharper for the parallel passage contactor made according to this Invention. Similar results were found for all contactors made with adsorbent material sheets. Data in Table 6 show that they all have faster adsorption kinetics (higher intrinsic kinetic constant values) than the 1 mm granular activated carbon. This allows for using the PSA system at shorter cycle times when the contactors are made with carbon sheet materials. The sheet materials also show improved separation performance over granular

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carbon, as indicated by shorter HETP lengths in Table 6. However, the permeability of packed granular beds is higher than that of contactors made from spiral wound adsorbent layers plus separator mesh structures. As a result, the pressure drop per theoretical plate is lower for the granular carbon bed. In conclusion, at comparable adsorption capacity for CO_2, the contactors made with adsorbent sheet materials afford faster kinetics (shorter cycle times) and better separation (require lower column length), at the expense of higher pressure drop.

EXAMPLE 10

[0062] This Example shows the making of a parallel passage contactor with spiral configuration and without using a separator between adjacent layers of carbon adsorbent sheets. A 400 μm thick carbon adsorbent sheet containing 80 wt % MSP 20 from Kansai Coke & Chemicals Company, 10 wt % Black Pearls 2000 from Cabott Corporation and 10 wt % PTFE binder was manufactured according to Example 2. The carbon sheet was then aligned parallel to a 200 μm thick stainless steel perforated plate containing a pattern of alternating circular holes of 500 μm diameter separated by distances no shorter than 2 mm. The carbon layer and the patterned perforated plate were passed together between the rolls of a calender. As a result, the carbon sheet acquired a regular pattern of imprinted bosses, with heights of about 100 μm, and the overall thickness of the carbon layer, including the elevated bosses, became 300 μm. This carbon layer was then spiral wound around a central rod (0.63 cm diameter) to form parallel passage contactors as described in Example 7, with the difference that a polypropylene spacer was not used. The results of CO_2 breakthrough data analysis are shown in Table 6. In comparison with all other parallel passage contactors containing a polypropylene mesh spacer, the embossed structure without spacer demonstrates higher gas permeability at comparable carbon packing density, CO_2 adsorption capacity, and intrinsic kinetic constant values. As a result of all these factors, the separation efficiency was higher and the energy penalty (expressed as pressure drop per theoretical plate) was lower than for of all other contactors made with an inert separator mesh.

[0063] Examples 11 - 13 show that processing zeolite in a sheet form does not substantially reduce the N_2 adsorption properties of the raw zeolite powder.

EXAMPLE 11

[0064] A zeolite sheet material contained 90 % zeolite 13X in Na form and 10 % PTFE was obtained by blending 100 g of raw Na-X zeolite powder with 16.6 g of Teflon T30 in presence of water, followed by intensive mixing to cause PTFE fibrillation, biaxial calendaring to form the sheet, and drying. The sheets (0.25 mm thick) were air dried overnight at room temperature and for more 3 hours in air at 125 C.

EXAMPLE 12

[0065] A zeolite sheet material contained 90 % zeolite 13X in Na form and 10 % PTFE was obtained as described in Example 11, except that water was replaced by white gas. The sheets (0.25 mm thick) were dried for 3 hours in nitrogen at 125 C.

EXAMPLE 13

[0066] The zeolite containing sheet materials from Examples 11 and 12 were subsequently heat treated at higher temperatures in a TGA apparatus under a He stream. For comparison, the raw Na-X zeolite powder was treated in the same way. The results are shown in Figure 9. All samples eliminate water between about 100 and about 250 C. The water content is about 1 wt % for raw zeolite powder and between 5 - 8 wt % for sheet zeolite materials. The dried zeolite powder is stable above 400 C, while the PTFE component of the sheet zeolite materials from Examples 11 and 12 starts decomposes above a temperature of about 400 C

[0067] Based on this result, drying of raw zeolite powder and sheet formed materials was carried out at 340 C under a He stream in a microbalance. After drying, the temperature was reduced to 45 C and He gas was replaced by N_2. A sudden weight increase was seen with all samples. The weight uptake represents the amount of N_2 adsorbed, and the derivative of the weight change is a measure of instantaneous rate of adsorption. The data are shown in Figure 9 for the raw Na-X zeolite and in Figures 10 and 11 for zeolite sheets made according to procedures from Examples 11 and 12, respectively. For all samples, the cycles of adsorption and desorption of N_2 are very reproducible. The equilibrium amounts of N_2 adsorption were 0.0095 g N_2 / g zeolite for powdered Na-X zeolite (Figure 9) and 0.0073 g N_2 / g zeolite for the two zeolite sheet formed samples (Figures 10 and 11). The rate of adsorption were estimated to about 0.008 g N_2 min^{-1}/g zeolite for raw Na-X zeolite (Figure 9) and about 0.006 g N_2 min^{-1}/g zeolite for the two two zeolite sheet formed samples (Figures 10 and 11).

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Claims

1. An adsorbent material comprising adsorbent particulates and a polymer binder, fabricated into a reinforcement-free, self-supported, flexible, coherent sheet. Said sheet is configured for use as a parallel passage contactor.

2. The adsorbent material of claim 1 where the adsorbent particulates consist of fine particles from a first group, either alone or admixed with larger particles from a second group, or of particles from the second group alone.

3. The adsorbent material of claim 2 where the fine adsorbent particulates from the first group include carbon nanoparticles, inorganic oxides nanoparticles, and ceramic nanoparticles and have the characteristic length of nanoparticles in the range from 10 to 200 nm.

4. The adsorbent material of claim 2 where the larger adsorbent particles from the second group include activated carbon, inorganic oxides, ceramic materials, or synthetic polymeric resins and have the characteristic length of in the range from 0.2 μm to 100 μm.

5. The adsorbent material of claim 1 where the adsorbent particulates have the BET surface area, as measured by nitrogen adsorption, in the range of 200 to 2500 m^2/g, and the micropore volume in the range 0.2 to 1 cm^3/g.

6. The adsorbent material of claim 3 where the carbon nanoparticles are surface modified with diazonium salts derivatives to attach specific chemical groups with enhanced gas adsorption or reaction properties.

7. The adsorbent material of claim 3 where the inorganic oxides nanoparticles are surface modified to enhance gas adsorption or reaction.

8. The adsorbent material of claim 4 where the larger adsorbent particles are impregnated with inorganic salts, inorganic oxides, inorganic acids, inorganic bases, organic acids, amines, amides, acid chlorides for enhanced gas adsorption or reaction properties.

9. The adsorbent material of claim 1 where the sheet thickness is in the range of 50 to 1000 μ.

10. The adsorbent material of claim 1 where the open porosity (void volume fraction) of the sheet is in the range of 30 to 95%.

11. The adsorbent material of claim 1 where the sheet surface area to total sheet volume ratio is in the range 200 to 2500 m^2/cm^3 and the sheet micro pore volume to total sheet volume ratio is in the range 0.1 to 0.9.

12. The adsorbent material of claim 2 where polymer fibril binder is polyethylene, polypropylene, polytetrafluoroethylene (PTFE), polyvinylchloride (PVC), polyvinylidenechloride (PVDC), polyvinylidenefluoride (PVDF), polyamide, cellulose, cellulose derivates, or any other natural or synthetic polymer that is capable of suspending adsorbent particles in a random manner.

13. The adsorbent material of claim 2 where the binder is present in the range of 3 - 30 wt %.

14. The adsorbent material of claim 2 where the sheet tensile strength is greater than 2 kg/cm^2 and where the sheet is flexible and bendable.

15. The adsorbent material of claim 2 where the adsorbent particulates from either the first or the second group are one of the following forms of carbon: carbon nanotubes, carbon fullerenes, carbon black, activated carbon particles, activated carbon fibers.

16. The adsorbent material of claim 15 where the electrical resistivity of the adsorbent material sheet is lower than 200 ohm-cm and the current distribution is uniform.

17. The adsorbent material of claim 1 where the adsorbent particulates are clays and natural or synthetic zeolites.

18. The parallel passage contactor of claim 1 where the sheets are spiral wound or layered with gaps between adjacent sheets to allow the flow of gas parallel to the sheet surface.

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19. The parallel passage contactor of claim 18 where the sheets are separated by polymer netting, by polymer bumps screen printed on the sheet, by corrugation of the sheet, by indents and embosses formed in the sheets, or configured in a honeycomb design.

20. The parallel passage contactor of claim 18 where an impermeable casing surrounds the contactor and provides connections for gas inlet and outlet.

21. The parallel passage contactor of claim 19 where the sheet is made from the adsorbent material of claim 16.

22. The parallel passage contactor of claim 21 where the sheet is electrically contacted at opposing ends.

23. The parallel passage contactor of claim 20 where the air permeability measured between inlet and outlet is greater than 10^{-15} m^2.

24. The parallel passage contactor of claim 20 where the ratio of total micropore volume to total parallel passage contactor volume is in the range 0.05 to 0.7.

25. The parallel passage contactor of claim 20 used in pressure swing adsorption.

26. The parallel passage contactor of claim 20 used in thermal swing adsorption.

27. The parallel passage contactor of claim 22 used in electrical swing adsorption.

28. The parallel passage contactor of claim 20 used as heterogeneous catalyst support.

29. The parallel passage contactor of claim 20 used in gas separation or concentration in rapid cycle pressure swing adsorption systems.

30. The parallel passage contactor of claim 20 used for gas filtration devices such as gas masks, clean air rooms, cabin air, and indoor air filters.

31. The parallel passage contactor of claim 20 used for air dehumidification.

32. The parallel passage contactor of claim 20 used for separation of air components.

33. An adsorbent material comprising adsorbent particulates and a polymer binder, fabricated on a substrate by tape casting or printing to form a sheet. Said sheet is configured for use as a parallel passage contactor.

34. The parallel passage contactor of claim 33 where the substrate thickness is less than 60 microns.

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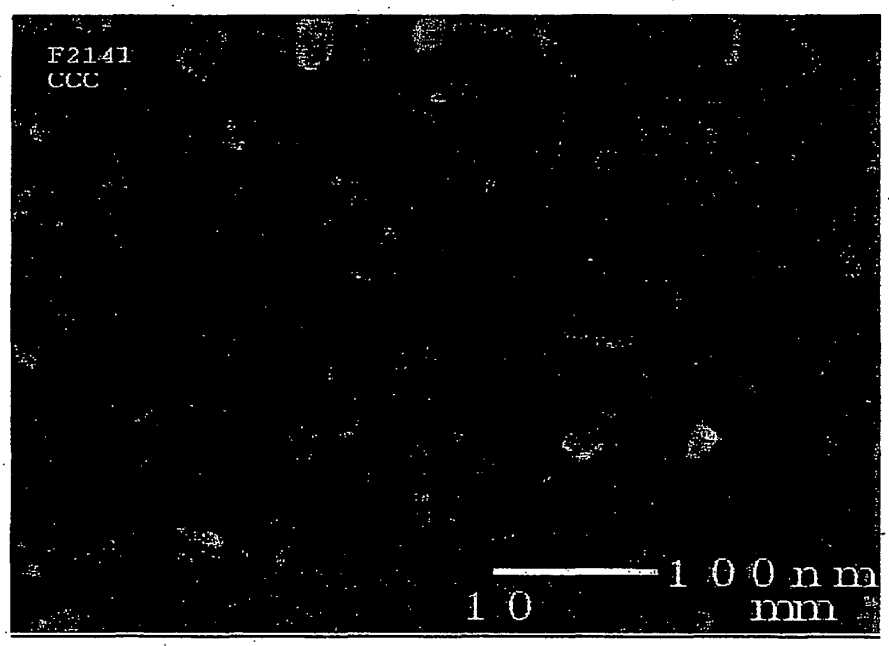


Figure 1

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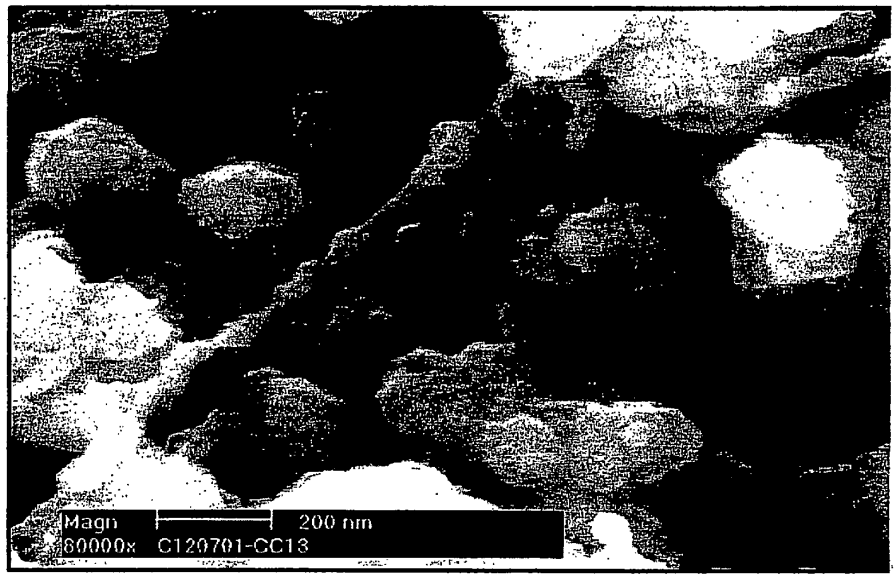


Figure 2

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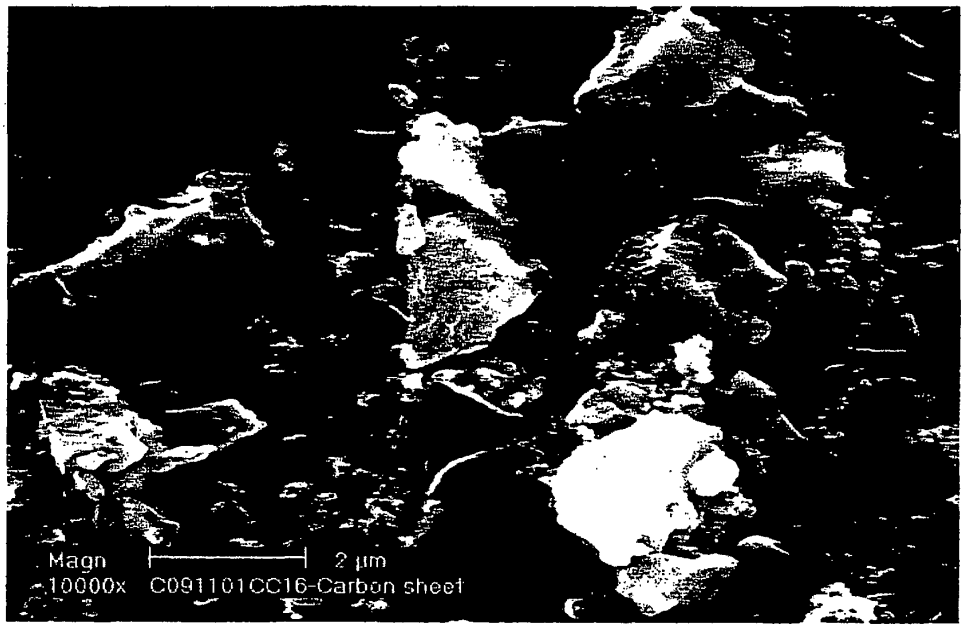


Figure 3

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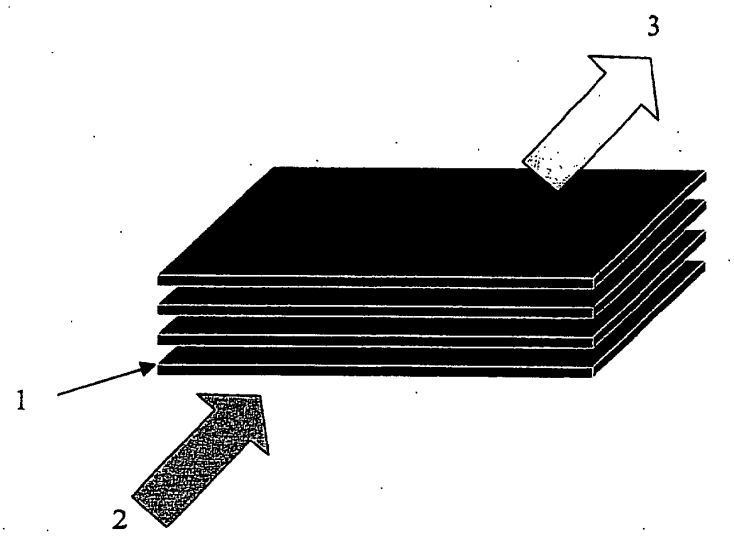


Figure 4

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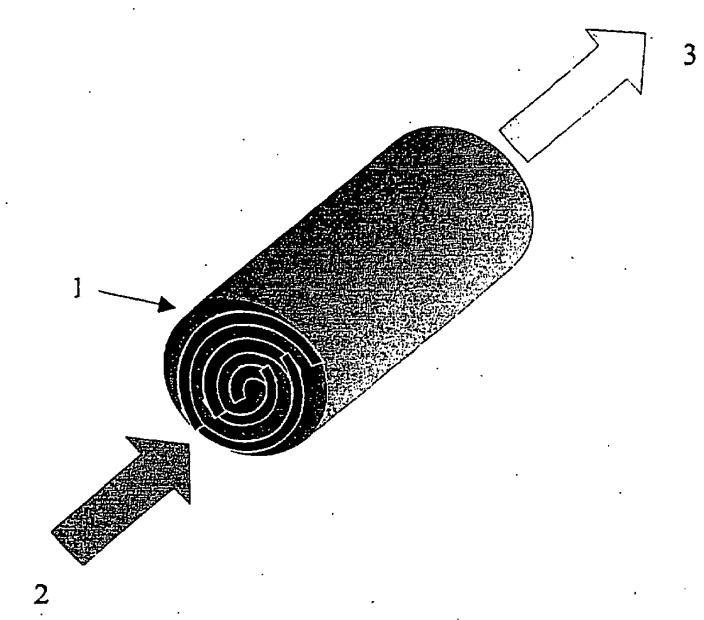


Figure 5

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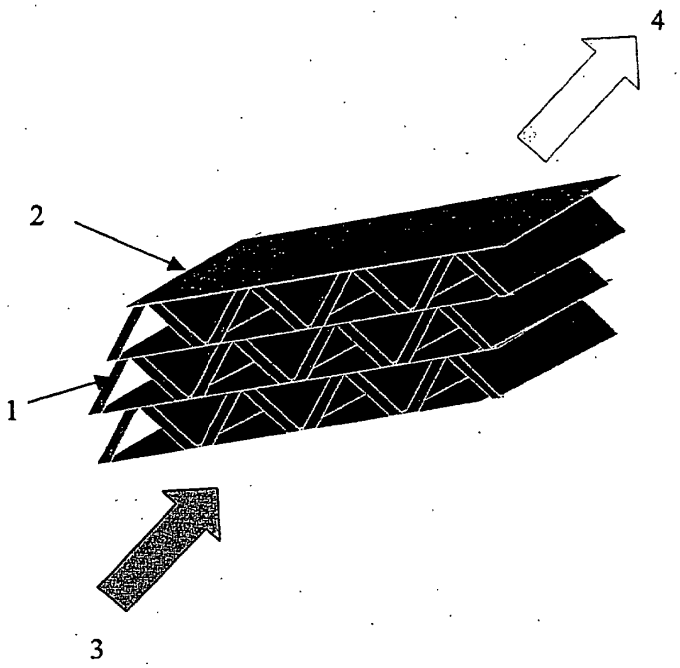


Figure 6

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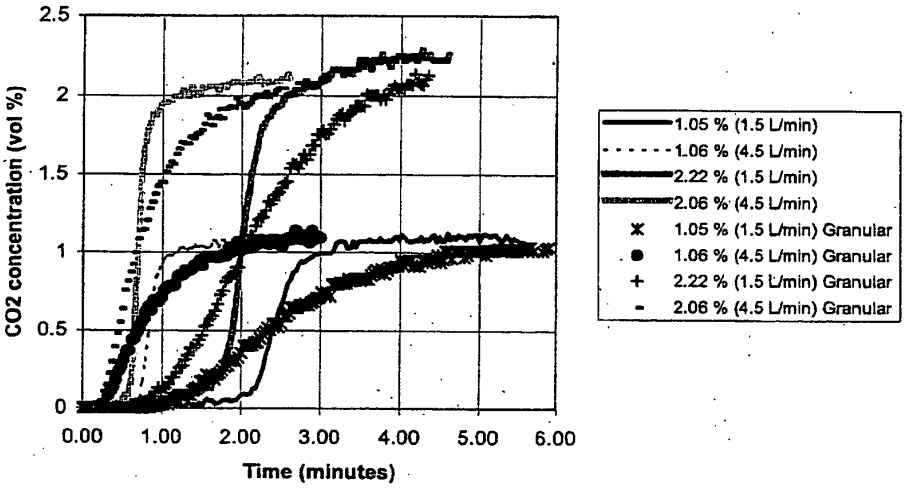


Figure 7

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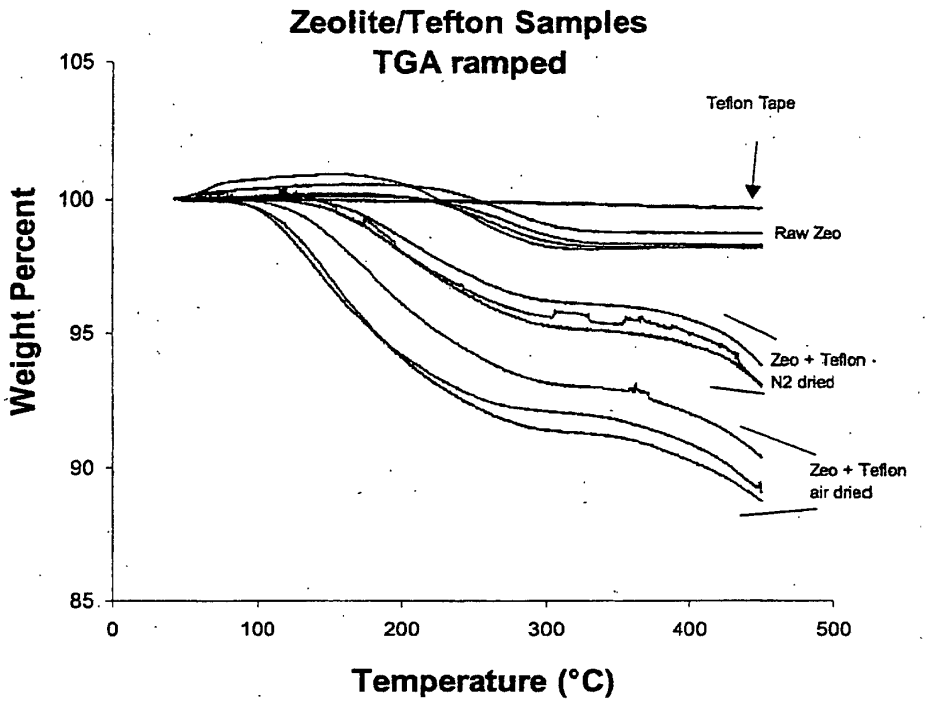


Figure 8

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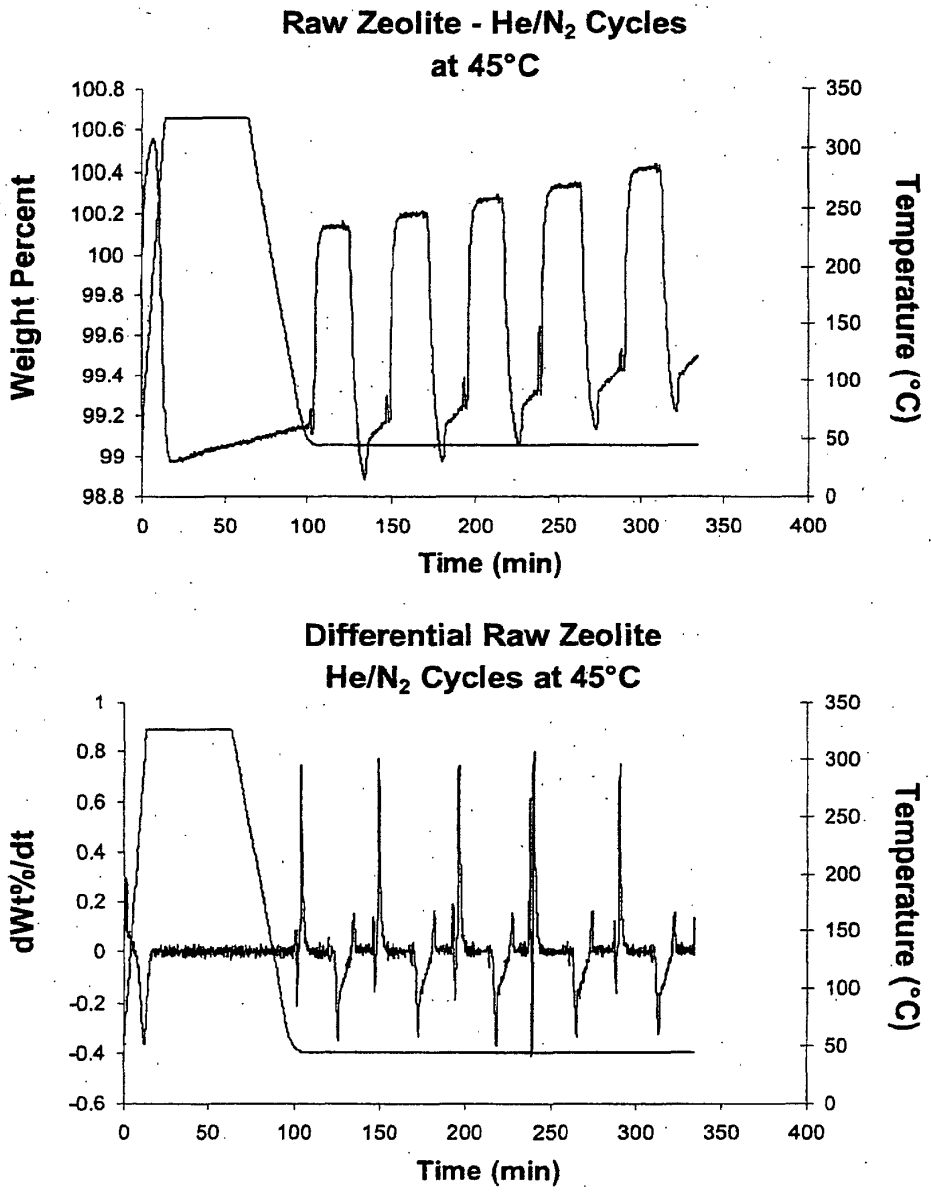


Figure 9

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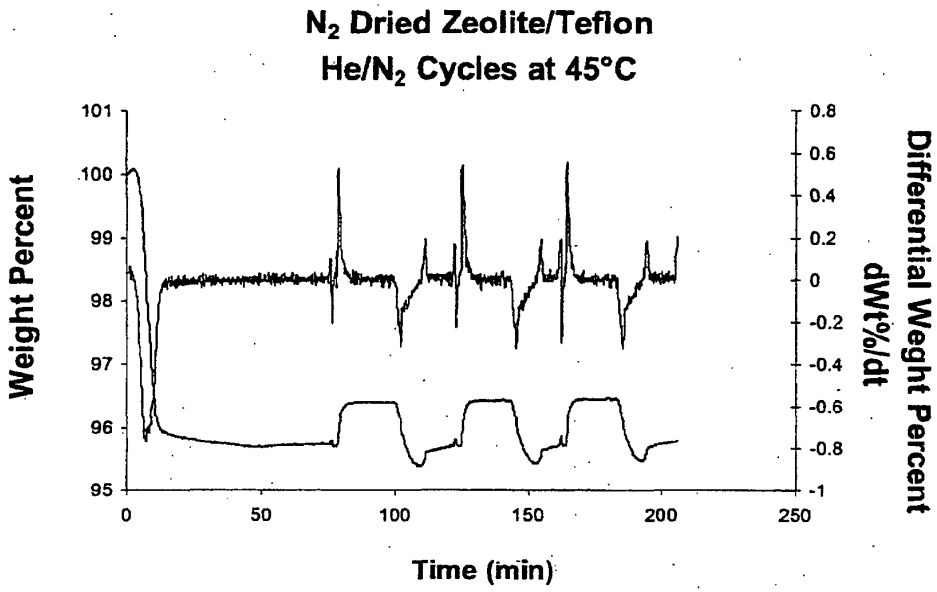


Figure 10

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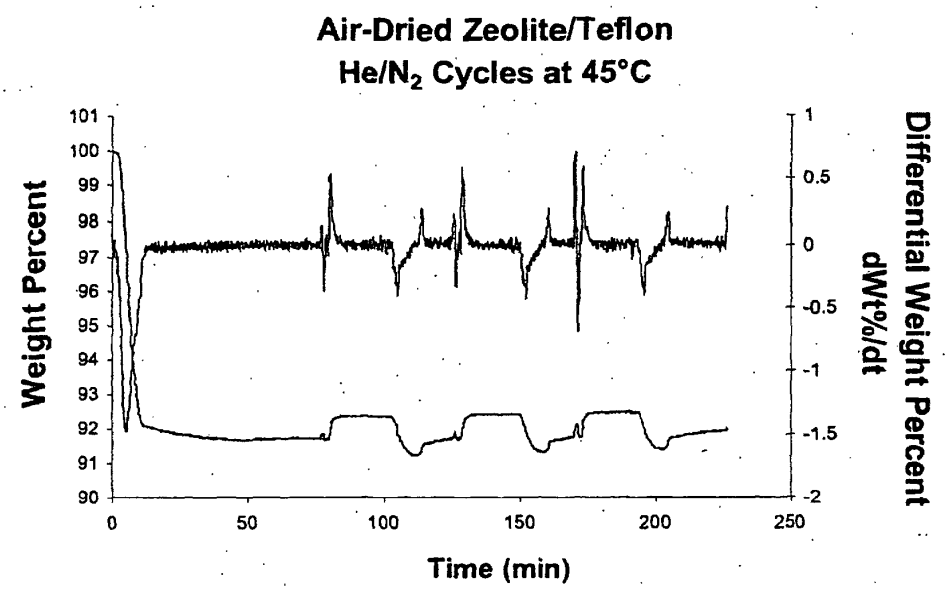


Figure 11

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 01 8329

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	US 5 071 610 A (BALSIMO WILLIAM V ET AL) 10 December 1991 (1991-12-10) * abstract * * column 3, line 55-60 * * column 7, line 27-29 * * column 9, line 23-46 * * column 12, line 39-48 * * column 14, line 24-47 *	1,2,4, 7-13, 17-19, 28,30-32	B01D53/04 B01J20/28
D,X	US 4 153 661 A (REE BUREN R ET AL) 8 May 1979 (1979-05-08) * column 4, line 54 - column 5, line 17; claims 1,6-8,10; example 24 *	1-4,8-17	
X	US 5 738 790 A (HANSEN PAUL E ET AL) 14 April 1998 (1998-04-14) * abstract; claims 1,12,14 * * column 2, line 34-62 *	1,2,4,7	
X	US 5 891 402 A (HOBSON ALEX R ET AL) 6 April 1999 (1999-04-06) * abstract; claims 1-9; figures 1,4 *	1-4,7, 18-20, 24,28, 30,33	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B01D B01J
X	US 5 972 077 A (BURCHELL TIMOTHY D ET AL) 26 October 1999 (1999-10-26) * abstract; claims 1,2; figure 2 *	1,5,10, 27	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	17 October 2003	Degen, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 01 8329

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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17-10-2003

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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1336241

PATENT SPECIFICATION (11) 1336241

NO DRAWINGS

(19)

(21) Application No. 469/71 (22) Filed 5 Jan. 1971
(31) Convention Application No. 10146 (32) Filed 5 Feb. 1970
(31) Convention Application Nos. 17353 and 17354
(32) Filed 26 Feb. 1970
(31) Convention Application No. 31412 (32) Filed 13 April 1970
(31) Convention Application No. 69398 (32) Filed 7 Aug. 1970 in
(33) Japan (JA)
(44) Complete Specification published 7 Nov. 1973
(51) International Classification C02B 1/18
(52) Index at acceptance
CIC 211 212 215 216 251 253 254 30X 400 406 40X 414
CIA K4

(54) PURIFICATION PROCESS

(71) We, OSAKA SODA CO. LTD., a Japanese body corporate of 53, 1-chome, Edobori, Nishi-ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for removing metals from gaseous (including vaporous) or liquid (including slurry) materials.

Various metal-containing gases and liquids are known. Examples include concentrated aqueous alkali solutions obtained by the electrolysis of alkali salts in a mercury cell; hydrogen gas and synthetic hydrochloric acid synthesized from hydrogen gas and chlorine gas; waste water and waste gases formed during the electrolysis of alkali salts in a mercury cell; waste liquids and waste gases which are produced during the smelting of zinc, mercury, copper and other metals; waste water of the plating industry; waste liquors containing catalysts or decomposed products thereof, which have been used in polymerisation reactions and other catalytic reactions; various waste liquors of the synthetic chemical industry which use metal compounds; and other metal-containing, and especially heavy metal-containing waste gases and liquids, which are produced in a broad range of inorganic and organic chemical industries and the mining industry. It is desirable to recover the metals not only for their own intrinsic value but also to prevent environmental pollution.

Usually metals are removed from materials containing them by adding a precipitating agent or a flocculating agent to the material in order to precipitate or flocculate the metal, or by using an adsorbent such as active carbon to adsorb the metal. These methods, however, suffer various disadvantages; for example it can be difficult to separate the precipitate or flocculate from the waste liquid being treated and there is a need for large scale apparatus.

Metals, particularly mercury, have been removed from gases by cooling the gas to a low temperature at normal pressure or superatmospheric pressure (3 to 5 kg/cm²) and condensing metal vapour or by passing the gas through a layer packed with active carbon or a molecular sieve to adsorb the metal. Once again these methods suffer various disadvantages; for example they may require large-scale cooling equipment to cool the gas or large quantities of adsorbents are required.

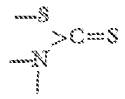
Chemical methods have also been employed. For example mercury has been removed from hydrogen gas as mercuric chloride by treatment with a hypochlorite or has been removed by treatment with a sulfuric acid-potassium permanganate solution. Control of these methods is difficult and recontamination of the gas can take place.

We have found that metals can be removed from a gaseous or liquid metal-containing material by a method which comprises contacting the material with a solid treating agent comprising a carrier having adsorbed thereon an organic compound

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which is capable of forming a mercaptide of the metal to be removed and which either contains an —SM group, where M is hydrogen or an alkali metal, or an

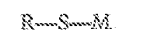


group or is an N,N'-substituted thiourea in which the substituents are bonded to nitrogen through carbon atoms.

The treating agent utilised in accordance with the invention can readily be prepared from available materials and retains its activity over prolonged periods. The concentration of metal in the metal-containing material can be reduced to values of the order of a few ppb (parts per 10^9 parts).

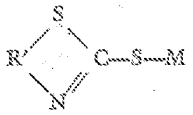
Examples of compounds which contain an —SM group, M being as hereinbefore defined are:

(1) Compounds of the formula



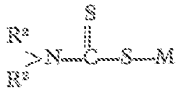
wherein R is an aromatic group or a group having a terminal —CH= or —CH_2— group.

(2) Thiazole compounds of the formula



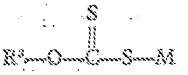
wherein R' is an aromatic group.

(3) Dithiocarbamic acids and their salts of the formula



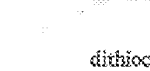
wherein each R^a is a C_1—C_{10} alkyl group, for example methyl, ethyl or n-butyl, or the two R^a groups together represent an alkylene group, for example pentamethylene.

(4) Xanthates of the formula

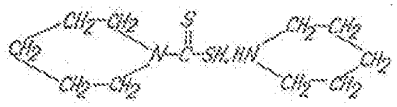


wherein R' is butyl or isopropyl.

Specific examples of compounds which contain an —SM group are: —2-aminoethanethiol; butyl-mercaptan; cyclohexylamine salt of 2-mercaptobenzothiazole; L-cysteine; 2,3-dimercapto-1-propanol; glutathione; 2-mercaptobenzothiazole and its alkali metal salts; 2-mercaptoethanol; dl-mercaprosuccinic acid; pipecoline pipecolyl



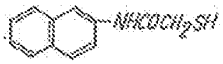
dithiocarbamate ($CH_3C_5H_9NC$—$SH.NC_5H_9CH_3$); piperidine pentamethylene dithiocarbamate



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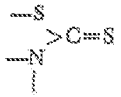
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thioacetic acid; thioglycolic acid and its alkali metal salts; thionalide

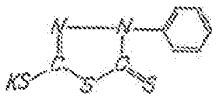


thiophenol and its alkali metal salts; and isopropyl xanthic acid and its alkali metal salts.

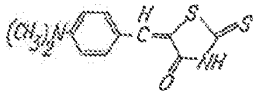
Specific examples of compounds which contain an



group are:
Bismuthiol II

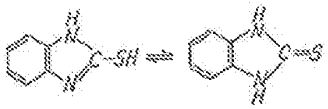


p-Dimethylaminobenzylidenerhodanine

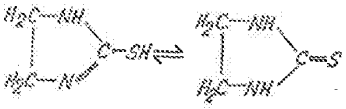


The N,N'-substituted thioureas preferably are those in which the substituents are aromatic groups or C_1—C_{10} alkyl groups. Specific examples of N,N'-substituted thioureas are:

2-Mercaptobenzimidazole (O-Phenylene thiourea)



2-Mercaptoimidazole (Ethylenethiourea)



Thiocarbanilide (Diphenylthiourea)



Di-orthotolylthiourea

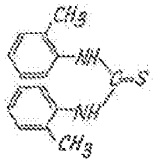
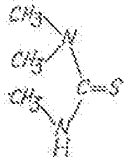


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Trimethylthiourea



The process of the invention may be carried out using a carrier on which is adsorbed not only the compound capable of forming a mercaptide of the metal to be removed but also an organic compound which is capable of forming a chelate compound of the metal to be removed and which contains an —OH group and one or more groups selected from —N= and —NH_2 groups. Examples of such compounds are:— anthranilic acid; oxine (8-hydroxyquinoline); and 2-methyl oxine (8-hydroxyquinaldine).

The organic compounds which can be used in the present invention include both water-soluble and water-insoluble compounds. They can be dissolved in suitable inert solvents and then deposited on the carrier by adsorption. Solvents which may be used include water, aqueous alkaline solutions containing an inorganic alkaline substance such as an alkali metal hydroxide, alkali metal carbonate, alkali metal bicarbonate or ammonia; methanol, ethanol, propanol, butanol and other C_1—C_{10} aliphatic alcohols; halogenated lower (C_1—C_4) hydrocarbons such as dichloromethane, trichloromethane, and trichloroethylene; di- lower alkyl (C_3—C_4) ketones such as acetone; carbon tetrachloride; and chloroform.

The preferred solvents are those which can be readily removed after the organic compounds have been deposited on the carrier material by, for example, water-washing, washing with dilute aqueous acid solutions, evaporation, vacuum drying and air drying. A solvent need not be used when the organic compound is normally liquid.

The carrier can be contacted with the organic compound or a solvent solution thereof by any suitable method, for example, immersion of the carrier or passage of the organic compound or solution through a column packed with the carrier. The organic compound is usually deposited on the carrier at room temperature but, if desired, the operation can be carried out at elevated temperatures, such as from 30° to 70° C.

After the organic compound has been deposited, the resulting solid treating agent can be used directly but, if desired, it may be used after treatment to remove solvent contained therein.

The carrier which constitutes the substrate of the solid treating agent can be a natural or artificial material. Preferred carriers are carbon, in such forms as active carbon and bone black, silica gel, zeolite and silica alumina gels containing at least 50% by weight of silica gel. If desired, organic polymeric adsorbents and molecular sieves can be used as the carrier material, but these are less desirable because of their high cost. Carriers such as alumina, magnesia and naturally occurring quartz sand can also be used, but they do not give such good results.

The particle size of the carrier can be varied over a broad range and sizes of 2 to 180 mesh (Tyler sieve), and preferably 6 to 150 mesh, may be used. The amount of the organic compound deposited on the carrier can also vary over a broad range, and amounts of from 1 to 30% by weight, preferably 2 to 20% by weight, based on the carrier may be used. The particle size of the carrier and the amount of organic compound deposited thereon can be adjusted to suit the type of carrier, of organic compound, and of material to be treated, the method used to contact the metal-containing material and the contact time.

There is no special restriction on the method to be used in contacting the solid treating agent and the metal-containing material in accordance with the invention. Any method which is capable of bringing about sufficient contact can be utilized. Although batch methods can be employed it is preferred to employ a continuous method such, for example, as treatment in a column.

For example, a metal-containing material can be passed downwardly or upwardly through a column packed with the solid treating agent; a gaseous metal-containing material may be passed through a fluidized bed of the solid treating agent; or a liquid metal-containing material can be sprayed onto the treating agent. The contact

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treatment can be carried out in a single stage or in a multistage fashion by providing a plurality of contact zones through which the metal-containing material is passed. The temperature of the contact treatment is not critical and suitable temperatures are from 5 to 35° C. The contact time can readily be varied to suit the conditions of the treatment. In general, the optimum conditions can be readily determined experimentally over a range of SV (space velocity)=0.2 to 20 l/hr when the metal-containing material is in the liquid phase and over a range of SV=100 to 5000 l/hr when the metal-containing material is gaseous.

Metals which can be removed from gaseous or liquid metal-containing materials in accordance with the invention include Hg, Au, Bi, Cd, Co, Cr, Cu, Ni, Pb, Zn, Ag, Mn, Fe, Mo, Ti, Mg and Al.

The organic compound should be chosen with the particular metal to be removed in mind. For example, thionalide, 2-mercaptobenzothiazole and p-dimethylaminobenzilidene-rhodanine are preferably used in the case of Hg, Cu, Au, Ag, Cd and Pb; oxine and 2-mercaptobenzothiazole in the case of Bi, Co, Ni and Zn. When the material to be treated contains a plurality of metals, a mixture of organic compounds can be used.

When the metal-containing material is a liquid, it is possible to pretreat the material with an anion exchange resin and thereafter contact the metal-containing material with the solid treating agent. In general, when the content of metal is high and recovery of the metal is also intended, a pretreatment of this kind is desirable. Since the recovery of the metal from the anion exchange resin is a relatively simple matter, the metal contained in the metal-containing material being treated can largely be recovered by such a pretreatment, after which the smaller amount of metal contained in the residual liquid can be contacted with the solid treating agent to effect its removal. Anion exchange resins which can be used include those having as the exchange group

$$—N—(CH_2)_nX,\ —N<\begin{matrix}(CH_2)_nX\\ C_nH_nOH,\end{matrix},\ —N(Q)_2,\ —NH(Q)\ \text{and}\ —NH_2,$$

wherein X is an anion such as Cl^- or OH^- and Q is an alkyl group such as CH_3 or C_2H_5.

The pretreatment operation can be carried out by passing the metal-containing liquid through a column packed with the anion exchange resin. Alternatively, the anion exchange resin can be placed in a tank filled with the metal-containing liquid, the mixture stirred and the resin then separated from the treated liquid.

The process of the invention can be applied to the treatment of a wide variety of metal-containing materials, including both acidic and basic materials. For example, the process can be applied to the removal of Hg from concentrated aqueous alkali solutions obtained in the mercury cell electrolysis of alkali salts; the removal of Hg from hydrogen gas evolved during such an electrolysis; the removal of Hg from hydrochloric acid synthesized from such hydrogen gas and chlorine gas; the removal of Hg from the various waste gases and water produced during the mercury cell electrolysis of alkali salts; the removal of Hg, Cd, Mn, Cr, Cu and Fe from the various waste gases and water which are produced during the smelting of various metals; the removal of Cr and Cu from the waste water of the plating industry; the removal of Hg, Cd, Mn, Cr, Cu and Fe from waste liquids containing catalysts or decomposition products thereof, as well as from the waste gases and water produced in the synthetic chemical industry; and the removal of metals contained in a wide range of other gaseous and liquid materials.

The following Examples and Controls serve to illustrate the invention. In the Examples mesh sizes are Tyler Standard Screen sizes.

Example 1

A saline solution prepared from mercuric chloride and sodium chloride (mercury content 13.9 mg per litre) was passed at the rate of 130 cc per hour through a tube of 8 mm diameter containing 10 grams of silica gel having 500 mg of 2-mercaptobenzothiazole adsorbed thereon. This test was repeated ten times. In every case the mercury concentration in the effluent was less than 5 ppb.

Control 1

Example 1 was repeated except that the silica gel had no 2-mercaptobenzo-

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thiazole adsorbed thereon. The test was repeated ten times and in every instance the mercury concentration of the effluent was above 13000 ppb.

Example 2

One hundred mg of thionalide in solution in 100 ml of dichloroethane were passed through a glass tube of 8 mm inside diameter packed with 5 grams of active carbon, thereby effecting retention of the thionalide on the active carbon, followed by removal of the solvent by blowing in air. A solution containing 5.6 mg per litre of mercury was passed through this thionalide-supporting carrier at the rate of 130 ml per hour, whereupon the mercury concentration of the effluent became less than 50 ppb.

Examples 3 to 24

Experiments were carried out using as the method of contact either the column method of Example 1 or a batch method in which 200 ml of a saline solution of the metal to be removed is mixed with a sample of the solid treating agent and the mixture is then gently stirred for one hour and various combinations of the organic compound and carrier, with various metals to be removed. The results obtained are shown in Table 1.

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TABLE 1

Solid Treating Agent

Experiment No	Organic Compound used		Amount deposited (wt. %)	Solvent used	Carrier	
		Name			Name	Weight (g)
Example 3	2-mercaptobenzothiazole		10	CH_2Cl_2	active carbon	5
" 4	thionalide		2	$CHCl_3$	"	5
" 5	2-mercaptobenzothiazole		10	CH_2Cl_2	"	5
" 6	p-dimethylaminobenzylidene rhodanine		2	$(CH_3)_2CO$	"	5
" 7	thionalide		2	$CH\ Cl_3$	"	5
" 8	2-methylaxine plus 2-mercaptobenzothiazole		12	CH_2Cl_2	"	5
" 9	2-mercaptobenzothiazole		20	3% aq NaOH sol	"	5
" 10	2-mercaptobenzothiazole		10	acetone	"	5000
" 11	2-mercaptobenzothiazole (Na salt)		8	water	"	30
" 12	bismuthiol II		7.5	water	bone black	40

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TABLE 1 (Continued)

Solid Treating Agent

Experiment No		Organic Compound used: Name	Amount deposited (wt. %)	Solvent used	Carrier: Name	Carrier: Weight (g)
Example	13	Na salt of diethyldithiocarbamic acid	5	Water	active carbon	40
do	14	Na salt of isopropyl xanthic acid	4.5	do	do	30
do	15	pipecoline pipecolyl dithiocarbamate	3.5	3% aq NaOH sol	do	40
do	16	2,3-dimercapto-1-propanol	3.0	water	do	40
do	17	2-mercaptoethanol	2.8	do	do	30
do	18	Na salt of 2-mercaptobenzothiazole	2.3	do	silica gel	100
do	19	thionalide	3.0	$CHCl_3$	active carbon	5
do	20	bismuthiol II	7.5	water	do	5
do	21	2-mercaptobenzothiazole plus anthranilic acid	total 10	3% aq NaOH sol	do	5
do	22	p-dimethylaminobenzylidene rhodanine plus 3-mercaptobenzothiazole	total 15	acetone	do	5
do	23	oxine plus pipecoline pipecolyl dithiocarbamate	total 15	do	do	5
do	24	8-hydroxy quinaldine plus p-dimethylamino-benzylidene rhodanine	5	do	do	5

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TABLE 1 (Continued)

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method) 1/hr	Material treated: Metal to be removed	Material treated: Property	Metal Concentration (ppb): Before Treatment	Metal Concentration (ppb): After Treatment
Example 3	6.5	Hg	aq sol	5600	5
4	10	Hg & Cu	"	Hg 5600 Cu 2500	50 10
5	5.0	Hg & Fe	"	Hg 5600 Fe 300	5
6	7.0	Hg	"	13,900	5
7	7.8	Cd	"	200	30
8	8.0	Hg	"	5500	5
9	10.5	Hg	"	10,200	5
10	(contact time 1 hr)	Hg	aq slurry	25,000	250
11	(contact time 2.5 hr)	Hg & Cd	aq sol	Hg 8200 Cd 600	7 40
12	(contact time 2.5 hr)	Hg & Cu	"	Hg 5500 Cu 500	9 30
13	2.1	Hg & Cu	"	Hg 5600 Cu 1200	8 54
14	2.1	Hg	"	8300	6

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TABLE 1 (Continued)

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method) l./hr	Material treated		Metal Concentration (ppb)	
		Metal to be removed	Property	Before Treatment	After Treatment
Example 15	1.1	Hg	aq sol	7800	8
do 16	1.0	Hg	do	2500	10
do 17	1.0	Hg	do	2700	12
do 18	2.0	Hg & Cd	do	Hg 8200 Cd 600	8 50
do 19	10	Hg Ag Pb	do	9600 1200 4100	50 70 75
do 20	8.0	Al Cd Cu Hg	do	1600 750 1200 9800	100 40 55 20
do 21	7.0	Co Zn Cd Ni Hg	do	900 1500 3500 700 7700	50 55 25 40 7
do 22	7.5	Ag Bi	do	2400 420	35 15
do 23	6.0	Mn Cr Fe	do	1200 720 2900	60 75 25
do 24	6.5	Mo Ti Mg Ag	do	950 1300 750 1200	60 75 80 30

IFW Document ID: <dd_____1336241A__i_>

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Examples 25 to 48 and Control 2

Experiments were carried out on acidic or basic mercury-containing materials. As the former, mercury-containing concentrated aqueous hydrochloric acid solutions were used while, as the latter, mercury-containing aqueous alkali solutions were used. The results obtained are shown in Table 2. Also shown in Table 2 are the results obtained as Control 2 wherein the experiment was carried out exactly as in Example 47 except that an organic compound was not deposited on the active carbon.

TABLE 2

Experiment No.		Solid Treating Agent: Organic Compound Used: Name	Amount deposited (wt. %)	Solvent used	Carrier: Name	Carrier: Weight (g)
Example	25	Na salt of 2-mercaptobenzothiazole	10	water	active carbon	160
do	26	2-mercaptobenzothiazole	abt 20	3% aq NaOH sol	do	40
do	27	pipecoline pipecolyl dithiocarbamate	abt 10	acetone	do	20
do	28	thionalide	abt 2.5	dichloro-methane	do	20
do	29	p-dimethylaminobenzylidene rhodanine	abt 4.0	acetone	do	10
do	30	2-mercaptobenzothiazole	abt 2.0	3% aq NaOH sol	bone black	10
do	31	bismuthiol II	abt 3.0	water	active carbon	20
do	32	thiophenol	abt 1.0	ethanol	do	10
do	33	piperidine pentamethylene thiocarbamate	abt 5.0	acetone	do	10
do	34	2-mercaptoimidazole	abt 2.0	methanol	do	10

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TABLE 2 (Continued)

Solid Treating Agent

Experiment No.	Organic Compound Used: Name	Amount deposited (wt. %)	Solvent used	Carrier: Name	Carrier: Weight (g)
Example 35	sodium diethyldithiocarbamate	abt 5.0	water	active carbon	20
do 36	2-mercaptobenzothiazole	abt 3.0	acetone	silica gel	10
do 27	p-dimethylaminobenzylidene rhodanine	abt 1.5	do	zeolite	20
do 38	sodium diethyldithiocarbamate	abt 5.0	6% aq NaOH sol	active carbon	150
do 39	2-mercaptobenzothiazole	10	acetone	do	40
do 40	L-cysteine	6.0	water	powdered active carbon	50
do 41	sodium salt of 2-mercaptobenzothiazole	abt 5.0	do	active carbon	40
do 42	glutathione (reduced type)	abt 3.0	do	powdered active carbon	50
do 43	L-cysteine	abt 2.0	weak alkali	molecular sieve	40

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TABLE 2 (Continued)

Experiment No		Solid Treating Agent: Organic Compound used: Name	Amount deposited (wt. %)	Solvent used	Carrier: Name	Carrier: Weight (g)
Example	44	bismuthiol II	1.5	water	active carbon	40
do	45	sodium salt of thiophenol	1.0	weak alkali	powdered active carbon	50
do	46	2-mercaptobenzothiazole	abt 1.5	acetone	zeolite	40
do	47	thioglycolic acid	abt 1.0	water	active carbon	40
do	48	thionalide	abt 2.5	dichloro-methane	powdered active carbon	50
Control 2		—	—	—	active carbon	40

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TABLE 2 (Continued)

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method) 1/hr	Material treated: Metal to be removed	Material treated: Property	Metal concentration (ppb): Before treatment	Metal concentration (ppb): 120 hrs later
Example 25	(contact time 2 hrs)	Hg	conc HCl	2800	7
do 26	11.0	Hg	do	1700	4
do 27	(contact time 2 hrs)	Hg	do	1700	6
do 28	(do 2.5 hrs)	Hg	do	1700	30
do 29	(do 2.0 hrs)	Hg	do	1700	5
do 30	(do 2.0 hrs)	Hg	do	1300	12
do 31	(do 3.0 hrs)	Hg	HCl 35%	1300	24
do 32	(do 2.0 hrs)	Hg	do	1300	30
do 33	(do 2.5 hrs)	Hg	do	1300	15
do 34	(do 2.5 hrs)	Hg	do	1300	25
do 35	(do 2.5 hrs)	Hg	do	1700	30
do 36	(do 2.5 hrs)	Hg	do	1700	10
do 37	(do 2.5 hrs)	Hg	do	1300	8
do 38	(do 3 hrs)	Hg	NaOH 25%	150	30
do 39	0.7	Hg	NaOH 48%	250	15

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TABLE 2 (Continued)

Experiment No.	Time contacted with liquid material being treated (batch method) or space velocity (column method) 1/hr	Material treated		Metal concentration (ppb)	
		Metal to be removed	Property	Before treatment	120 hrs later
Example 40	1.5	Hg	KOH 48%	120	10
do 41	2.0	Hg	NaOH 48%	120	10
do 42	0.8	Hg	do	200	30
do 43	1.2	Hg	do	100	15
do 44	0.5	Hg	do	100	15
do 45	0.4	Hg	do	150	30
do 46	0.5	Hg	KOH 45%	200	27
do 47	0.4	Hg	NaOH 46%	150	25
do 48	1.5	Hg	NaOH 48%	150	30
Control 2	0.4	Hg	---	150	120

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Example 49

Sixty grams of 2-mercaptobenzothiazole were dissolved in 1.2 litres of a caustic soda solution of 3% concentration, after which the resulting solution was passed through 300 grams of active carbon of 6 to 20 mesh to effect retention of the former on the latter. The amount adsorbed was about 18% by weight based on the active carbon.

After water-washing and air drying the 2-mercaptobenzothiazole-adsorbed active carbon particles, they were packed in an acrylic resin tube of 60 mm inside diameter and about 25 cm high. This was followed by passing hydrogen gas containing 9.1 mg per cubic meter of mercury through the tube at a space velocity of 2500 1/hr at room temperature, whereupon the mercury content of the hydrogen gas after passage through the tube was 0.001 mg/m^3 6 hours later, 0.002 mg/m^3 30 hours later and 0.002 mg/m^3 90 hours later.

Examples 50 to 59 and Control 3

Experiments were carried out as in the hereinabove described Example 49, varying the organic compound the class of the carrier and the material being treated. The results obtained are shown in Table 3 below, along with the results of Example 49. Also presented are the results of Control 3, which was also carried out as in Example 49 but without deposition of an organic compound on the carrier.

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TABLE 3

Solid Treating Agent

Experiment No.		Organic Compound Used				Carrier	
		Name	Amount deposited (wt. %)	Solvent used	Name	Weight (g)
Example	49	2-mercaptobenzothiazole	18	3% aq NaOH sol	active carbon	300
Control	3	—	—	—	do	300
Example	50	p-dimethylaminobenzylidene rhodanine	abt 4.0	acetone	do	25
do	51	thionalide	3.0	dichloroethane	do	25
do	52	2-mercaptobenzothiazole	2.0	5% aq NaOH sol	bone black	40
do	53	2-mercaptobenzothiazole	1.0	5% aq NaOH sol	silica gel	75
do	54	2-mercaptobenzothiazole	5.0	do	active carbon	20
do	55	pipecoline pipecolyl dithiocarbamate	3.0	acetone	zeolite	30
do	56	2-mercaptobenzothiazole plus pipecoline pipecolyl dithiocarbamate	6.0	do	active carbon	25
do	57	2-mercaptobenzothiazole	10.0	3% aq NaOH sol	do	25
do	58	thiophenol	1.0	ethanol	do	25
do	59	sodium salt of 2-mercaptobenzothiazole	5.0	water	do	40

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TABLE 3 (Continued)

Experiment No.	Space velocity (1/hr)	Material treated: Metal to be removed	Material treated: Property	Metal concentration (μg/m³): Before treatment	Metal concentration (μg/m³): After treatment: 6 hrs later	Metal concentration (μg/m³): After treatment: 90 hrs later
Example 49	2500	Hg	H_2	9100	1	2
Control 3	2500	Hg	H_2	9100	2700	9100
Example 50	1100	Hg	H_2	14,100	2	4
do 51	1800	Hg	H_2	10,600	1	3
do 52	1700	Hg	H_2	11,500	2	8
do 53	1100	Hg	H_2	8400	2	10
do 54	2000	Hg	air	1500	2	7
do 55	1400	Hg	H_2	8200	3	9
do 56	2100	Hg	H_2	11,100	3	9
do 57	850	Hg	HCl	2100	1	2
do 58	1000	Hg	H_2	8600	4	12
do 59	2100	Hg	H_2	9200	3	7

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Example 60

An acrylic resin tube of 80 mm inside diameter was packed with 3 grams of an anion exchange resin. The height of the layer was about 1000 mm. When waste water containing 15,700 ppb of mercury was passed through this tube at a space velocity of 12 1/hr, the mercury concentration 20 hours later was 150 ppb and 120 hours later was 560 ppb.

Further when this treated liquid was passed through an acrylic resin tube of 120 mm inside diameter, which had been packed with a fixed layer (layer height of 1050 mm) of a treating agent consisting of 8.2 kg of 10—30 mesh bone black on which had been deposited by adsorption 0.7 kg of 2-mercaptobenzothiazole, the mercury concentration 20 hours later was 2ppb and 120 hours later was 5 ppb.

Example 61

A polyvinyl chloride column having an inside diameter of 280 mm was packed with 52 kg of an anion exchange resin. The layer height was about 1200 mm. When waste water containing 9400 ppb of mercury was passed through this column at a space velocity of 10 1/hr, the mercury concentration 25 hours later was 120 ppb and 170 hours later was 860 ppb. Further, when this treated liquid was passed through a polyvinyl chloride column having an inside diameter of 600 mm, which had been packed with a fixed layer (packing height 950 mm) of a treating agent consisting of 125 kg of 10—40 mesh active carbon on which had been deposited by adsorption 22 kg of 2-mercaptobenzothiazole, the mercury concentration 25 hours later was 2 ppb and 170 hours later was 3 ppb.

Now, when the adsorbed mercury was desorbed and recovered and the anion exchange resin was regenerated but the fixed layer of the treating agent was left intact and the treatment of waste water containing 8200 ppb of mercury was carried out under substantially identical conditions as hereinabove, the mercury concentration in the waste water after 25 hours of treatment with the anion exchange resin was 340 ppb. When this waste water was further treated with the fixed layer of the treating agent, the mercury concentration was 3 ppb. On the other hand, the mercury concentration after 170 hours was 900 ppb after treatment with the anion exchange resin and 5 ppb after treatment with the treating agent. Further, when waste water containing 8000—10,000 ppb of mercury was treated under identical conditions while repeatedly carrying out the desorption and recovery of mercury of the anion exchange resin and its regeneration step, the number of days duration that the treating agent could stand use, i.e. the number of days until the mercury concentration in the waste water subsequent to the treatment with the fixed layer of the treating agent reaches 10 ppb, was 200 days.

Examples 62—65

Experiments were carried out as in Example 60 varying the carrier, the organic compound deposited thereon and the material treated. The results obtained are shown in Table 4.

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TABLE 4

Experiment No.	Pretreatment: Amount used of anionic exchange resin (g)	Solid Treating Agent: Organic Compound Used: Name	Amount deposited (wt %)	Solvent used	Carrier: Name	Carrier: Weight (g)
Example 62	63	thiomilide	1.6	acetone	silica gel	120
do 63	1700	pipecoline pipecolyl dithiocarbamate	5.0	3% aq NaOH sol	active carbon	1000
do 64	400	2-mercaptobenzothiazole	5.0	do	do	1600
do 65	63	p-dimethylaminobenzylidene rhodanine	4.0	acetone	do	40

TABLE 4 (Continued)

Experiment No.	Contact time with material treated or space velocity: Resin column (1/hr)	Contact time with material treated or space velocity: Treating agent column (1/hr)	Material treated: Metal to be removed	Material treated: Property	Metal concentration (ppb): Before treatment	Metal concentration (ppb): After passage through resin column or after contact with resin	Metal concentration (ppb): After passage through treating agent column (120 hrs later) or after contact with treating agent
Example 62	3.0	1.9	Hg	aq waste water	7000	240	5
do 63	(contact time abt 3 hrs	(contact time abt 2.5 hrs)	Hg	do	11,600	900	4
do 64	(contact time abt 4 hrs)	(contact time abt 2 hrs)	Hg	aq slurry	5200	500	7
do 65	2.0	2.0	Hg	aq sol	10,200	350	4

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Examples 66 to 70 and Control 4

Fifty grams of thionalide in solution in 150 ml of dichloromethane were passed through a glass column of 8 mm inside diameter packed with 15 grams of a carrier material to cause retention on the carrier of the thionalide, followed by air drying and water-washing the carrier. A solution containing 5600 ppb of mercury and 1500 ppb of copper was passed through the packed column, after which the metal concentration was measured with the results shown in Table 5. As can be seen from the results given in this Table, better results are had by the use of carbon, silica gel and zeolite, as compared with the other readily available carrier materials such as alumina and magnesia.

TABLE 5

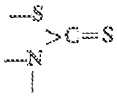
Experiment No.		Carrier	Organic compound	Metal Concentration (ppb)			
				Before treatment		After treatment	
				Hg	Cu	Hg	Cu
Example	66	active carbon	thionalide	5600	1500	50	10
do	67	silica gel	do	5600	1500	65	15
do	68	zeolite	do	5600	1500	60	15
do	69	alumina	do	5600	1500	590	550
do	70	magnesia	do	5600	1500	1260	520
Control 4		active carbon	none	5600	1500	2100	1000

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WHAT WE CLAIM IS:—

1. A process for removing metals from a gaseous or liquid metal-containing material which comprises contacting the material with a solid treating agent comprising a carrier having adsorbed thereon an organic compound which is capable of forming a mercaptide of the metal to be removed and which either contains an —SM group, where M is hydrogen or an alkali metal, or an



group or is an N,N'-substituted thiourea in which the substituents are bonded to nitrogen through carbon atoms.

2. A process according to claim 1 wherein the carrier is carbon, silica gel, silica-alumina gel containing at least 50% by weight of silica gel, or a zeolite.

3. A process according to claim 1 or 2 wherein the metal to be removed is one or more of Hg, Au, Bi, Cd, Co, Cr, Cu, Ni, Pb, Zn, Ag, Mn, Fe, Mo, Ti, Mg and Al.

4. A process according to any one of claims 1 to 3 wherein the metal-containing material which is treated is a liquid and has been pretreated with an anion exchange resin.

5. A process according to any one of the preceding claims wherein the organic compound is any compound specifically named herein as such.

6. A process according to any one of claims 1 to 5 wherein the carrier also has adsorbed thereon a second organic compound which is capable of forming a chelate compound of the metal to be removed and which contains an —OH group and one or more groups selected from —N= and —NH$_2$ groups.

7. A process according to claim 6 wherein the second organic compound is anthranilic acid, oxine or 2-methyl oxine.

8. A process for removing metals from a metal-containing material according to claim 1 substantially as hereinbefore described.

9. Materials when purified by a process as claimed in any one of the preceding claims.

10. A process according to claim 1 wherein mercury is removed from a gas.

11. A process according to claim 1 wherein a heavy metal is removed from an aqueous solution.

12. A process according to claim 1 wherein mercury is removed from concentrated hydrochloric acid.

13. A process according to claim 1 wherein mercury is removed from an aqueous solution or slurry which has been pretreated with an anion exchange resin.

14. A process according to claim 1 wherein mercury is removed from an alkali solution.

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ABSORBENT ARTICLE WITH FOLDING BACK SECTION

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Abstract of JP2008023365 (A)

PROBLEM TO BE SOLVED: To provide a urine pad, a urine incontinence product, and a diaper which make good use of material by the contribution of the whole surface of a part which abuts on the skin to absorb urine and are compact even if they are folded back. ;SOLUTION: In an absorbent article which has a liquid-permeable surface sheet, a liquid impermeable rear surface sheet, and an absorber body which absorbs and fixes body fluid arranged between these both sheets, the absorber body contains an absorptive polymer. An inflectional structure part is formed by arranging two or more linear closed up parts which consist of one kind or two or more kinds of them selected from a part where the basis weight of the absorber body is low and density is low, a part where the blending quantity of the absorbable polymer is small, a slit line part, and a cutoff line part at spaces along a longitudinal direction and a width direction. In the absorbent article, a turndown section is formed by setting this inflectional structure part as a return line and folding back both lateral borders and one edge part of the absorbent article inward at least once. In the absorbent article, a pouched structure is formed by joining both lateral borders of the turndown section of this one edge part. ;COPYRIGHT: (C)2008,JPO&INPIT

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最終頁に続く

(54)【発明の名称】折り返し部を有する吸収体製品

(57)【要約】
【課題】肌に当接する部分の全面が尿の吸収に寄与することによって材料の無駄がなく、かつ折り返してもコンパクトな尿パッド、尿失禁製品及びおむつを提供する。
【解決手段】液透過性の表面シートと、液不透過性の裏面シートと、これら両シートの間に配置された体液を吸収固定する吸収体本体とを有する吸収体製品において、
前記吸収体本体は、吸収性高分子を含有し、長手方向及び幅方向に沿って、吸収体本体の坪量が低くかつ密度が低い部分、吸収性高分子の配合量が少ない部分、スリット線部分及び切取線部分から選ばれる１種又は２種以上からなる複数本の線状の肉薄化部分が間隔を置いて配列されて屈曲構造部分を形成しており、吸収体製品は、該屈曲構造部分を折り返し線として吸収体製品の両側縁部及び一方の端縁部を少なくとも１回内側に折り返して折り返し部が形成され、該一方の端縁部の折り返し部の両側縁部が接合されて袋状構造が形成されていることを特徴とする吸収体製品。
【選択図】　図１１

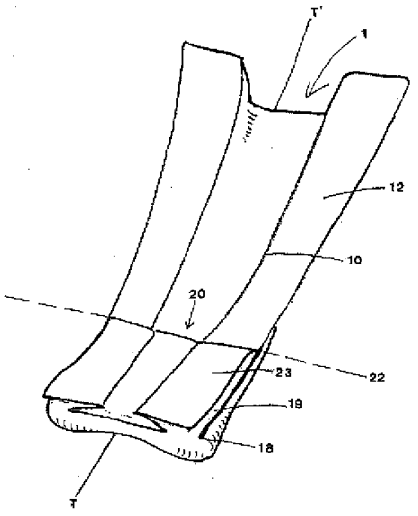


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【特許請求の範囲】
【請求項1】
液透過性の表面シートと、液不透過性の裏面シートと、これら両シートの間に配置された体液を吸収固定する吸収体本体とを有する吸収体製品において、
前記吸収体本体は、吸収性高分子を含有し、長手方向及び幅方向に沿って、吸収体本体の坪量が低い部分、吸収性高分子の配合量が少ない部分、スリット線部分及び切取線部分から選ばれる１種又は２種以上からなる複数本の線状の肉薄化部分が間隔を置いて配列されて屈曲構造部分を形成しており、吸収体製品は、該吸収体本体に形成された屈曲構造部分を折り返し線として吸収体製品の両側縁部及び一方の端縁部を少なくとも１回内側に折り返して折り返し部が形成され、該一方の端縁部の折り返し部の両側縁部が接合されて袋状構造が形成されていることを特徴とする吸収体製品。
【請求項2】
前記一方の端縁部の折り返し部は、前記線状の屈曲構造部分からなる複数の折り返し線に沿って該端縁部を内側と外側に交互に折り返して形成されている折り返し部であることを特徴とする請求項１記載の吸収体製品。
【請求項3】
前記一方の端縁部の折り返し部は、該折り返し部の対向する裏面シート同士が接合されている折り返し部であることを特徴とする請求項１又は請求項２に記載の吸収体製品。
【請求項4】
前記両側縁部の折り返し部は、前記線状の屈曲構造部分からなる複数の折り返し線に沿って該両側縁部を内側と外側に複数回折り返して形成されている折り返し部であることを特徴とする請求項１～請求項３のいずれか１項に記載の吸収体製品。
【請求項5】
前記吸収体本体に、吸収体本体が身体に沿って湾曲しやすいように切り込みが形成されていることを特徴とする請求項１～請求項４のいずれか１項に記載の吸収体製品。
【請求項6】
前記吸収体製品の長手方向に沿った両側縁部に伸縮弾性体が配置されていることを特徴とする請求項１～請求項５のいずれか１項に記載の吸収体製品。
【請求項7】
前記吸収体本体が、少なくとも５０重量以上の吸水性高分子を含有する、吸水性高分子とセルロースパルプの混合体からなり、前記屈曲構造部分はその部分の坪量及び密度を他の部分より低くすることによって形成されていることを特徴とする請求項１～請求項６のいずれか１項に記載の吸収体製品。
【請求項8】
前記吸収体本体は、不織布基材にミクロフィブリルセルロースと吸水性高分子をラインコートしたシート状吸収体を有しており、その屈曲構造部分は前記シート状吸収体における不織布基材だけの部分であることを特徴とする請求項１～請求項７のいずれか１項に記載の吸収体製品。
【請求項9】
前記吸収体本体が、分離可能に取り付けられた水解性シートからなることを特徴とする請求項１～請求項８のいずれか１項に記載の吸収体製品。

【発明の詳細な説明】
【技術分野】

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【0001】
本発明は、吸収体製品に関するものであり、さらに詳しくは、尿パッド、尿失禁製品、おむつを提供しようとするものである。
【背景技術】
【0002】
従来、尿の横漏れを防止する手段として立体的にギャザーを配置する方法と、実用新案登録３０５５５４５号公報、特開平４-０５１９５２号公報などのように吸収体を折り返して防漏壁を形成する方法が知られている。
【0003】
これらの吸収体製品では吸収体本体を折り返して防漏壁を作るために高い吸収面積が確保できる。しかしながら、吸収体本体の折り返し部分は嵩高になり、コンパクトにすることができなかった。さらに、従来の均一密度の吸収体本体を折り返した場合、折り返し線は吸収体本体が潰れるために密度が高くなり、吸液、膨張によって、折り目を体液が通過しにくくなるという問題があった。
【特許文献1】実用新案登録３０５５５４５号公報
【特許文献2】特開平４-０５１９５２号公報
【発明の開示】
【発明が解決しようとする課題】
【0004】
本発明の目的は、肌に当接する部分の全面が尿の吸収に寄与することによって材料の無駄がなく、かつ折り返してもコンパクトな尿パッド、尿失禁製品及びおむつを提供するものである。
【課題を解決するための手段】
【0005】
本発明は、基本的には、吸収体製品が、吸収体本体に形成されている屈曲構造部分を折り返し線として吸収体製品の両側縁部及び一方の端縁部を少なくとも１回内側に折り返して折り返し部が形成され、該一方の端縁部の折り返し部の両側縁部が接合されて袋状構造を有すること特徴とする吸収体製品に関する発明であり、以下の発明から選択される発明である。
【0006】
（１）液透過性の表面シートと、液不透過性の裏面シートと、これら両シートの間に配置された体液を吸収固定する吸収体本体とを有する吸収体製品において、
前記吸収体本体は吸収性高分子を含有し、長手方向又は長手方向と幅方向に沿って、坪量が低い部分、吸水性高分子の配合量が少ない部分又は吸収体本体が配置されていない部分からなる複数本の線状の肉薄化部分が間隔を置いて配列されて屈曲構造部分を形成しており、該吸収体本体の長手方向の屈曲構造部分の一つを第１折り返し線として、吸収体製品全体の両側縁部が内側に折り返されて第１折り返し部が形成され、該第１折り返し部内における前記第１折り返し線と平行な吸収体本体の屈曲構造部分を第２折り返し線として前記吸収体製品の第１折り返し部が外側に折り返されて第２折り返し部が形成されていることを特徴とする吸収体製品。
【0007】
（２）前記吸収体本体の第１折り返し部は、前記第１折り返し線と平行な折り返し線となる複数の屈曲構造部分を有しており、該吸収体本体の複数の屈曲構造部分に沿って吸収体製品全体が外側あるいは内側にさらに折り返されて複数の折り返し部が該第１折り返し部において形成されていることを特徴とする（１）項記載の吸収体製品。
【0008】
（３）前記吸収体製品は、前記吸収体本体の幅方向に沿って形成されている前記肉薄化部分からなる屈曲構造部分を折り返し線として吸収体製品の端縁部を内側に折り返して折り返し部を形成し、該折り返し部の両側縁部を接合して袋状構造が形成されていることを特徴とする（１）項又は（２）項に記載の吸収体製品。

【0009】
（４）前記端縁部を内側に折り返して形成されている折り返し部が、該折り返し部内に配列されている吸収体本体の屈曲構造部分に沿ってさらに外側に折り返され、該折り返し部の対向する液不透過性の裏面シート同士が接合されていることを特徴とする（３）項記載の吸収体製品。
【0010】
（５）前記吸収体製品の長手方向一端側の液透過性表面シート上に、液不透過性シートが、該液透過性表面シートの両側縁部分及び該一端縁部分を覆って接合されていることを特徴とする（１）項～（４）項のいずれか１項に記載の吸収体製品。
【0011】
（６）前記吸収体製品の両側縁部の長手方向中央部において、長手方向第１折り返し部内の対向する表面シート同士が接合されていることを特徴とする（１）項～（５）項のいずれか１項に記載の吸収体製品。
【0012】
（７）前記吸収体製品の長手方向の少なくとも一端部側の両側縁において、長手方向第１折り返し部の内側の対向する表面シート同士が接合されていることを特徴とする（１）項～（６）項のいずれか１項に記載の吸収体製品。
【0013】
（８）前記吸収体本体に、吸収性本体が身体に沿って湾曲しやすいように切り込みが形成されていることを特徴とする（１）項～（７）項のいずれか１項に記載の吸収体製品。
【0014】
（９）前記吸収体製品の長手方向に沿った両側縁部に伸縮弾性体が配置されていることを特徴とする（１）項～（８）項のいずれか１項に記載の吸収体製品。
【0015】
（１０）前記吸収体製品の両側縁部における吸収体本体上の液透過性表面シート上に液不透過性シートを配置したことを特徴とする（１）項～（９）項のいずれか１項に記載の吸収体製品。
【0016】
（１１）前記吸収体本体が、少なくとも５０重量％以上の吸水性高分子を含有する、吸水性高分子とセルロースパルプの混合体からなり、前記屈曲構造部分は該部分の坪量を他の部分より低くすることによって形成されていることを特徴とする（１）項～（１０）項のいずれか１項に記載の吸収体製品。
【0017】
（１２）前記吸収体本体は、不織布基材にミクロフィブリルセルロースと吸水性高分子をラインコートしたシート状吸収体を有しており、その屈曲構造部分は前記シート状吸収体における不織布基材だけの部分であることを特徴とする（１）項～（１１）項のいずれか１項に記載の吸収体製品。
【0018】
（１３）前記吸収体本体が、分離可能に取り付けられている水解性シートからなることを特徴とする（１）項～（１２）項のいずれか１項に記載の吸収体製品。
【0019】
（１４）前記（１）項～（１３）項に記載された吸収体製品のうち、同一構造の吸収体製品２個を表面シート同士を対向させて両側縁同士及び一端縁同士を接合して形成されている袋状構造を有することを特徴とする吸収体製品。
【0020】
（作用）
本発明の吸収体製品は、吸収体本体を折り返すことによって防漏壁を形成するものである。折り返し線を有する吸収体本体は屈曲構造であり、折り返しによっても嵩高にならず、かつ防漏壁に吸収性があるために体液吸収に有効な面積が大きく、結果としてコンパクトな吸収体製品を構成している。

【発明の効果】
【0021】
本発明によれば、吸収体本体の折り返し線が屈曲構造であるため、折り返し易く、嵩高にならず、結果としてコンパクトにすることができる。さらに、折り返しの角部の密度が高くなり過ぎず、吸液、膨張によって、折目を体液が通過しにくくなるという問題が内吸収体製品を得ることができる。
【0022】
（作用）
本発明の吸収体製品は、吸収体本体を折り返すことによって防漏壁を形成するものである。折り返し線を有する吸収体本体は屈曲構造であり、折り返しによっても嵩にならず、かつ防漏壁に吸収性があるために体液九州に有効な面積が多き無、結果としてコンパクトな吸収体製品を構成している。
【発明を実施するための最良の形態】
【0023】
本発明の吸収体製品における吸収体本体は、木材パルプや非木材パルプを綿状にしたフラッフパルプを主材としたものに吸水性高分子（ＳＡＰ）を併用したものでよく、その他に吸収紙単独、又は熱融着繊維等の混合物や積層物が用いられ。また、吸水性高分子の飛び出し防止のために全体をティシュで包み込んだ積層構造としてもよい。また、より薄く、コンパクトにするためには、吸水性高分子５０重量%以上を含有した構成からなるものを用いることが好ましい。
【0024】
さらに、本発明の吸収体製品に好適な吸収体本体は、不織布基材と吸水性高分子とミクロフィブリルセルロースとからなるシート状複合体から構成されているものであってもよい。そのようなシート状の複合体の具体例としては、吸水性高分子とミクロフィブリルセルロースをプロピレングリコールやメタノールと水の溶液に分散した塗工液を、ポリエチレン系、ポリプロピレン系、ポリエステル系、その他の熱可塑性樹脂やレーヨン、コットンなど一般に不織布に用いられる材料を原料とした不織布に塗工した吸水性高分子を主成分とするシート状吸収体などが挙げられる。
【0025】
ミクロフィブリルセルロースとは、木材パルプを高シェア下で開繊して得られる平均繊維長０．１ｍｍ以下の極微細繊維である。前記シート状吸収体は、吸水性高分子を不織布にコーティングして得られるので、任意の幅のラインコートが可能である。本発明の吸収体本体には、前記シート状吸収体を複数枚重ねて用いてもよい。また、塗エパターンは全面コートとラインコートの組合わせ、ラインコートのみなど選択することができる。
【0026】
また、前記吸収体本体に水解性素材を用いてもよい。水解性にする場合の前記吸収体製品の構成例としては、例えば、表面シートとしてレーヨン、パルプ、ＣＭＣ－Ｃａなどを用いた水解紙シートを用い、吸収コアとしてフラッフパルプ、カーリーファイバーと生分解性吸水性高分子や少量であれば生分解性がない吸水性高分子などを用いたもの、水解紙上に吸水性高分子をコーティングしたものなどを用い、バックシートとして、ティシュにＰＶＡをラミネートした難透水性シートなどを用いたものを挙げることができる。
【0027】
本発明の吸収体本体は、容易に折り返すことが可能な屈曲構造部分を有している。容易に折り返すことが可能であれば、均一な折り返し加工をすることができる。また、折り返して生ずる厚み変化が吸収体の厚み（Ｄ）の整数倍からあまり外れない。すなわち、ｎ重に折り重ねた厚みが、ｎ×Ｄからあまり外れない結果として折り返しても厚ぼったくならないようにすることができる。
【0028】
容易に折り返すことを可能にする屈曲構造部分とは、吸収体本体の折り返し予定線部分が、その他の部分と比較して坪量差、吸水性高分子含有量のある部分として形成されてい

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る線状部分である。例えば、該屈曲構造部分の坪量が他の部分より低ければ容易に屈曲して折り返すことが可能であるし、吸水性高分子含有量が他の部分より低いか、又は含まれない場合も同じ効果が得られる。また、厚さが均一の場合は、屈曲構造部分の密度が他の部分より低ければ容易に折り返すことができる。

屈曲構造をより積極的に形成するために、吸収体本体にスリットを入れたり、部分的に切断してもよい。

【0029】

また、吸収体本体が吸水性高分子を不織布基材にラインコートしたものの場合は、ラインコートされた部分は剛性が高く、ラインコートされていない部分は柔軟であるために屈曲しやすい。その上、ラインコート部分の厚みが非ラインコート部より厚いために非ラインコート部を折り返しても折り重ねた厚さに微小な変化しか与えずに済ますことが可能となる。

これら屈曲構造は折り返し線として機能させるために、実質的に線状に配置して形成される。

【0030】

また、吸収体本体に屈曲構造部分を複数配置しても、必ずしもそれらを全て折り返し線として利用する必要はない。屈曲構造部分は吸収体本体に任意の本数を任意の位置に配置することができる。本発明のように、吸収体本体を屈曲構造にすることによって、吸収体製品を折りやすくかつ折り目を保ちやすくすることが可能となる。

【0031】

本発明の吸収体製品は、吸収体本体の折り返し線で吸収体製品が少なくとも一度内側に折り返される。さらにその第１の折り返し線より外側の第２の折り返し線で内側か外側に折り返し、必要であればさらに複数の折り返し線で内側か外側に折り返しすることができ、折り返し線を増やすことによって任意の数の折り返しを形成することができる。

【0032】

前記吸収体製品の折り返しは、長手方向に沿って（長手方向に沿った折り返し線で）折り返してもよいし、幅方向に沿って折り返してもよい。また、長手方向に沿って折ってから幅方向に沿って折ってもよく、その逆に幅方向に沿って折り返した後、長手方向に沿って折り返してもよい。

【0033】

本発明の吸収体製品の構造は、本発明の主旨に沿って任意に選択することが可能であるが、好ましい構造として具体例を挙げるならば、吸収体製品が吸収体本体の長手方向第１折り返し線部分で内側に折り返されて長手方向第１折り返し部を形成し、その長手方向第１折り返し部上の長手方向第２の折り返し線部分で外側に折り返され、長手方向第２の折り返し部を形成し、吸収体製品の長手方向一端縁が吸収体製品の長手方向と直交する幅方向第１折り返し線部分で内側に折り返され、対向する前記長手方向第２折り返し部の外縁同志が接合されることによって袋状構造に形成されているものである。前記幅方向第１折り返し線は、幅方向の屈曲構造部分で形成し、この部分に沿って折り返すことが好ましいが、屈曲構造部分以外で折り返して形成してもよい。

【0034】

また、吸収体製品が吸収体本体の長手方向第１折り返し線部分で内側に折り返されて長手方向第１折り返し部を形成し、その長手方向第１折り返し部上の長手方向第２折り返し線部分で外側に折り返され、長手方向第２折り返し部を形成し、さらに吸収体製品上の一方の端縁部領域に液不透過性シートを配置し、該液不透過性シートを吸収体製品の両側縁及び端縁で接合してもよい。この場合も一端が袋状構造になった吸収体製品を得ることができる。

【0035】

さらに例を挙げるならば、吸収体製品を、吸収体本体の長手方向第１折り返し線部分で内側に折り返して長手方向第１折り返し部を形成し、その長手方向第１折り返し部上の長手方向第２折り返し線部分で外側に折り返して長手方向第２折り返し部を形成した２個の

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吸収体製品Ａ、Ｂを表面シートの面同士を対向させた状態で互いの両側縁及び一方の端縁同士を接合した袋状構造をもった吸収体製品とすることもできる。この際、ＡとＢの長さは同じでもよく、一方が他方よりも短くてもよい。

【0036】

前記のように、屈曲構造部分で折り返すことによって、複数回折り重ねた場合でも折り返し部の厚み変化を小さくすることができる。一方、従来の均一密度の吸収体本体を折り返した場合、折り目が嵩高になってしまい、複数回折り重ねると吸収体製品をコンパクトにし難くなる。さらに従来の吸収体本体では折り返し線部分は吸収体本体が潰れるために密度が高くなり、吸液、膨張によって折り目を体液が通過し難くなる。本発明は前記従来の吸収体本体における問題点を改良するものである。

【0037】

前記のように、吸収体本体が木材パルプや非木材パルプを綿状にしたフラッフパルプを主材としたものに吸水性高分子を併用したものの場合、屈曲構造の折り返し線を得るには、坪量を下げること、又は屈曲構造部分への吸水性高分子の配合比を下げるか、配合しない等の方法をとればよい。

【0038】

吸収体本体が不織布基材と吸水性高分子とミクロフィブリルセルロースとからなるシート状複合体から構成される場合、屈曲構造の折り返し線を得るには、不織布基材上に吸水性高分子とミクロフィブリルをラインコートし、非塗工部分を折り返し線とすればよい。また、塗工量の高い部分と低い部分を形成するようにラインコートして、低塗工量部分を折り返し線としてもよい。

【0039】

液透過性の表面シートには、一般的に衛生材料に用いられる素材を採用することができる。例えば、ポリエチレン系、ポリプロピレン系、ポリエステル系、その他の熱可塑性樹脂を原料とした合成繊維などからなる不織布、穴あき不織布、メッシュシートなどのシートを選択することができる。

【0040】

本発明の吸収体本体の裏面に配置する液不透過性の裏面シートは、液不透過性のシート単独でも複数の不織布とともに積層して用いてもよい。液不透過性の裏面シートとしては、液体不透過性のポリエチレンシート、好ましくは微孔を設けたポリエチレンシート、熱可塑性樹脂にフィラーを加えて延伸したシートのような透湿性のある液体不透過性シートを用いて透湿性を付与すると蒸れが少なく快適である。

【0041】

前記液不透過性の裏面シートの外側に手触り感を好適にし、フィルム独特の擦れ音をださないように、不織布を貼り付けてもよい。その不織布はポリエチレン系、ポリプロピレン系、ポリエステル系などの熱可塑性樹脂を原料とした合成繊維からなる不織布を用いることができる。

【0042】

本発明の吸収体本体の裏面に使用する液不透過性の裏面シートの外側に廃棄の際に吸収体製品を丸めて留めることができるように係留手段を具備させてもよい。係留手段としては例えば、粘着テープ、メカニカルファスニングテープ、紐、バンドなどが挙げられる。

【0043】

本発明の吸収体製品は、その長手方向第１折り返し部の内側で対向している表面シート同士が部分的に接合されていてもよい。長手方向第１折り返し部が部分的に接合されることによって吸収体本体を着用者により密着させたり、保形性を良好にすることが可能となる。例えば、女性用の尿パットを設計する場合には吸収製品の長手方向中央部で長手方向第１折り返し部内側表面シートを接合すると、着用者の体に合った吸収体製品を得ることができる。男性用吸収体製品も前記のように得ることができるが、例えばパンツ型おむつの補助として併用する尿パットの場合は前身頃での吸収を主目的とした吸収体製品が適する。その場合、吸収体製品の長手方向の一方の端縁において長手方向第１折り返し部の表

面シートが接合されると、その部分を股下に位置するように吸収体製品を配置したときに着用感、フィット性、吸収前後の保形性が良好となり好ましい。接合の方法は、不織布を接合するために常用される方法でよいが、例えばホットメルトによる接着やヒートシール、超音波による融着が挙げられる。

【0044】

本発明の吸収体本体には、切り込みを入れることによって身体に沿って湾曲しやすく設計することができる。切り込みの方向は、吸収体製品の流れ方向に交差してもよいし、流れ方向に沿ってもよいし、両方向に入れてもよい。また、前記切り込みは吸収体本体の任意の位置に、任意の本数入れることができる。

【0045】

本発明の吸収体製品における伸縮弾性体としては、天然ゴム、合成ゴムなどからなる糸ゴム、平ゴム、弾性ネット状シートを用いることができる。伸縮弾性体は着用者の体線に沿うように吸収体製品を湾曲させたり、吸収体本体が折り返されてできる防漏壁の起立を補う役目をする。

【0046】

本発明の吸収体製品は、その表面シートの両側縁に液不透過性シートを配置してもよい。本発明の吸収体製品は最終折り返し部が着用者に触れ易い構造になるので、その部分の表面シートが着用者に直接触れると、排尿後の着用感が悪くなるので、液不透過性シートを用いるのが好ましい。また、同時に吸収体製品端縁からのしみ出しを防止する役割もする。素材としては前記の吸収体本体裏面に用いる液不透過性の裏面シートと同様のものを用いることができるが、ポリエチレン系、ポリプロピレン系、ポリエステル系などの熱可塑性樹脂を原料とした合成繊維を原料として、一般にＳＭＳと呼ばれるスパンボンド法／メルトブロー法／スパンボンド法でサンドイッチにした不織布や、ＳＭＭＳなどが好適である。

【0047】

本発明の吸収体製品とは、赤ちゃん用おむつ、赤ちゃん用及び大人用尿パッド、大人用失禁用品などを意味する。

【実施例】

【0048】

以下、尿パッドを例にして、図面を参照して本発明の吸収体製品を詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

【0049】

図１は、本発明の尿パッドの外観斜視図、図２は、図１に示した尿パッドの展開平面図、図３は、図２に示した尿パッドをＶ－Ｖ’線に沿って切断した状態の横断面図、図４は、図１に示した尿パッドを畳んだ状態を上面から見た正面図、図５は、図４に示した尿パッドをＷ－Ｗ’線に沿って切断した状態の横断面図をそれぞれ示している。

【0050】

本発明の尿パッド１は、図３に示すように、液透過性の表面シート３と、液不透過性の裏面シート６と、これら両シートの間に配置された吸収体本体２とから基本的に構成されており、また、表面シート３の両側縁部には液不透過性シート４が取付けられており、さらに、吸収体本体２の両側縁から延出した裏面シート６部分と液不透過性シート４の間には、長手方向に沿って伸縮弾性体５が配置されている。

【0051】

本実施例では、吸収体本体２は、不織布からなる基材１５面にミクロフィブリルセルロースとＳＡＰを含む塗工液を塗工してＳＡＰ塗工部１４を形成したシート状吸収体１３により形成されている。この場合、シート状吸収体１３のＳＡＰ塗工部１４はライン塗工により形成されており、ＳＡＰ塗工部１４には、シート状吸収体１３を折り返す際の長手方向屈曲構造部分７となる非塗工部７が長手方向に４本形成されている。

【0052】

また、本実施例では、尿パッド１は、図１に示すように、長手方向第１折り返し線９に

沿って尿パッドの側縁部を内側に折り返して長手方向第１折り返し部１１を形成し、次いで第１折り返し部１１上の長手方向第２折り返し線１０に沿って外側へ折り返して長手方向第２折り返し部１２を形成し、さらに、一方の端部領域において折り返し部１１、１２の表面シート同士及び裏面シート同士が接合されている。

この場合、図２に示すように、ＳＡＰ塗工部に形成された４本の長手方向屈曲構造部分７のうち、内側の２本を長手方向第１折り返し線９とし、外側の２本を長手方向第２折り返し線１０として折り返されており、これらの線に沿って折り返された状態の断面は図５に示すとおりである。

【0053】

図６は、図２に示した尿パッドをＶ－Ｖ’線に沿って切断した状態の横断面図の、図３とは異なる例を示している。

図６において、シート状吸収体１３の下層（裏面シート側）にパルプとＳＡＰを混合したパルプマット層１６が配置されており、特に速い吸収速度が要求される場合に適した構造になっている。

【0054】

図７は、図１に示す尿パッド１の長手方向折り返し部１１、１２を両端部領域１７、１７で接合した例を示す外観斜視図である。このように、長手方向折り返し部１１、１２を両端部領域１７、１７で接合することによって、前身頃側及び後身頃側からの尿漏れを防止することができる。

【0055】

図８は、本発明の尿パッドの別の形態を示す外観斜視図、図９は、図８に示した尿パッドの展開平面図、図１０は図９に示した尿パッドをＸ－Ｘ’線に沿って切断した状態の横断面図をそれぞれ示している。

【0056】

尿パッド１は、図１０に示すように、その基本構成は先に述べた場合と同様であるが、吸収体本体２がシート状吸収体１３を２層積層して形成されている。このように、複数のシート状吸収体を積層して吸収体本体を形成することにより尿パッドの吸収量を向上させることができる。

【0057】

また、尿パッド１は、図８に示すように、長手方向第１折り返し線（図示せず）及び長手方向第２折り返し線１０に沿って尿パッドの側縁部を折り返し、長手方向第１折り返し部（図示せず）及び長手方向第２折り返し部１２を形成し、さらに、一方の端縁部を幅方向第１折り返し線１８に沿って内側に折り返して幅方向第１折り返し部１９を形成し、その両側縁部を長手方向第２折り返し部１２の側縁部と接合することにより、袋状構造部２０が形成されている。

【0058】

この場合、図９に示すように、尿パッド１は、ＳＡＰ塗工部に形成された４本の長手方向屈曲構造部分７のうち、内側の２本を長手方向第１折り返し線９とし、外側の２本を長手方向第２折り返し線１０として長手方向に折り返され、さらに、幅方向屈曲構造部７’を幅方向第１折り返し線１８として幅方向に折り返され、長手方向折り返し部１２及び幅方向折り返し部１９の相対する両側縁部２１、２１が接合される。

本実施例では、幅方向屈曲構造部分７’を幅方向第１折り返し線１８として尿パッド１の端縁部を折り返しているが、幅方向第１折り返し線は必ずしも屈曲構造にする必要はない。しかしながら、折り返し易くするために屈曲構造にしたり、切り込みを入れることは好ましい。

【0059】

図１１は、本発明の尿パッドの他の形態を示す外観斜視図であり、図１２は、図１１に示した尿パッドをＴ－Ｔ’線に沿って切断した状態を示す横断面図である。

【0060】

本実施例において、尿パッド１は、図８に示す尿パッドの幅方向第１折り返し部１９の

端縁部をさらに外側に折り返した構成になっている。すなわち、図１１に示すように、尿パッド１は、長手方向第１折り返し線（図示せず）及び長手方向第２折り返し線１０に沿って尿パッドの側縁部を折り返し、長手方向第１折り返し部（図示せず）及び長手方向第２折り返し部１２を形成し、次いで、一方の端縁部を幅方向第１折り返し線１８に沿って内側に折り返して幅方向第１折り返し部１９を形成し、さらに幅方向第１折り返し部１９の端縁部を幅方向第２折り返し線２２に沿って外側に折り返して幅方向第２折り返し部２３を形成し、折り返し部の両側縁部を接合することにより袋状構造部２０が形成されている。

この場合、図１２に示すように、尿パッド１は、吸収体本体２に形成された幅方向屈曲構造部分７’を幅方向第１及び第２折り返し線１８、２２として幅方向に折り返されて幅方向第１及び第２折り返し部１９、２３が形成され、折り返し部の相対する表面シート３同士及び裏面シート６同士が接合されている。

【0061】

本実施例の尿パッドは、実際の使用に当たっては、袋状構造部２０が股下部に位置するようにして使用する。このような構成の尿パッドは、表面シート３が着用者の肌に触れる面になるので、着用中のべたつき感を軽減することが可能となる。なお、本実施例では、長手方向第２折り返し部１２に伸縮弾性体を配置していないが、伸縮弾性体を配置したものであってもよい。

【0062】

図１３は、本発明の尿パッドのさらに別の形態を示す外観斜視図であり、図１４は、図１３に示した尿パッドをＳ－Ｓ’線に沿って切断した状態を示す横断面図である。

【0063】

本実施例において、尿パッド１は、図１４に示すように、吸収体本体２と裏面シート６のみを図１１及び図１２の場合と同様に折り返した後、その上面を覆って表面シート３が配置されている。このような構成の尿パッドは、図１３に示すように、袋状構造部２０の開口面が表面シート３で覆われているため、一度に多量の尿が排泄された場合、袋状構造部２０内に尿が保持され、漏れを防止することができる。

【0064】

図１５は、図１３に示した尿パッドの端縁部をさらに幅方向に２度折り返した形状になっている状態を示す外観斜視図であり、図１６は、図１５に示す尿パッドを長手方向のＲ－Ｒ’線に沿って切断した状態を示す横断面図である。幅方向の折り返しを内外交互に合計４回行うことによって袋状構造部２０を２箇所形成し、尿だまりとして機能させることができる。

【0065】

図１７は、本発明の尿パッドのさらに他の形態を示す外観斜視図であり、図１８は、図１７に示した尿パッドを展開した状態において長手方向に沿って切断した状態を示す横断面図である。

【0066】

本実施例において、尿パッド１は、図１７に示すように、一方の端縁部が幅方向第１折り返し線に沿って内側に折り返され、両側縁部２１が接合されて袋状構造部２０が形成されている。

この場合、図１８に示すように、尿パッド１は、吸収体本体２を構成するシート状吸収体１３に形成された幅方向屈曲構造部分７’を幅方向第１折り返し線１８として折り返される。

【0067】

図１９は、本発明の尿パッドを使いすておむつの吸収体として用いた例を示す外観斜視図であり、図２０は、図１９に示す使いすておむつをＵ－Ｕ’線に沿って切断した状態の尿パッドの折り返し部分を示す横断面図である。

【0068】

本実施例において、図１９に示すように、尿パッド１は、その長手方向両端部領域１７

、１７が幅方向第１折り返し線１８で内側に折り返されて幅方向第１折り返し部１９が形成され、さらに幅方向第１折り返し部１９の幅方向第１折り返し線１８の近傍が接合領域２４で接合された状態で、おむつ本体２５の長手方向中央領域に配置され、おむつ本体２５と接合されている。

この場合、図２０に示すように、尿パッド１は、吸収体本体２に形成された幅方向屈曲構造部分７’を幅方向第１折り返し線１８として端部領域１７が折り返されて幅方向第１折り返し部１９が形成され、さらに幅方向第１折り返し線１８の近傍の接合領域２４で表面シート３が接合されており、おむつ本体２５に接合されている。

【0069】

図２１は、本発明の尿パッドを使いすておむつの吸収体として用いた場合の、図１９とは異なる例を示す外観斜視図であり、図２２は、図２１に示す使いすておむつをＴ－Ｔ’線に沿って切断した状態の尿パッドの折り返し部分を示す横断面図である。

【0070】

本実施例において、図２１に示すように、尿パッド１は、股下領域において幅方向に襞部２６が形成されており、おむつ本体２５の長手方向中央領域に形成された一対の立体ギャザー２７の間に配置され、おむつ本体２５と接合されている。

この場合、図２２に示すように、尿パッド１の襞部２６は、吸収体本体２としてシート状吸収体１３を用い、基材１５上に形成された多数の幅方向屈曲構造部分７’の１つを幅方向第１折り返し線１８として折り返し、次いで、折り返し部分の幅方向屈曲構造部分７’の１つを幅方向第２折り返し線２２として折り返すことにより形成されている。

【0071】

図２３、２４、２５及び２６は、本発明の吸収体本体の折り返しの形態を示す模式図である。図２３は一度折り返した例であり、図２４は第２折り返し線で側縁部をさらに内側に折り返した例であり、図２５は図２４と同じ２度折り返しているが、第２折り返し線で側縁部を外側に折り返している。さらに図２６は６回内外交互に側縁部を折り返した例である。このように屈曲構造部分を折り返し線として吸収体本体を複数回折り返して吸収製品の吸収部分を構成することができる。

【0072】

図２７、２８、２９及び３０は、本発明の吸収体本体の屈曲構造と非屈曲構造の構成を示す模式図である。これら模式図でパルプとＳＡＰの混合マットで形成された吸収体本体を説明することができる。すなわち吸収体の坪量が低い部分を屈曲構造部分７とし、坪量が高い部分を非屈曲構造８とすることができる。図のように屈曲構造と非屈曲構造は複数形成することができ、屈曲構造部分の任意の位置を折り返し線として利用することができる。

【0073】

図３１、３２、３３及び３４は、本発明の吸収体本体の屈曲構造と非屈曲構造の構成を示す模式図である。これらの模式図で、パルプとＳＡＰの混合マットやＳＡＰ含有量が５０％以上の混合マットで形成された吸収体本体を説明することができる。これらはＳＡＰ濃度で屈曲構造部分と非屈曲構造部分を形成すればよい。すなわち、ＳＡＰが存在しないか又は濃度が低い部分を屈曲構造部分７とし、ＳＡＰ濃度が高い部分を非屈曲構造８とすることができる。図のように屈曲構造と非屈曲構造は複数形成することができ、屈曲構造部分の任意の位置を折り返し線として利用することができる。

【0074】

図３５、３６及び３７は、本発明の吸収体本体の屈曲構造と非屈曲構造の構成を示す模式図である。これら模式図でＳＡＰを塗工したシート状吸収体で形成された吸収体本体を説明することができる。これらについても前記の図３１～３４で示した例と同様に、ＳＡＰ濃度で屈曲構造部分と非屈曲構造部分を形成すればよい。すなわち、ＳＡＰを塗工していない部分を屈曲構造部分７とし、ＳＡＰを塗工した部分を非屈曲構造８とすることができる。また、ＳＡＰの塗工量の少ない、多いで屈曲構造と非屈曲構造を形成することができる。前記の例と同様に、屈曲構造と非屈曲構造は複数形成することができ、屈曲構造部

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分の任意の位置を折り返し線として利用することができる。

【0075】

図３８～図５０は、吸収体本体の折り返しの形態を示すものである。図３８は、前記図２７と同様の吸収体本体であり、図２７の屈曲構造部分７が破線で示した第１折り返し線９となる。このものの外縁部が折り返されたものを図３９に示す。図４０は、図２７の屈曲構造部分７の一対を第１折り返し線９としたものであり、その外縁部を内側に折り返した例が図４１で示すものであり、さらにその第１折り返し部１１の屈曲構造部分７を第２折り返し線１０として外側に折り返して第２折り返し部１２を形成した例が図４２に示されている。

【0076】

図４３は、図３４と同様の吸収体本体であり、屈曲構造部分７が破線で示した複数の折り返し線９となり、外縁部が交互に内・外の順に折り返されたものを図４４に示す。

【0077】

図４５は、図３５と同様のものであり、屈曲構造部分７が破線で示した第１折り返し線９となり、外縁部が内側に折り返されたものを図４６に示す。

【0078】

図４７は、図３６と同様のものであり、ＳＡＰ塗工面が下向きの状態になっている。ＳＡＰが塗工されていなし、屈曲構造部分７の一対を第１折り返し線９として内側に折り返し、さらにその第１折り返し部１１の屈曲構造部分７を第２折り返し線１０として外側に折り返して第２折り返し部１２を形成した例を図４８に示す。

【0079】

図４９は、図３７と同様のものであり、ＳＡＰ塗工面が下向きの状態になっている。屈曲構造部分７が破線で示した複数の折り返し線９となり、外縁部が交互に内外の順に折り返された例を図５０に示す。

【0080】

図５１、５２、５３は、本発明の吸収体本体の別の形態を説明するものであり、身体に沿って吸収体本体２を湾曲させるための切り込み部２８を吸収体本体２に設けた例である。吸収体本体の側縁部分に外向きにハの字に切り込み部を設けた例を図５１に示す。吸収体本体の側縁部分に直行して切り込み部を設けた例を図５２に示す。図５１と図５２の例では着用者の前身頃から後身頃にかけてのカーブに湾曲することが可能である。図５３は吸収体本体の長手方向に沿って切り込み部が設けられている。これによって吸収体本体が着用者の胴周り方向に湾曲することが可能である。前記の切り込み部は併用してもよく、それによって胴周り方向と股下周り方向に同時に湾曲させる効果がある。これらの切り込み部は、吸収体本体を厚さ方向に貫通していてもよいし、前記のごとく吸収体本体が複数のシート状吸収体が積層されて形成されている場合は上層のシート状吸収体に切り込み部を設ければ十分である。

【0081】

本発明によると、吸収体本体の折り返し線が屈曲構造であるために、折り返し易く、嵩高にならず、結果としてコンパクトな吸収体製品にすることができる。さらに、折り返しの角部の密度が高くなり過ぎず、吸液、膨張によって、折り目を体液が通過しにくくなるという問題がない吸収体製品を得ることが可能となる。

【0082】

本発明によると、容易に屈曲構造部を得ることが可能となる。

【0083】

本発明の吸収体製品によると、さらに防漏壁が増えるので、大きな吸収面積を持つコンパクトな吸収体製品が可能となる。

【0084】

本発明によると、袋状構造をもつ吸収体製品ができるので、尿を吸収体本体が完全に吸収するまで、袋状構造部分に一時貯留することが可能となる。

【0085】

本発明によると、吸収体製品に袋状構造部をより確実に形成することが可能となる。
【0086】
本発明によると、袋状構造部を形成するために、吸収体本体を容易に折り返すことが可能となる。
【0087】
本発明によると、袋状構造をもつ吸収体製品ができるので、尿を吸収体本体が完全に吸収するまで、袋状構造部分に一時貯留することが可能となる。
【0088】
本発明によると、袋状構造部分の内部全体が尿を吸収することができるので、さらに急速な尿の吸収が期待できる。
【0089】
本発明によると、吸収体本体を着用者により密着させたり、保形性を良好にすることが可能となる。
【0090】
本発明によると、吸収体本体を湾曲させ易くなり、着用者により密着させることが可能となる。
【0091】
本発明によると、吸収体本体を湾曲させ易くなり、着用者により密着させることが可能となる。また、吸収体本体が折り返されてできる防漏壁の起立を補う役目をする。
【0092】
本発明によると、着用感を向上することができる。
【0093】
本発明によると、薄い吸収体製品を得ることができる。
【0094】
本発明によると、極めて薄い吸収体製品を得ることができる。
【0095】
本発明によると、吸収体本体の設計を柔軟にすることができる。
【0096】
本発明によると、吸収体本体の廃棄方法を容易にすることができる。
【図面の簡単な説明】
【0097】
【図1】尿パッドの外観を表す斜視図である。
【図2】図１に示した尿パッドを展開した状態における平面図である。
【図3】図２に示した尿パッドをＶ－Ｖ’線に沿って切断した状態の横断面図である。
【図4】図１に示した尿パッドを折り返し部で小さく畳んだ状態の上面の正面図である。
【図5】図４に示した尿パッドをＷ－Ｗ’線に沿って切断した状態の横断面図である。
【図6】図３とは異なる例を示す、図２に示した尿パッドをＶ－Ｖ’線に沿って切断した状態の横断面図である。
【図7】図１に示した尿パッドの長手方向折り返し部の両端部を固定した状態を示す外観斜視図である。
【図8】本発明の別の尿パッドの外観を表す斜視図である。
【図9】図８の尿パッドを展開した平面図である。
【図10】図９に示した尿パッドをＸ－Ｘ’線に沿って切断した状態の横断面図である。
【図11】本発明の別の尿パッドの外観を表す斜視図である。
【図12】図１１に示した尿パッドをＴ－Ｔ’線に沿って切断した状態の横断面図である。
【図13】本発明の別の尿パッドの外観を表す斜視図である。
【図14】図１３に示した尿パッドをＳ－Ｓ’線に沿って切断した状態の横断面図である。
【図15】本発明の別の尿パッドの外観を表す斜視図である。
【図16】図１５に示した尿パッドをＲ－Ｒ’線に沿って切断した状態の横断面図である。
【図17】本発明の別の尿パッドの外観を表す斜視図である。

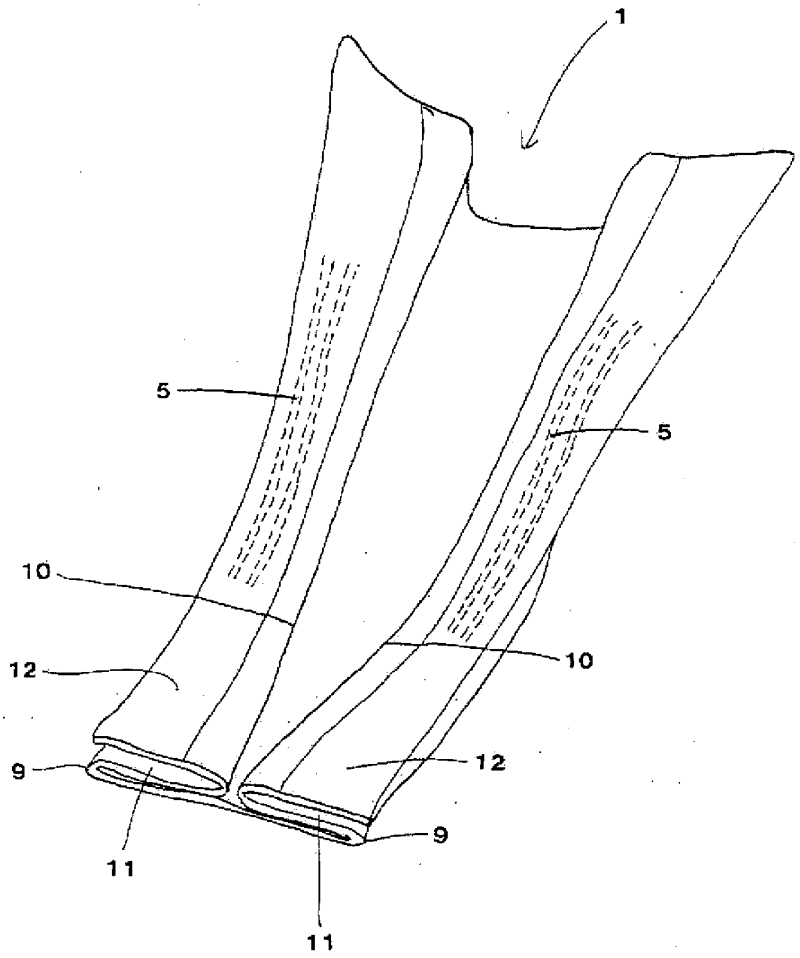
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【図18】図１７に示した尿パッドを展開した状態において長手方向に沿って切断した状態を示す横断面図である。
【図19】尿パッドを使いすておむつの吸収体として用いた場合の外観を示す斜視図である。
【図20】図１９に示すおむつをＵ－Ｕ’線に沿って切断した状態を示す横断面図である。
【図21】尿パッドを使いすておむつの吸収体として用いた場合の別の例の外観を示す斜視図である。
【図22】図２１に示すおむつをＴ－Ｔ’　線に沿って切断した状態を示す横断面図である。
【図23】吸収体本体の折り返し形態を説明する横断面図である。
【図24】吸収体本体の別の折り返し形態を説明する横断面図である。
【図25】吸収体本体の別の折り返し形態を説明する横断面図である。
【図26】吸収体本体の別の折り返し形態を説明する横断面図である。
【図27】吸収体本体の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図28】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図29】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図30】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図31】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図32】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図33】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図34】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図35】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図36】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図37】吸収体本体の別形態の屈曲構造部分と非屈曲構造部分を説明する吸収体本体の横断面図である。
【図38】吸収体本体を折り返す形態を説明する横断面図である。
【図39】図３８を折り返す形態を説明する横断面図である。
【図40】吸収体本体を折り返す別の形態を説明する横断面図である。
【図41】図４０を折り返す形態を説明する横断面図である。
【図42】図４０を折り返す形態を説明する横断面図である。
【図43】吸収体本体を折り返す別の形態を説明する横断面図である。
【図44】図４３を折り返す形態を説明する横断面図である。
【図45】吸収体本体を折り返す別の形態を説明する横断面図である。
【図46】図４５を折り返す形態を説明する横断面図である。
【図47】吸収体本体を折り返す別の形態を説明する横断面図である。
【図48】図４７を折り返す形態を説明する横断面図である。
【図49】吸収体本体を折り返す別の形態を説明する横断面図である。
【図50】図４９を折り返す形態を説明する横断面図である。
【図51】吸収体本体の切り込みを説明する上面正面図である。
【図52】吸収体本体に別の形態の切り込みが入ったものを説明する上面正面図である。

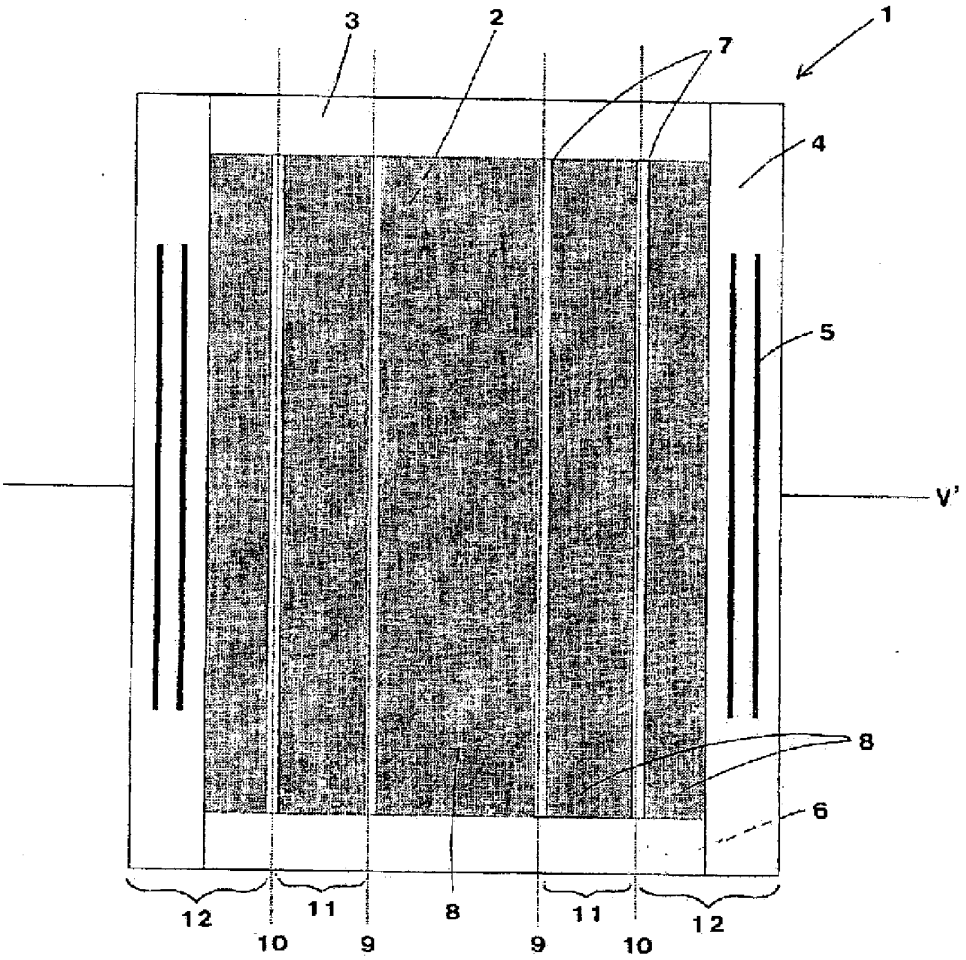
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【図53】吸収体本体に別の形態の切り込みが入ったものを説明する上面正面図である。
【符号の説明】
【0098】
１：尿パッド
２：吸収体本体
３：液透過性表面シート
４：液不透過性シート
５：伸縮弾性体
６：液不透過性裏面シート
７：長手方向屈曲構造部分
７’：幅方向屈曲構造部分
８：非屈曲構造部分
９：長手方向第１折り返し線
１０：長手方向第２折り返し線
１１：長手方向第１折り返し部
１２：長手方向第２折り返し部
１３：シート状吸収体
１４：ＳＡＰ塗工部
１５：基材
１６：パルプマット層
１７：端部領域
１８：幅方向第１折り返し線
１９：幅方向第１折り返し部
２０：袋状構造部
２１：側縁部
２２：幅方向第２折り返し線
２３：幅方向第２折り返し部
２４：接合領域
２５：おむつ本体
２６：襞部
２７：立体ギャザー
２８：切り込み部

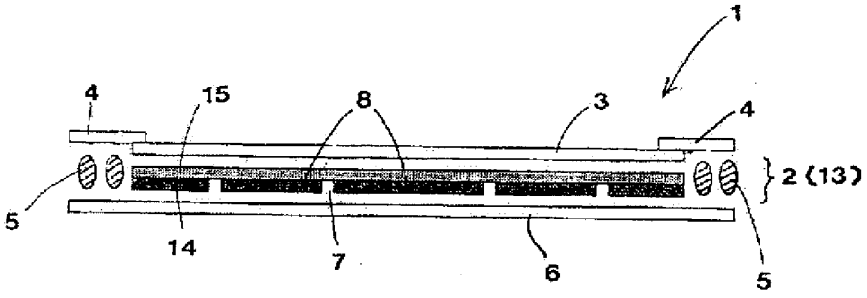
【図1】



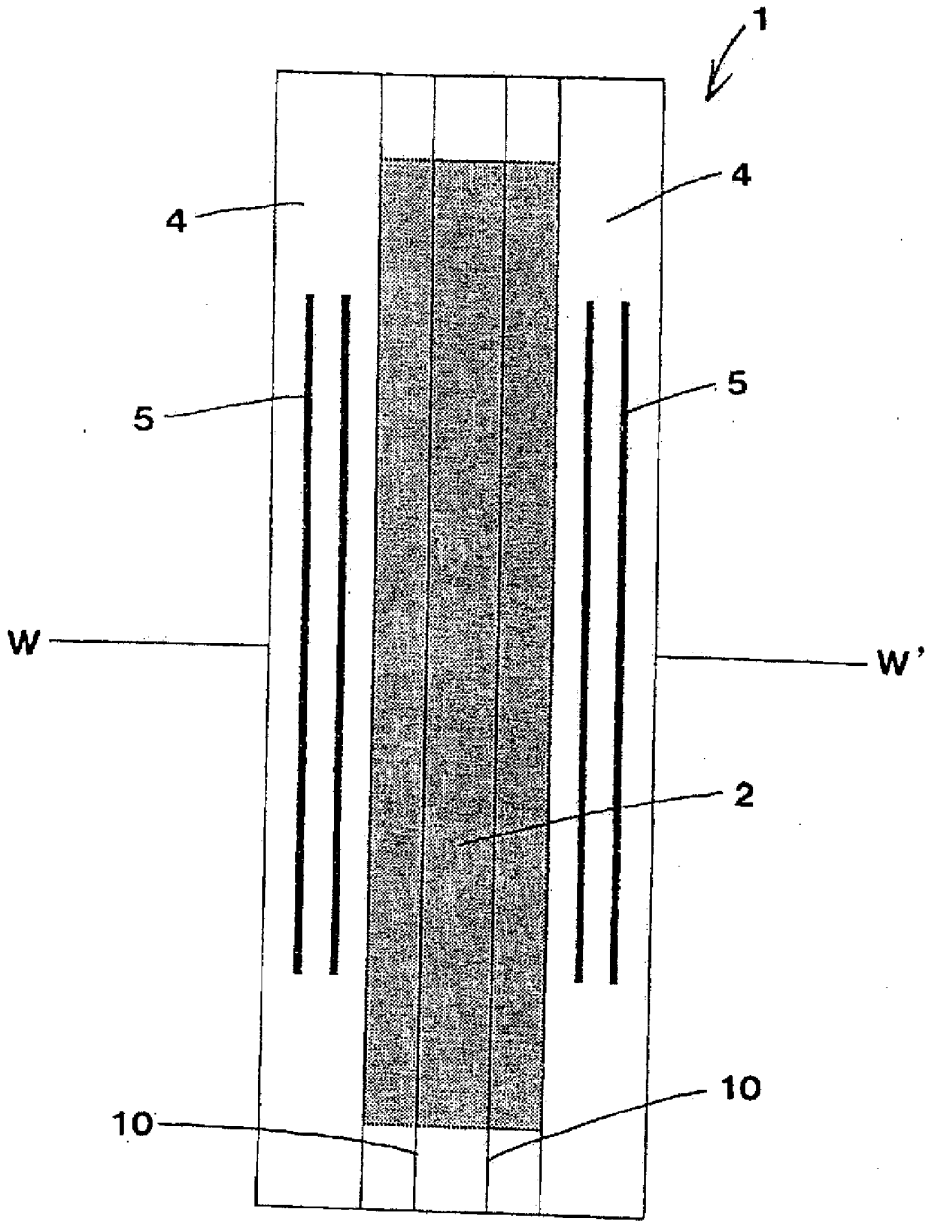
【図2】



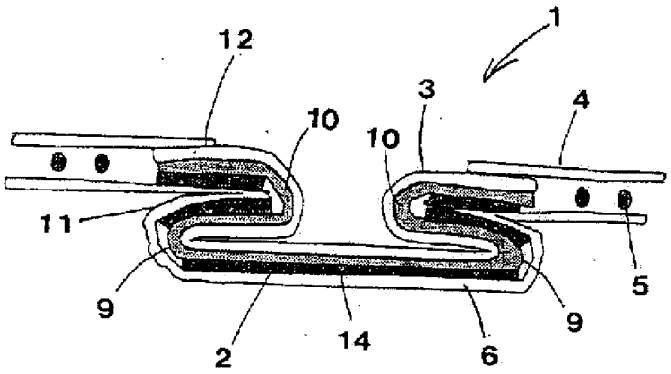
【図3】



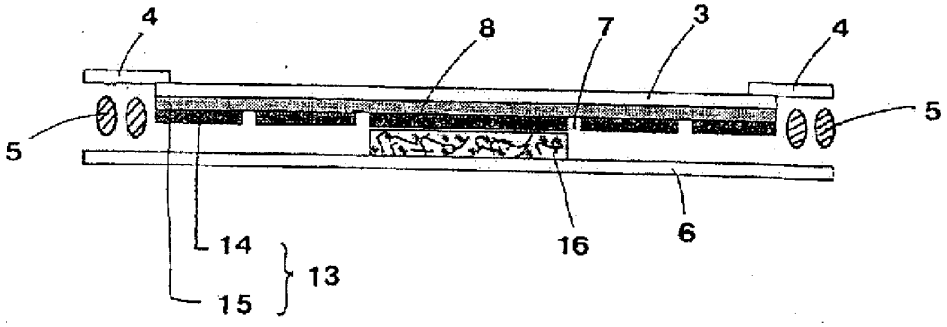
【図4】



【図5】



【図6】



【図7】

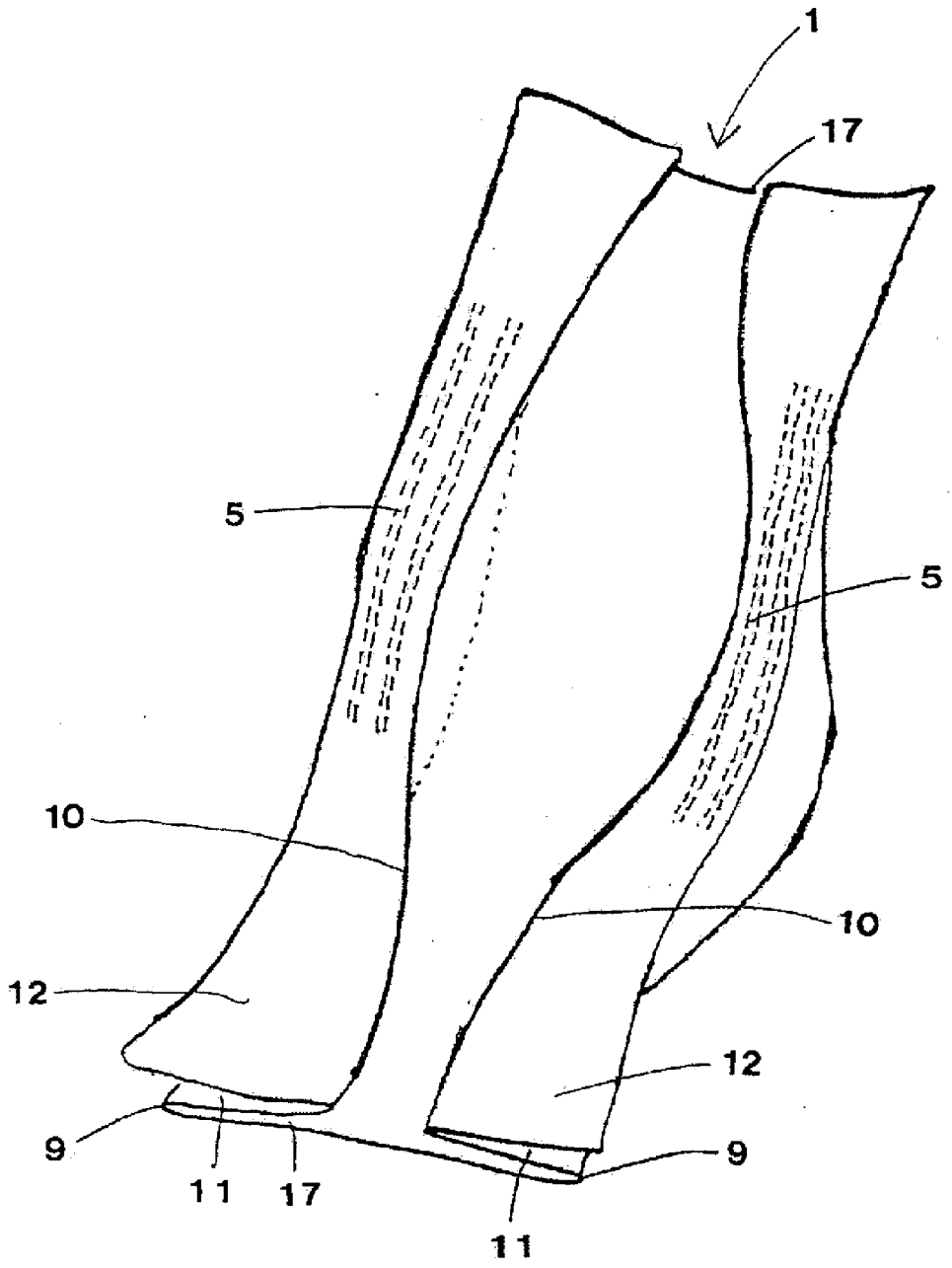
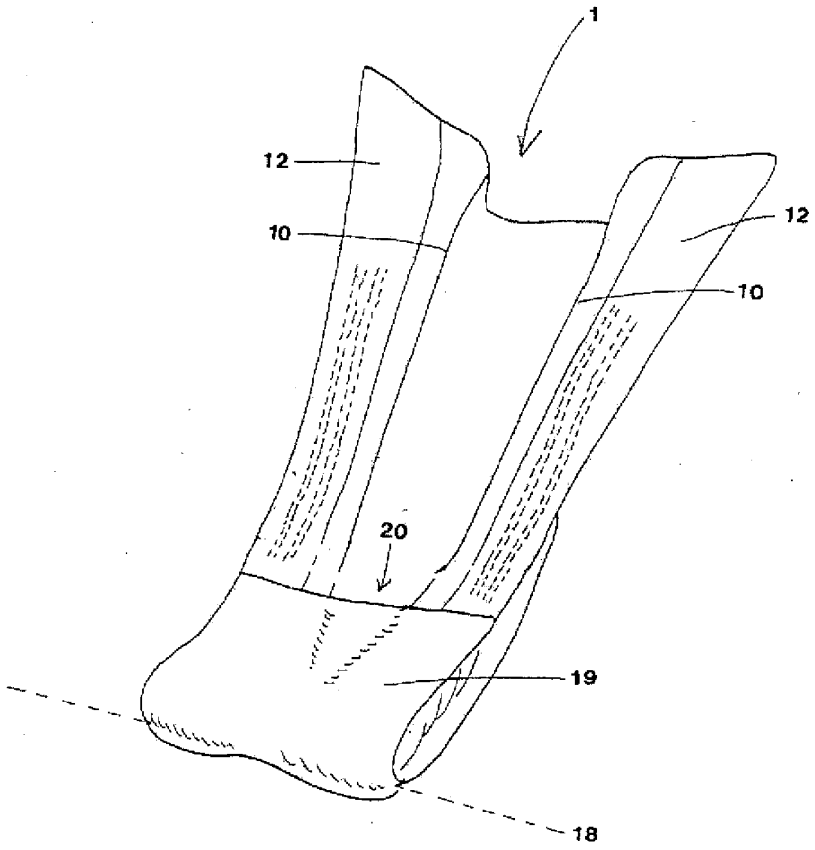
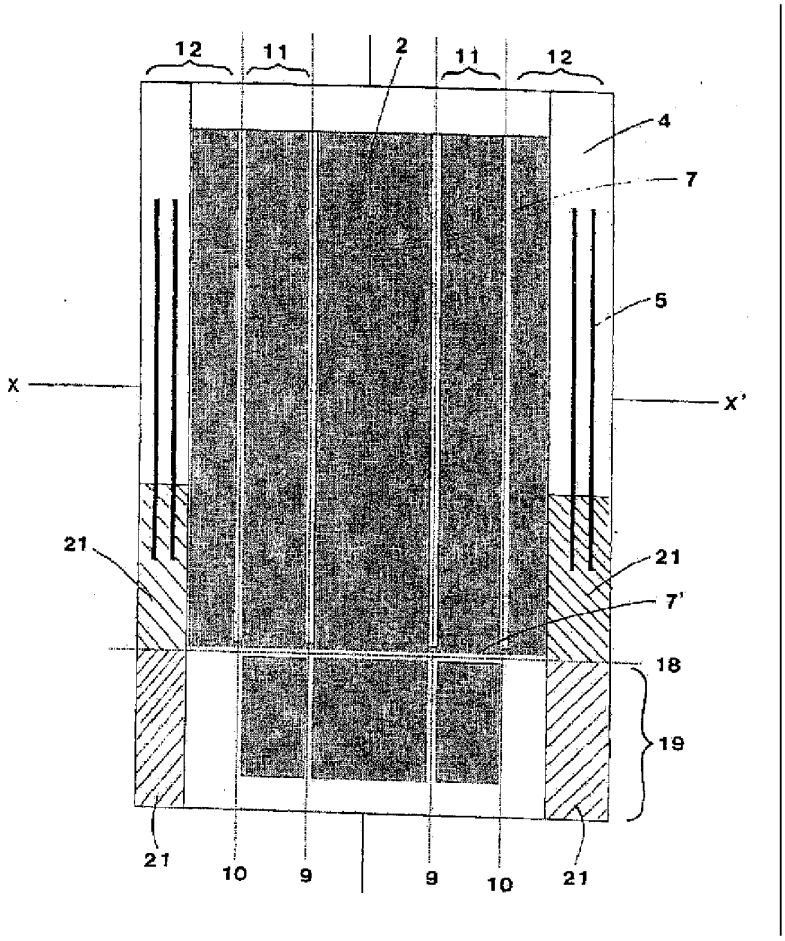


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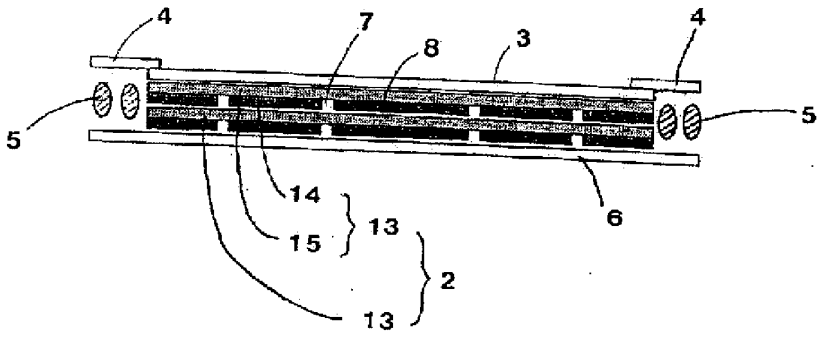
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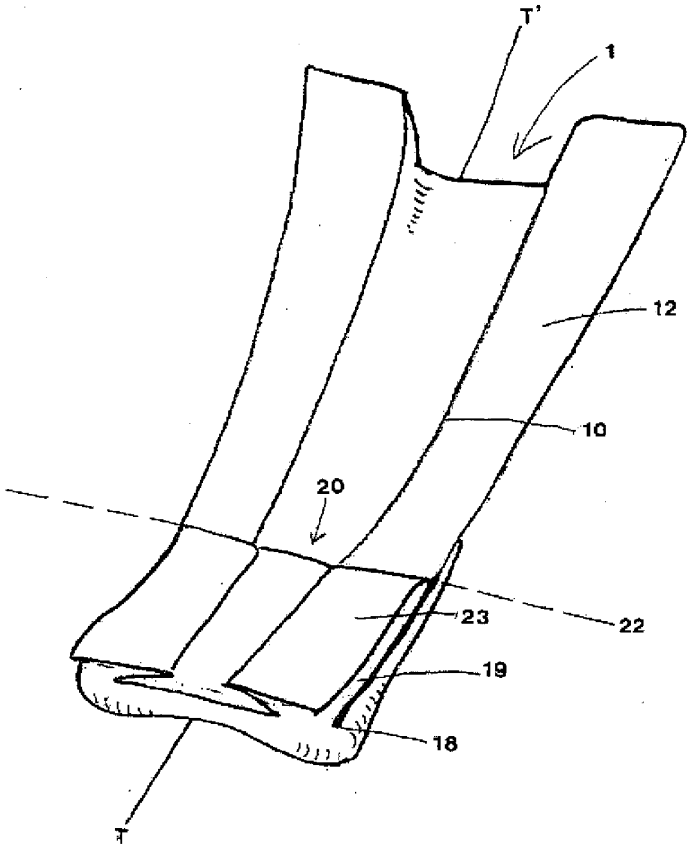
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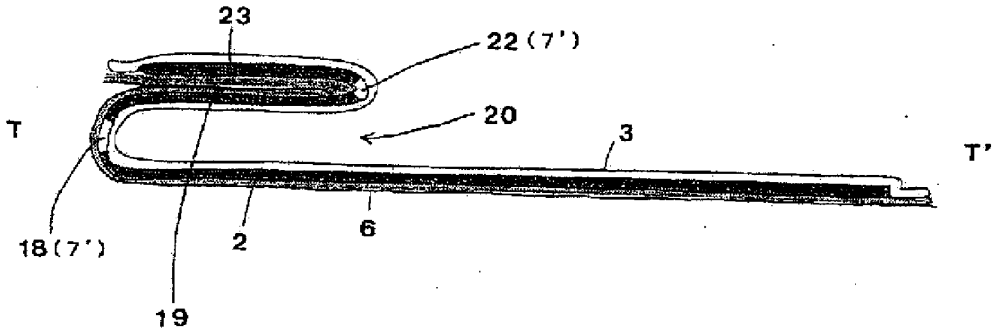
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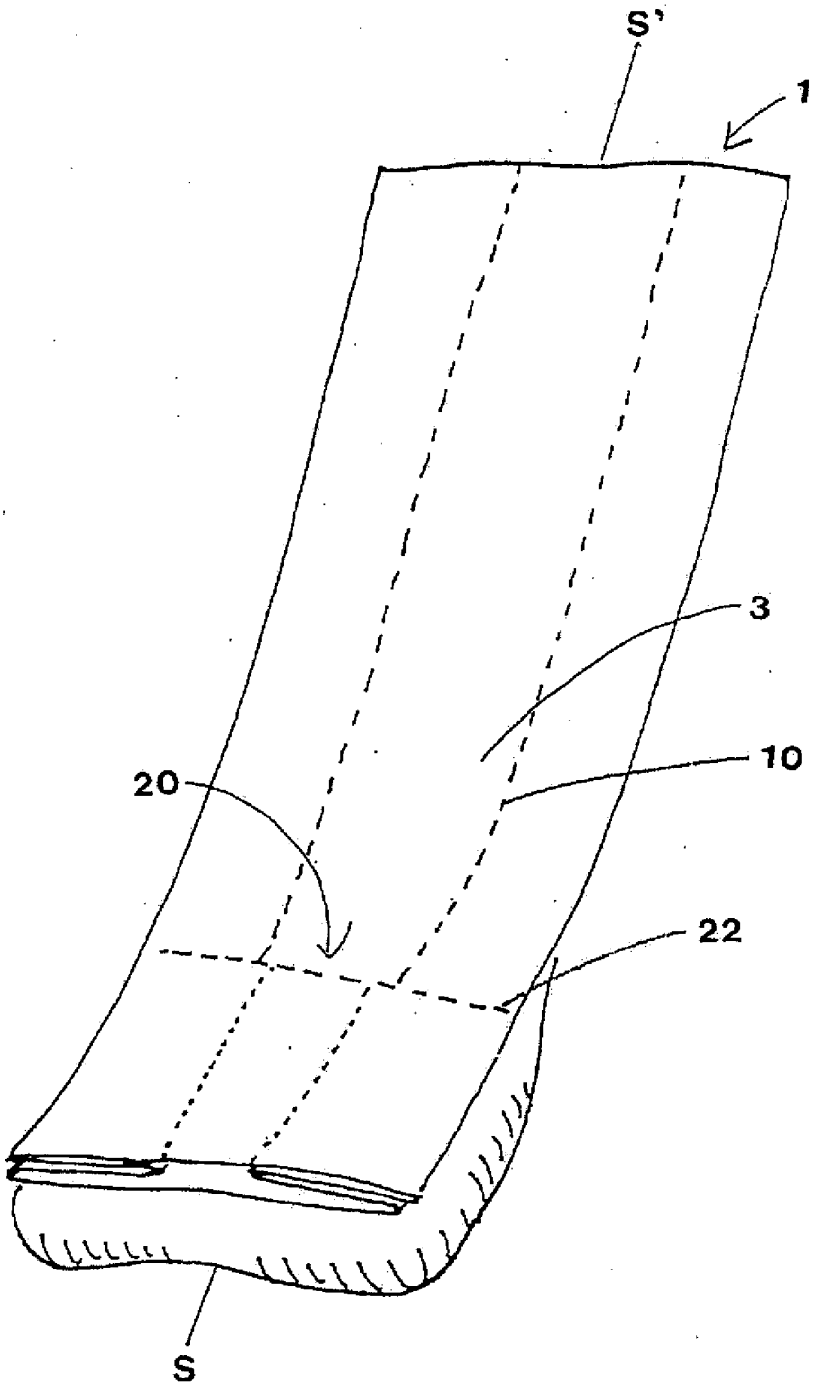
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【図12】



【図13】



【図14】

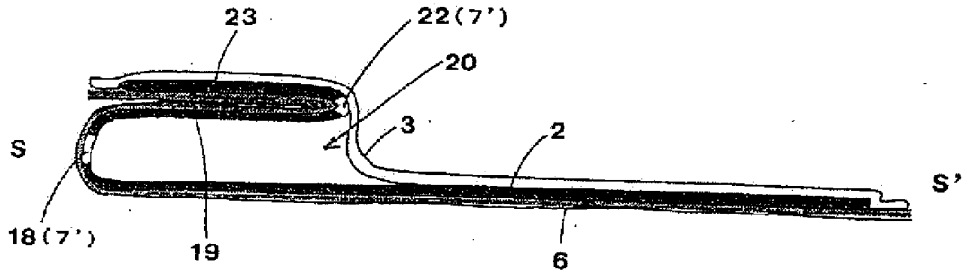
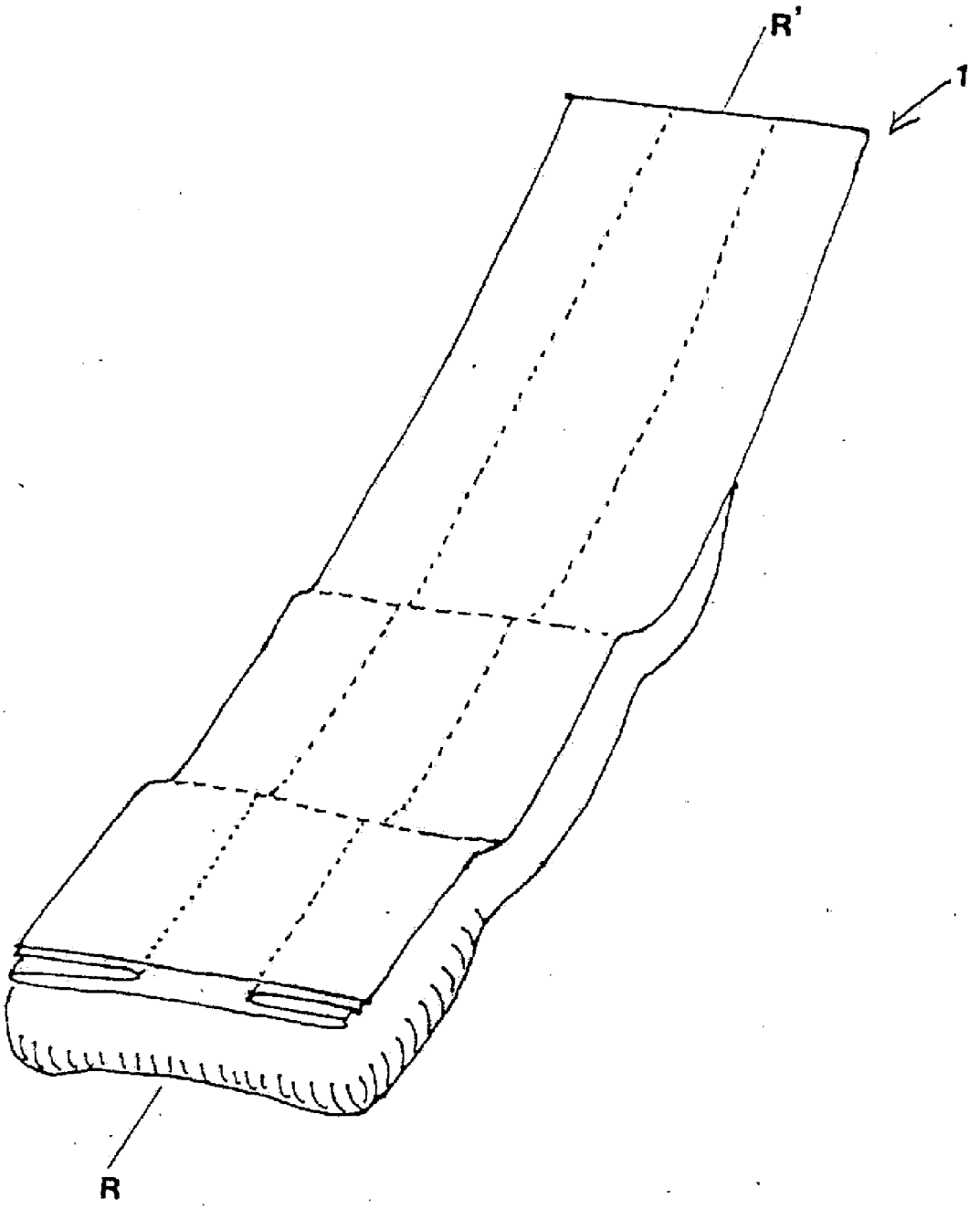
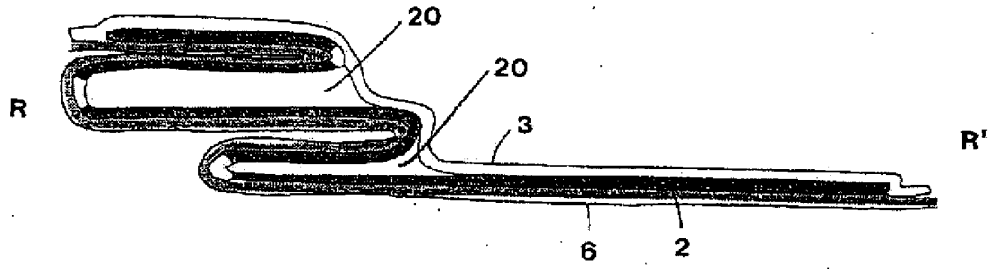


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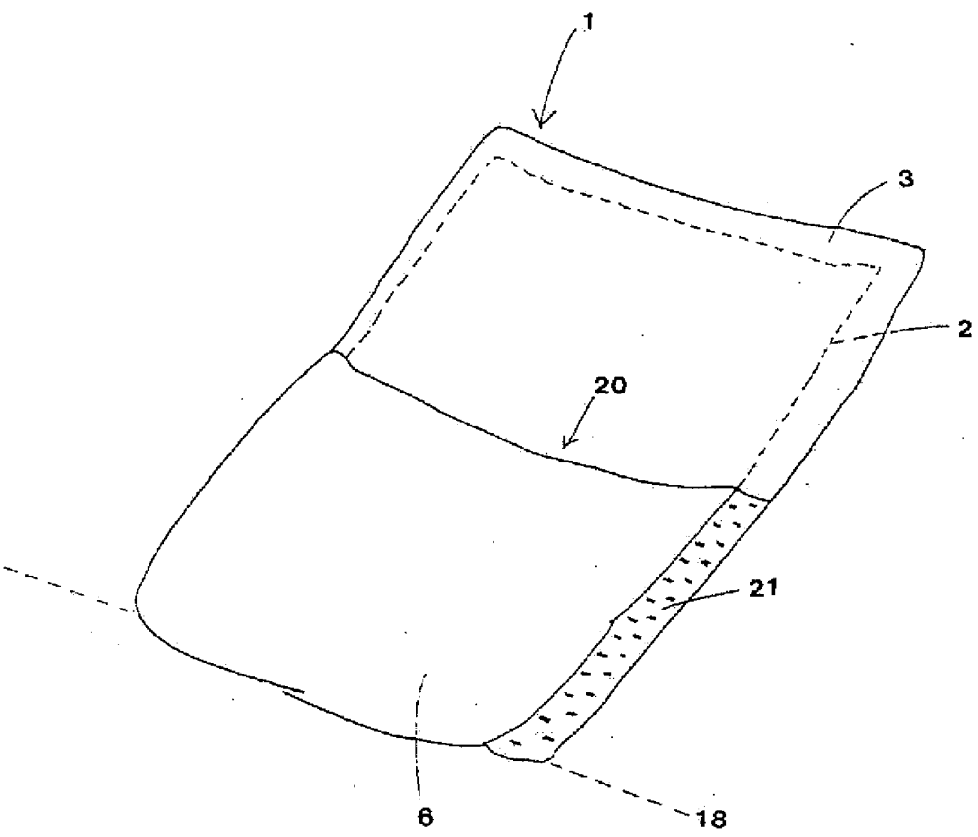
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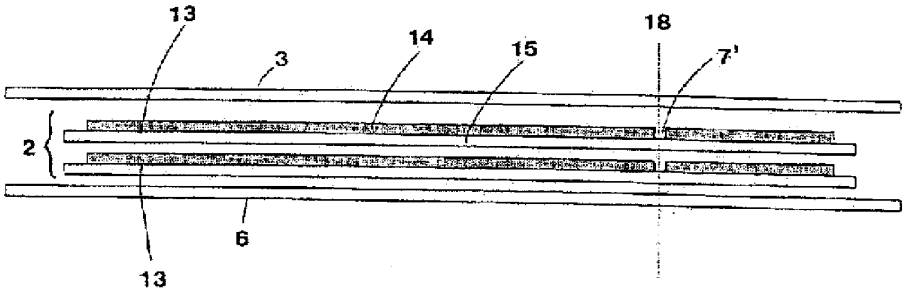
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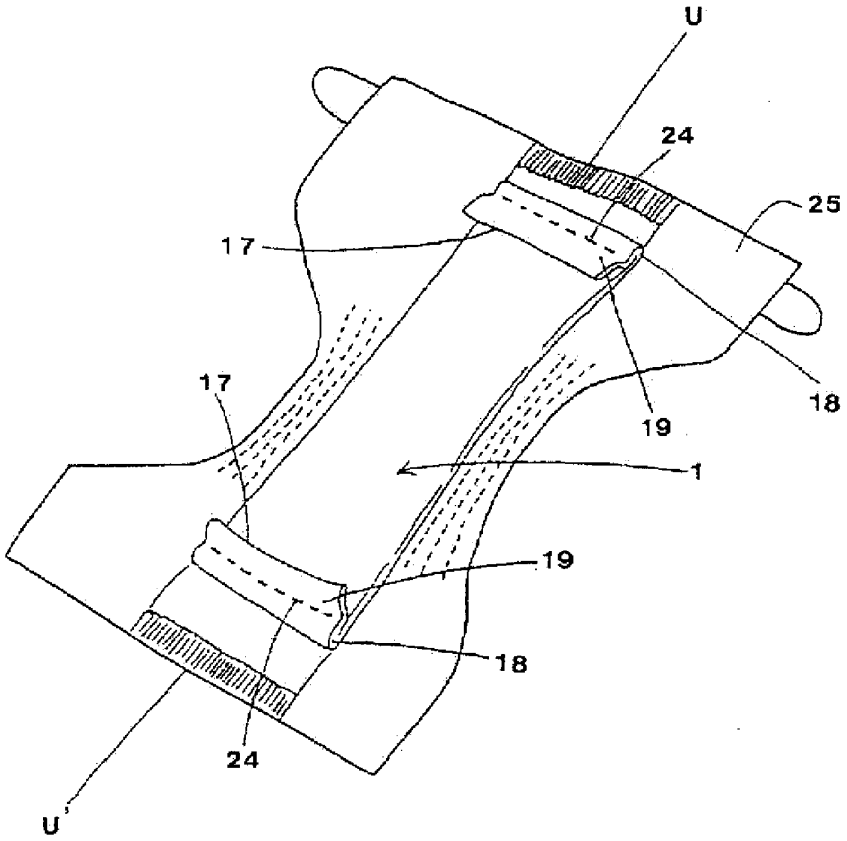
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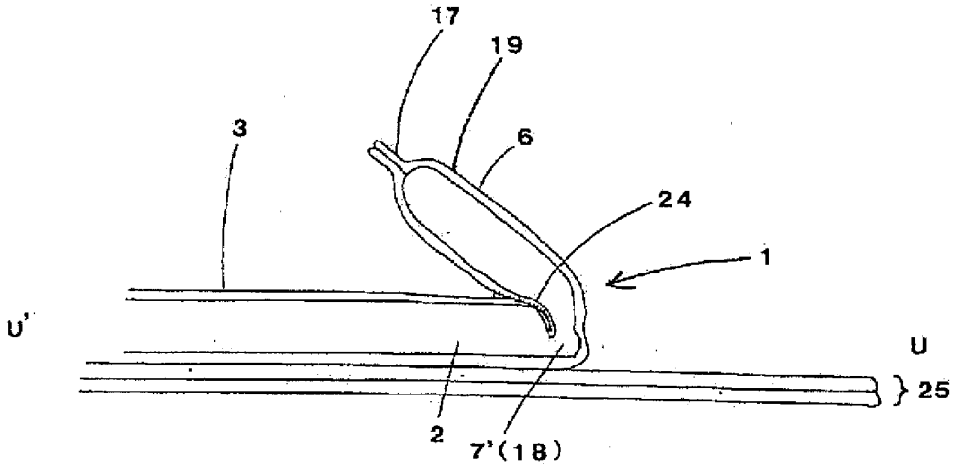
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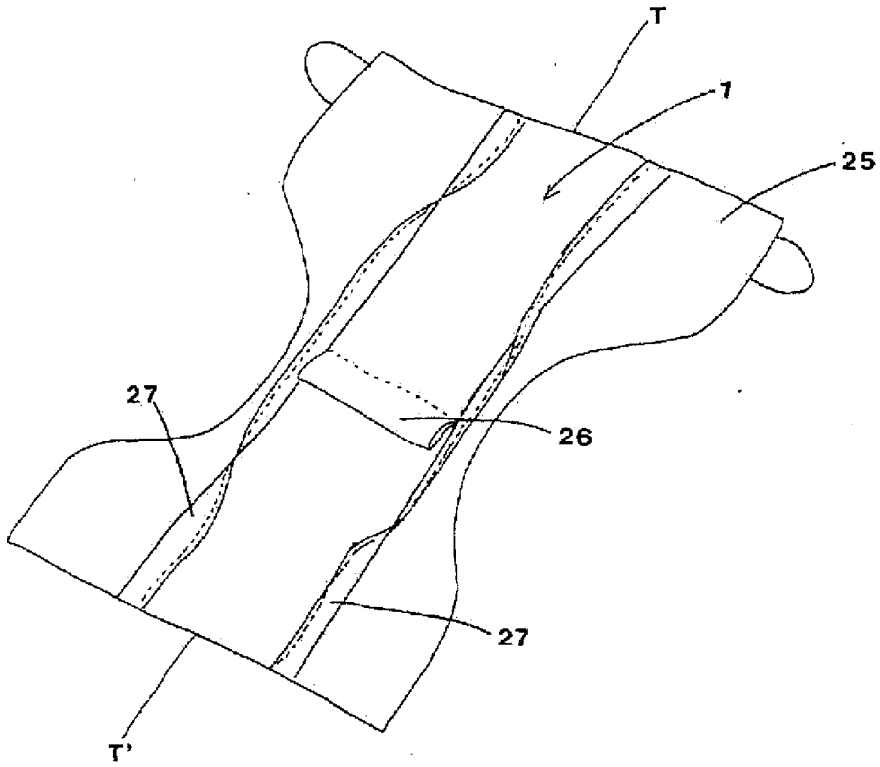
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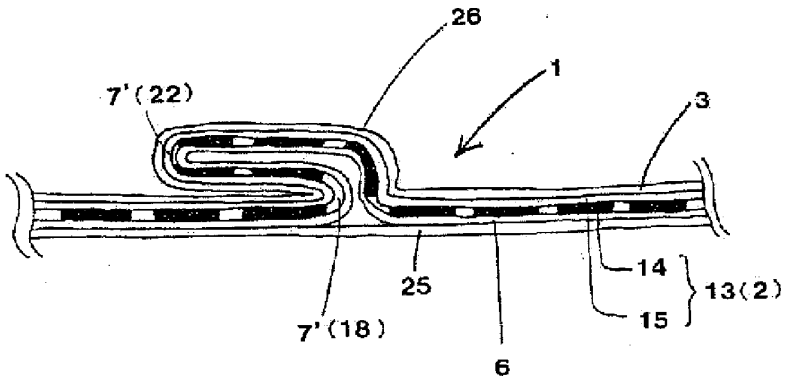
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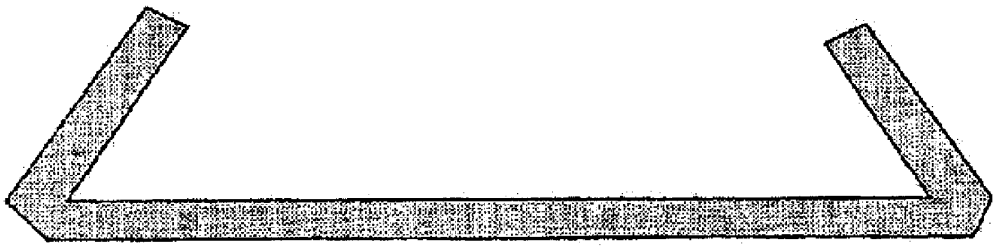
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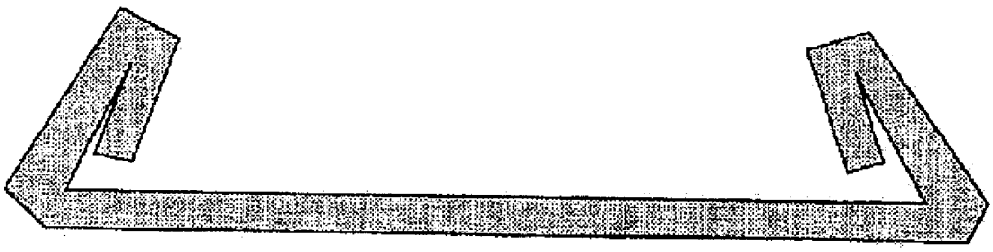
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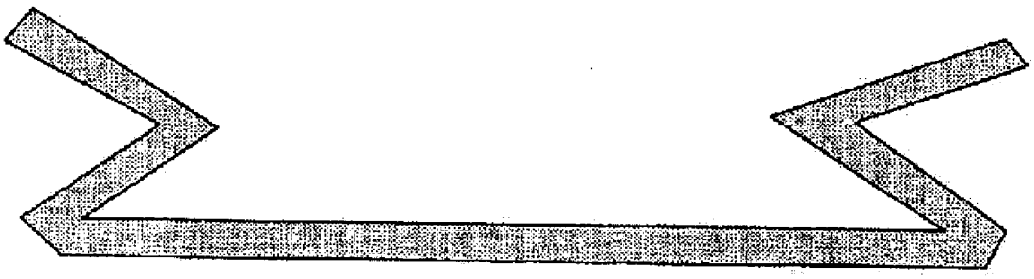
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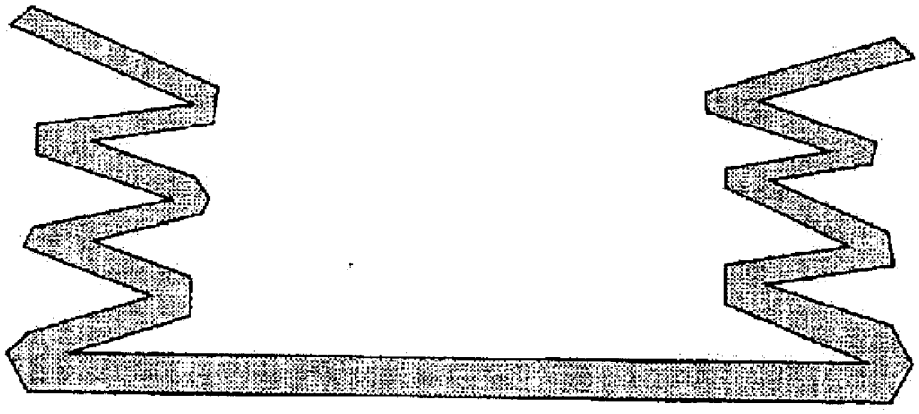
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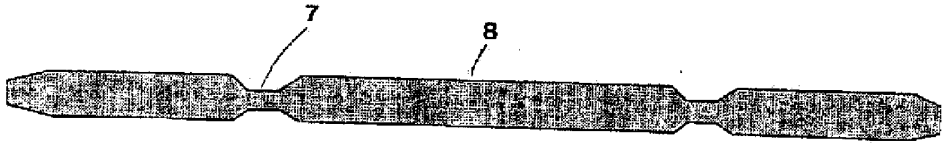
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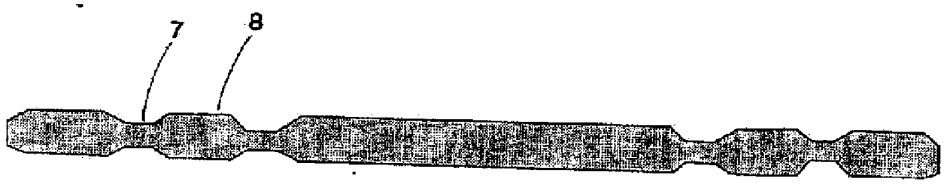
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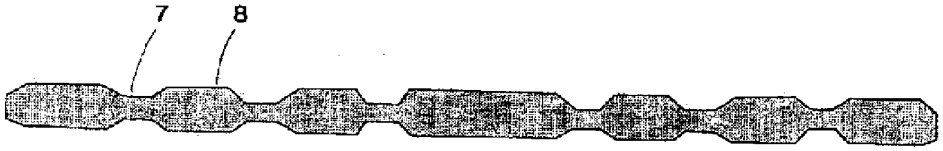
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【図29】



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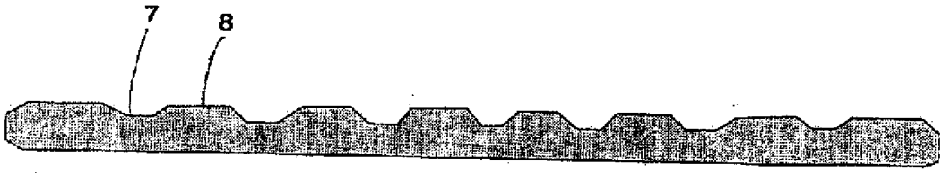
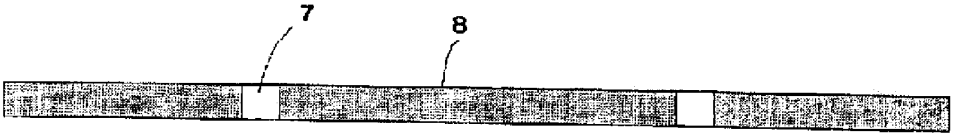
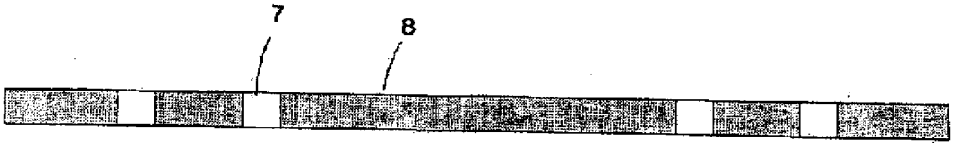


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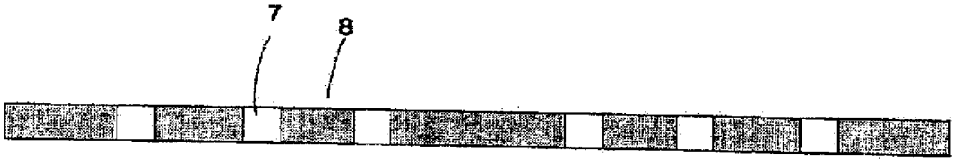
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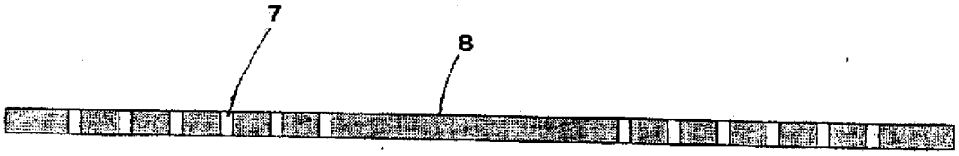
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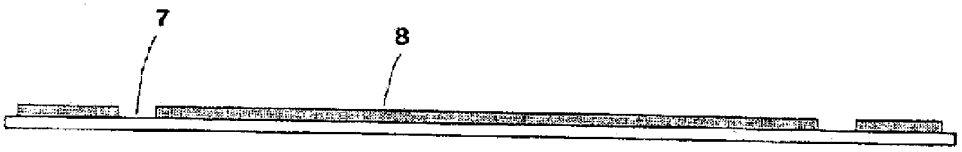
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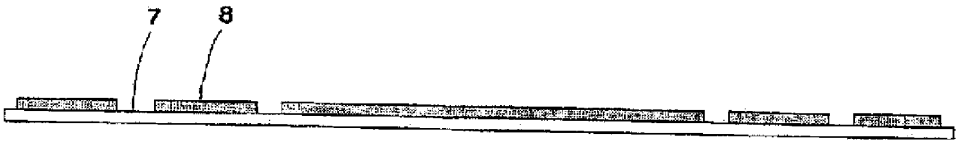
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【図35】



【図36】



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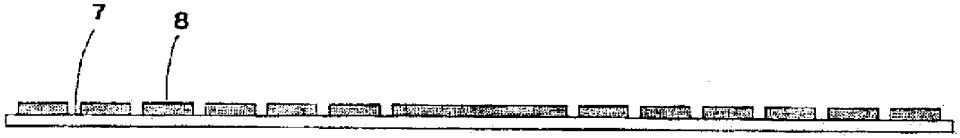
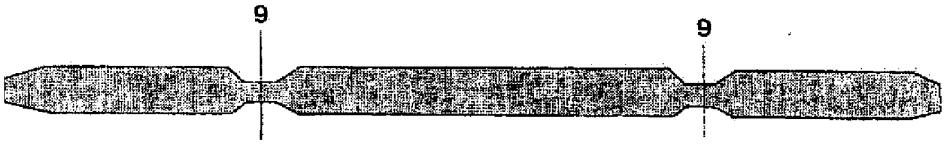
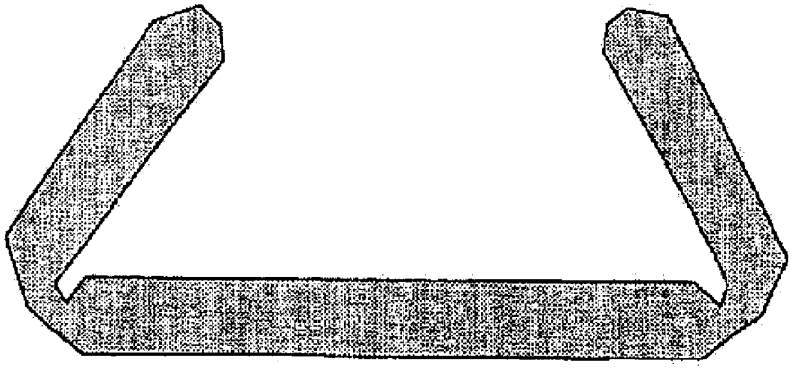


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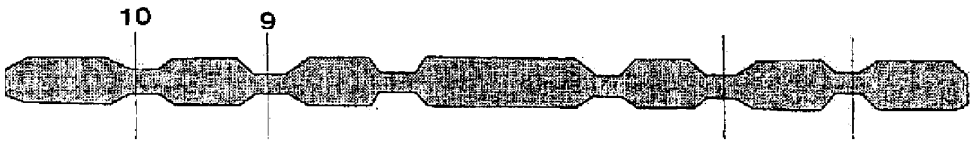
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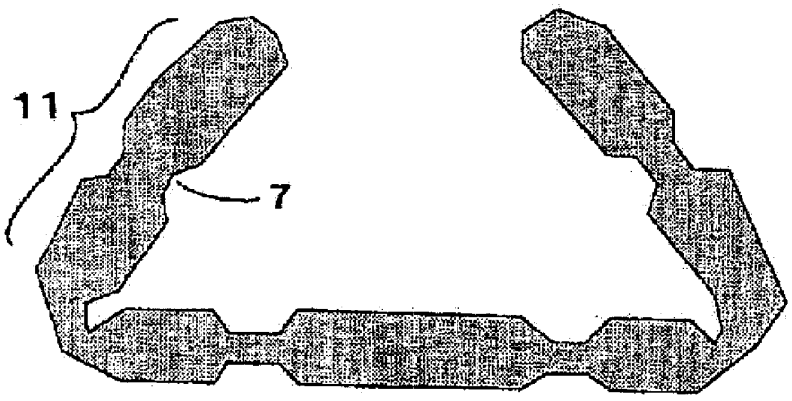
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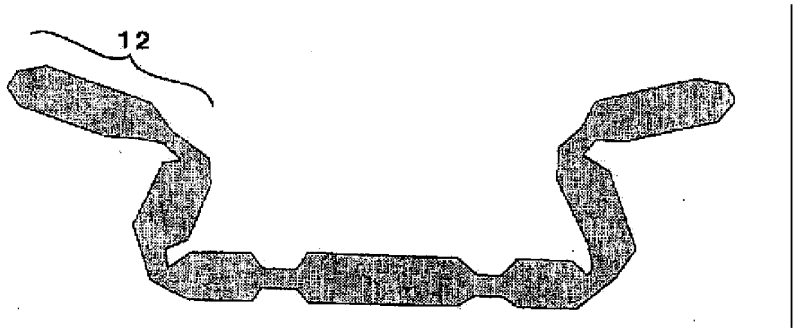
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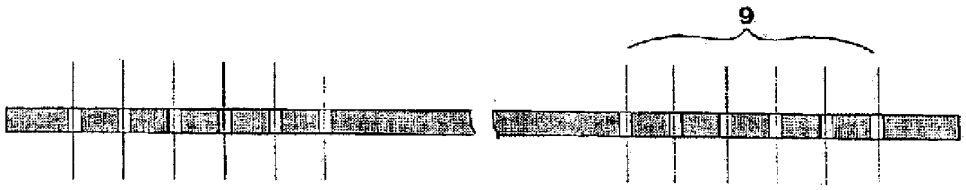
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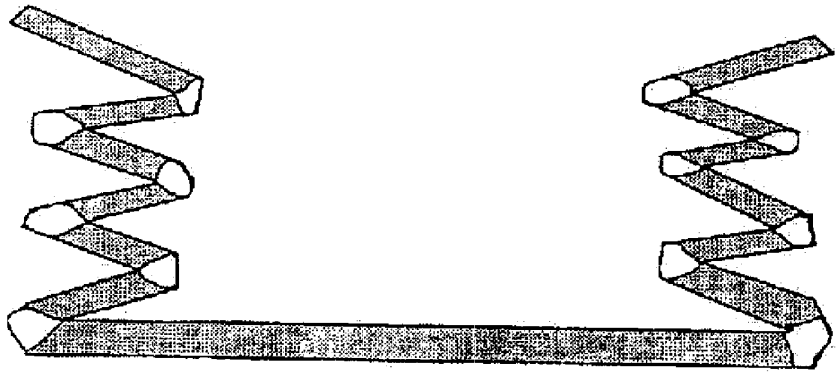
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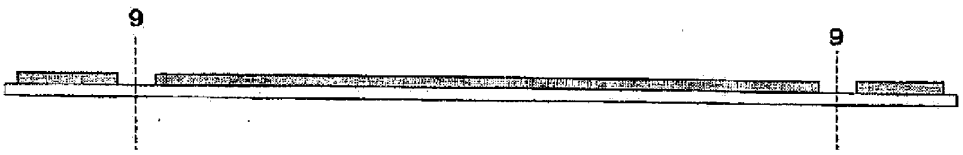
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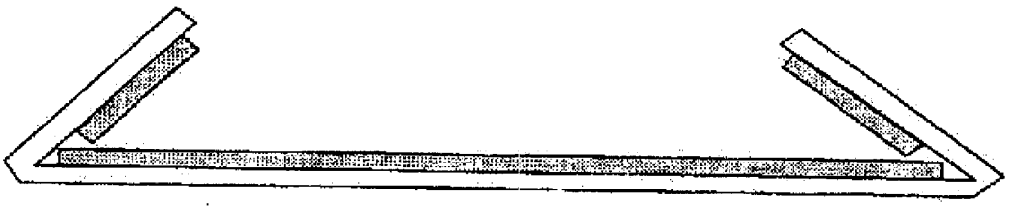
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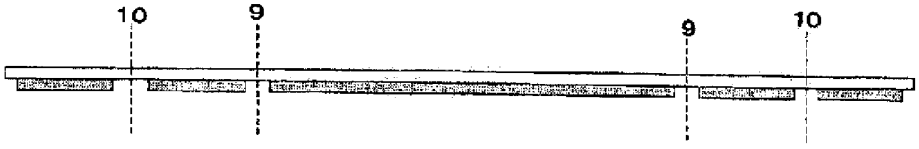
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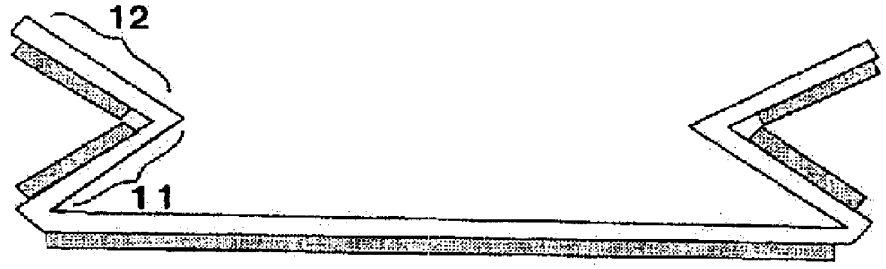
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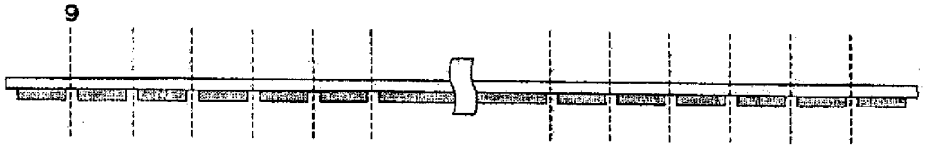
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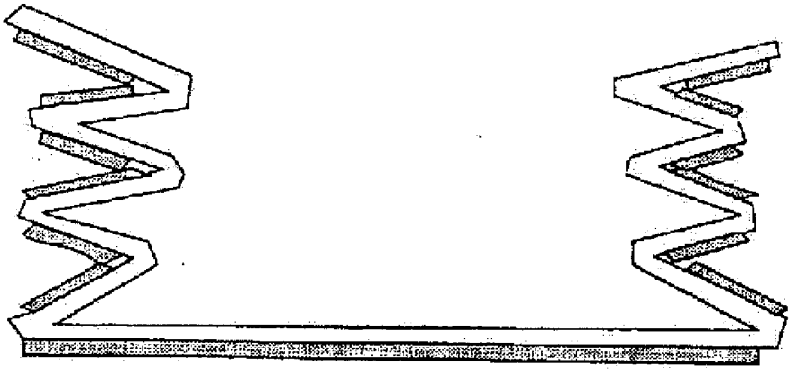
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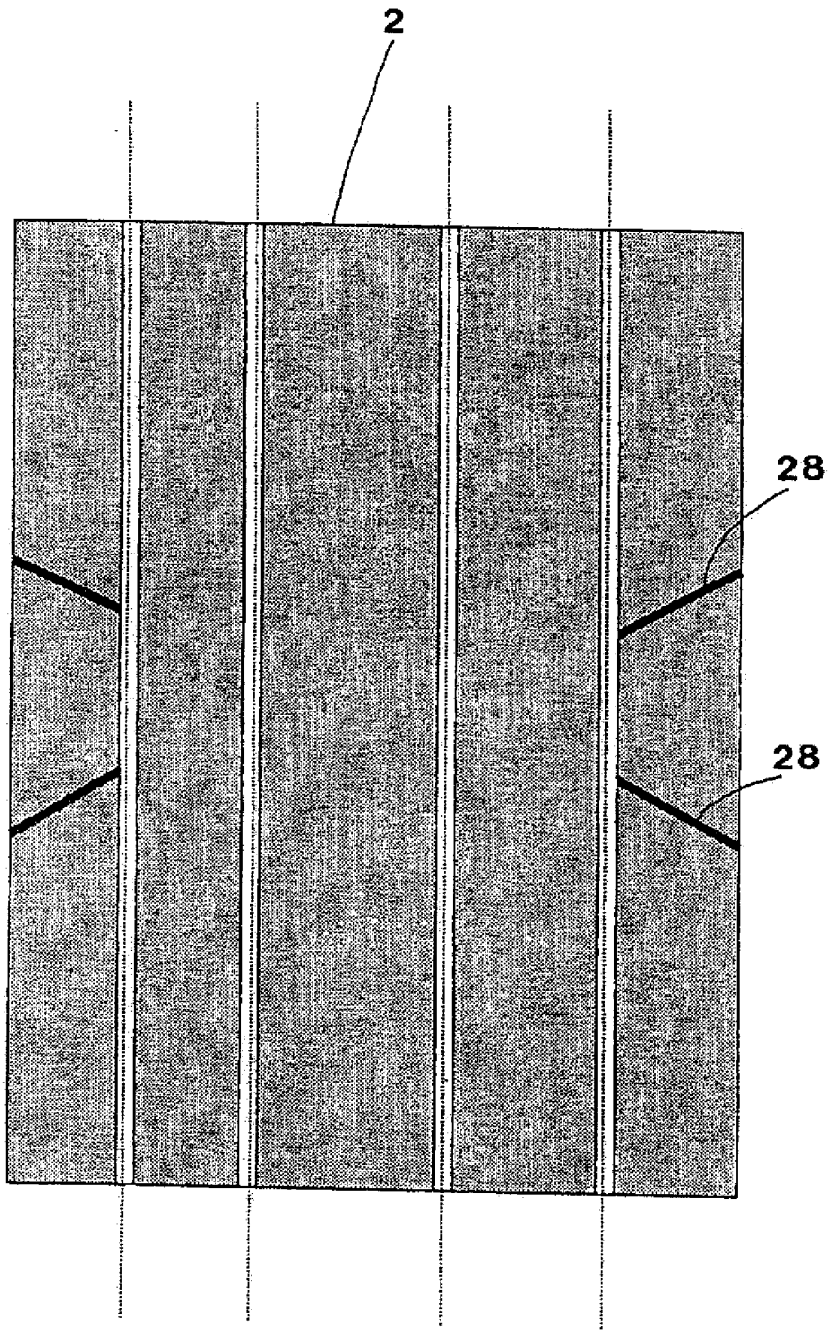
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【図50】



【図51】



【図52】

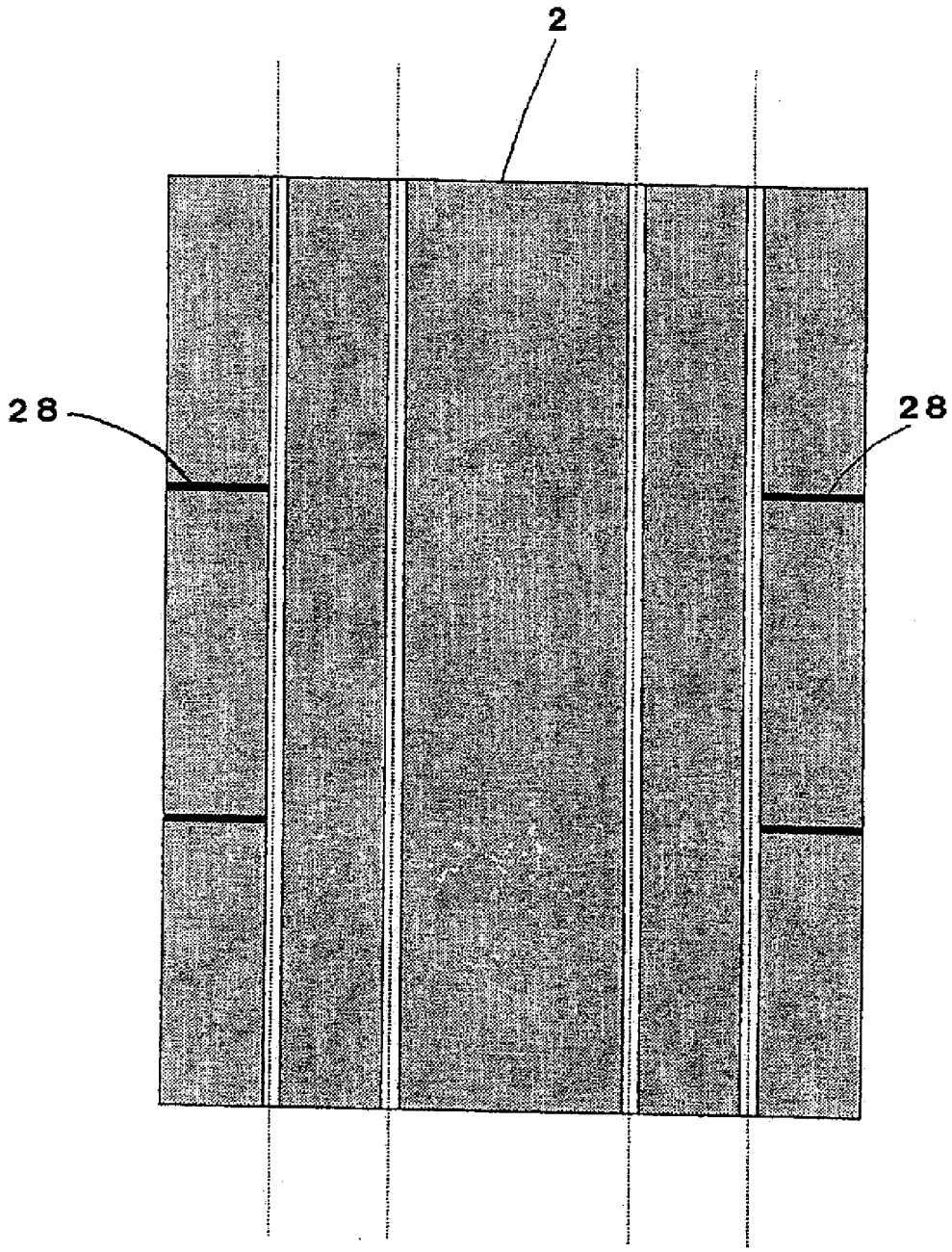
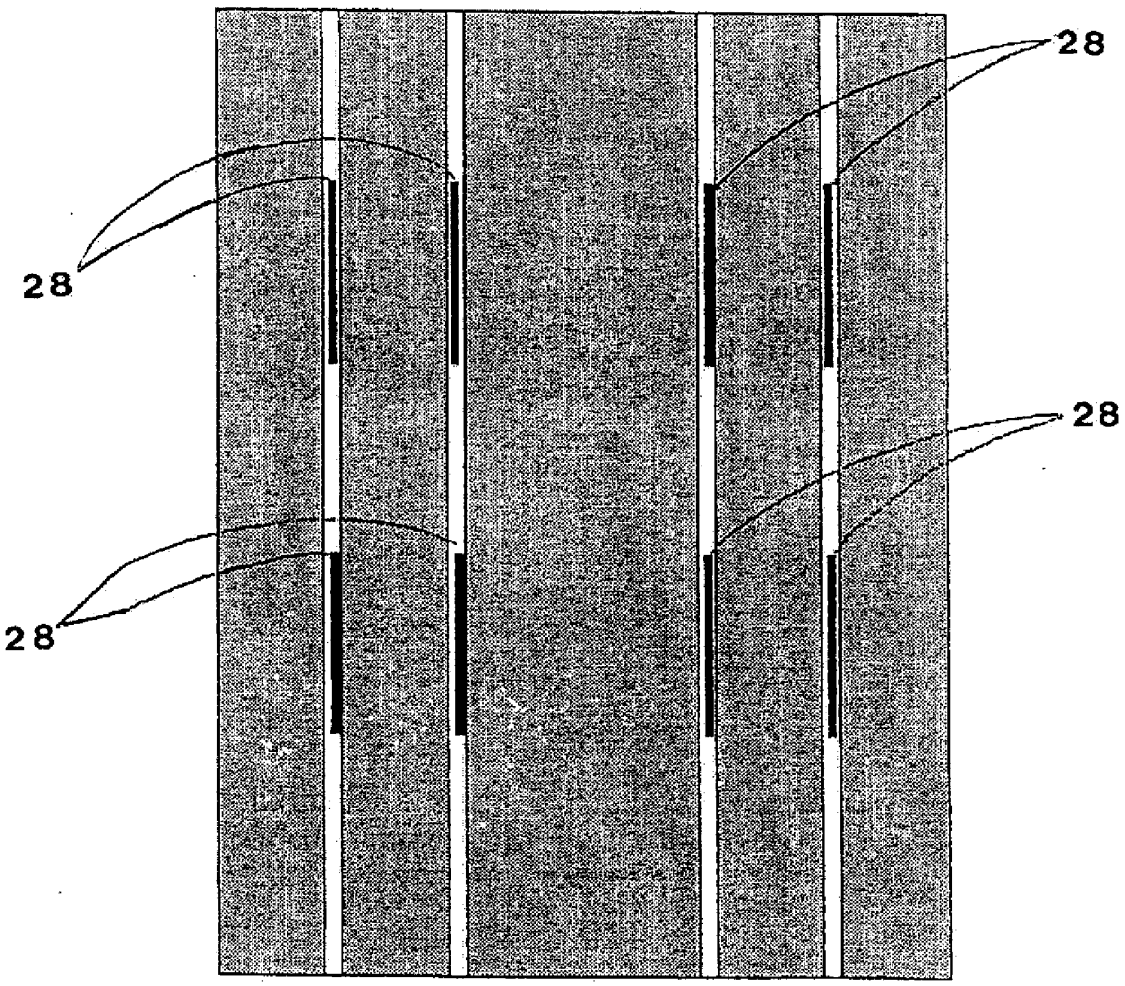


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【図53】



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Ｆターム(参考) 3B200 AA01 BA01 BA10 BA12 BA14 BA18 BB03 BB05 BB09 BB11
BB13 BB17 CA02 CA11 DA02 DA04 DA08 DA12 DB01 DB02
DB05 DB11 DB13 DB17 DB23
4C098 AA09 CC03 CC05 CC08 CC14 CE09 DD06 DD10 DD22 DD25
DD26 DD30

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Legal Status

(11)Publication number	64-058331
(43)Date of publication of application	06.03.1989
(51)Int.Cl.	B01D 53/36 B01J 21/18
(21)Application number	62-215024
(22)Date of filing	31.08.1987
(71)Applicant	MITSUI MINING CO LTD
(72)Inventor	KOMATSUBARA KATSUNOBU

(54)DENITRATION METHOD FOR EXHAUST GAS

(57)Abstract

PURPOSE: To increase SV value and enhance treatment capacity by using catalysts modified by means of making a carbon material of specific surface area of 20W1,500m2/g contact with ammonia and gas containing oxygen at the temperature of 150W450°C.

CONSTITUTION: A carbon material such as active carbon or the like with a specific surface area of 20W1,500m2/g is modified by making the same contact with ammonia of approximately 2vol.% or more and gas containing approximately 1vol.% or more with SV value approximately 50W10,000h-1 at the temperature of 150W400°C for 10min or more. As for components other than modified gas, nitrogen, carbon dioxide, water vapor or any others not affecting badly the carbon material such as combustion gas or the like can be used. Then, ammonia is added to exhaust gas, which is made in contact with catalysts of modified carbon material prepared at the temperature of approximately 60W200°C and denitrated. By said process, SV value of exhaust gas can be increased and treatment capacity is enhanced to a large extent to obtain a sufficient denitration effect.

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⑲日本国特許庁（JP）　⑪特許出願公開

⑫公開特許公報（A）　昭64－58331

⑤1Int.Cl.⁴	識別記号	庁内整理番号	④3公開　昭和64年(1989)3月6日
B 01 D 53/36	102	F－8516－4D	
B 01 J 21/18		A－8618－4G	

審査請求　未請求　発明の数 1　（全3頁）

⑤4発明の名称　排ガス脱硝方法

⑵1特　願　昭62－215024

⑵2出　願　昭62(1987)8月31日

⑦2発明者　小松原　克展　福岡県北九州市若松区響町1丁目3番　三井鉱山株式会社九州研究所内

⑦1出願人　三井鉱山株式会社　東京都中央区日本橋室町2丁目1番1号

明　細　書

1.発明の名称

排ガス脱硝方法

2.特許請求の範囲

1）比表面積20～1500 ㎡／gの炭素材をアンモニアおよび酸素を含有するガスと150～450℃の温度で接触せしめて改質した触媒を使用し、アンモニアの存在下に窒素酸化物を含む排ガスを処理することを特徴とする排ガス脱硝方法。

3.発明の詳細な説明

＜産業上の利用分野＞

本発明は燃焼排ガスや工場排ガスなどの窒素酸化物を含む排ガスから窒素酸化物を除去する方法に関する。

＜従来の技術＞

燃焼排ガスや工場排ガスなどの窒素酸化物を含む排ガス中に含有されている窒素酸化物の除去方法は、乾式法と湿式法に大別され、乾式法はさらに金属、セラミックス系触媒を使用した接触還元法と吸着法に分類される。

従来知られている種々の窒素酸化物除去技術の中で実用化されているものの大半は金属酸化物を触媒とし、250～400℃の温度範囲で操作されるアンモニアによる窒素酸化物の選択的接触還元法である。

この金属酸化物系脱硝法は処理温度が高いため、一連の排ガス処理設備において上流側に反応器を設置し、下流側で熱回収、湿式脱硫、排ガス再昇温（白煙防止）等を行わねばならず、排ガス処理工程は複雑であった。また脱硝反応器を上流側に設けるためそこに吹き込むアンモニアガスは、排ガス中の硫黄酸化物と反応し酸性硫安等を生成し、下流側設備における閉塞、腐食等を誘引しトラブルを起こすことが多かった。

近年になり、より低温の60～200℃で操作できる新しい窒素酸化物の除去方法として活性炭等の炭素材料を用いたアンモニア接触還元法が注目されている。炭素材料による窒素酸化物除去法の最大の利点は、脱硝温度が60～200℃と低いことである。すなわち排ガス中の顕熱を十分に回収した

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のち脱硝できるということである。

そのため炭素材料による脱硝設備は熱を回収したあとに設置可能であり、さらに活性炭等の炭素材料は従来知られているように脱硝機能に加えて脱硫機能も有しているので排ガス中に含まれる硫黄酸化物も同時に除去され、反応容器出口では硫黄酸化物はほぼ完全に除去されるので、酸性硫安の生成などによるトラブルの恐れがない。

しかしながら炭素材料による脱硝方法においては一般に反応速度が遅く、空間速度ＳＶを大きくとることができず、例えば窒素酸化物の除去率を８０％以上にしようとすれば、金属酸化物系の触媒を使用し、250～400℃で実施する場合ＳＶ値が3000～~~100000~~(30000)h^{-1}であるのに対し、炭素材料を使用する場合には100℃付近の低温処理ではＳＶを約200h^{-1}以下、200℃付近の処理においてもＳＶ1000以下とする必要がある。

＜発明の解決すべき問題点＞

本発明は前述のような特徴、欠点を有する炭素材料による脱硝方法をさらに改良し、ＳＶ値を大きくとることができ、処理能力を大幅に向上させた脱硝方法を提供することを目的とする。

＜問題を解決するための手段＞

本発明の方法は、比表面積20~1500㎡／ｇの炭素材をアンモニアおよび酸素を含有するガスと150～450℃の温度で接触せしめて改質した触媒を使用し、アンモニアの存在下に窒素酸化物を含む排ガスを処理することによる排ガス脱硝方法である。

本発明における炭素材としては、20～1500㎡／ｇの比表面積を有する木炭、石炭、コークス、活性コークス、活性炭など任意の炭素材を使用することができる。

これらの炭素材を、２容量％以上好ましくは５容量％以上のアンモニアと１容量％以上好ましくは３容量％以上の酸素を含むガスと150～400℃の温度で接触させて改質する。改質ガスの他の成分としては窒素、二酸化炭素、水蒸気あるいは燃焼排ガス等炭素材に対し悪影響を及ぼさないものであれば何を用いてもよい。接触温度が低すぎると改質が円滑に進行せず、また温度が高すぎると炭素材の損耗が起るので好ましくない。ガスとの接触時間は接触温度等他の条件により異なるが10分以上、好ましくは３時間以上とする。接触させるガス量としてはＳＶ値、すなわちガス量（$N㎥/h$）を改質反応装置の体積（㎥）で除した値が50～10000h^{-1}好ましくは50～1000h^{-1}である。

前記のようにして製造した改質炭素材はアンモニアの作用により窒素酸化物を還元分解する際の触媒として極めてすぐれた性能を有している。すなわち燃焼排ガスや工場排ガス等窒素酸化物を含有する排ガスにアンモニアを添加し、60～200℃の温度で本発明の改質活性炭と接触させることにより充分な脱硝効果を得ることができる。

以下実施例により本発明の方法をさらに具体的に説明する。

なお、以下の実施例における脱硝率はそれぞれの触媒反応が定常になった時点での数値に基づき、次の式に従って算出した。

脱硝率（％）＝（入口NO濃度－出口NO濃度）
÷（入口NO濃度）×100

実施例１

比表面積200㎡／ｇの石炭系活性炭Ａをアンモニア１０％、酸素１９％、窒素７１％の組成のガスと300℃で６時間接触させて処理し、改質活性炭Ｂとした。

NO 200ppm、NH_3 200ppm、O_2 ５％、H_2O １０％、残り窒素の組成のガスを試料Ａ、Ｂを触媒とし、温度130℃、ＳＶ400h^{-1}の条件で処理し脱硝率を測定した。その結果、試料Ａでの脱硝率が６１％であったものが試料Ｂでは８２％であった。

実施例２

改質処理ガスの組成をアンモニア１０％、酸素５％、窒素８５％のガスとした他は実施例１と同様にして改質処理、脱硝試験を行なった結果脱硝率は７５％であった。

実施例３

改質処理の温度をそれぞれ200℃、250℃、

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350℃および400℃とした他は実施例1と同様にして改質処理および脱硝試験を行なった結果、脱硝率はそれぞれ67%、72%、82%および81%であった。

実施例4

比表面積900㎡／gの石炭系活性炭Cを使用した他は実施例1と同様に改質処理および脱硝試験を行なった結果、脱硝率は60%であった。なお活性炭Cを用いた脱硝試験結果は2%であった。

実施例5

実施例1の改質ガスの窒素71%をそれぞれ二酸化炭素71%あるいは水蒸気71%とした他は実施例1と同様に改質処理および脱硝試験を行なった結果、脱硝率は両者とも試料Bと同等であった。

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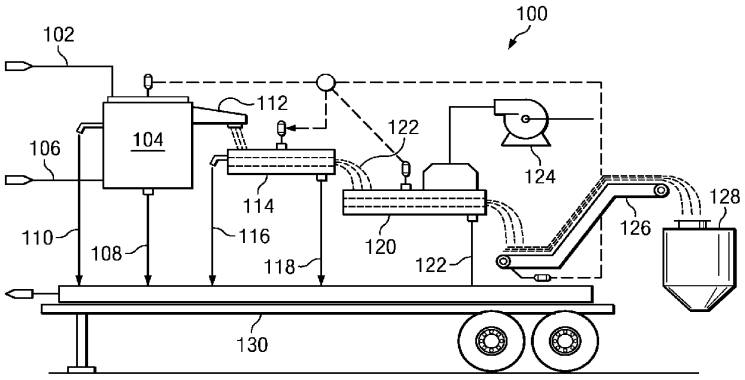


FIG. 1

(57) **Abstract**: A system for activating carbonaceous material including a carbonaceous material feedstock unit for producing a carbonaceous material of less than 5% mineral content; a digestion unit in communication with the carbonaceous material feedstock unit; an acid feedstock unit in communication with the digestion unit for providing an acid mixture solution; a separation unit in communication with the digestion unit for separating the digested carbonaceous material from the acid mixture solution; a dryer unit in communication with the separation unit for drying the digested carbonaceous material and separating the carbonaceous material; and a thermal unit for activating the carbonaceous material to produce activated carbonaceous material, the thermal unit having an inlet for receiving the carbonaceous material from the dryer unit and an outlet for exiting the activated carbonaceous material from thermal unit.

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TITLE

SYSTEM AND METHOD FOR ACTIVATING CARBONACEOUS MATERIAL

FIELD OF THE INVENTION

The field of the invention is directed to refining carbonaceous material and more specifically to activating carbonaceous material.

BACKGROUND OF THE INVENTION

Activated carbonaceous material, such as activated carbon, is a porous substance that has a large surface area and accordingly a large adsorption ability for a wide range of uses as an adsorbent for various purposes. For example, activated carbon may be used for adsorbing gases and vapors, recovering solvents, purifying gases, deodorizing gases, and contacting with liquids so as to treat water, decolor or purify solutions. Additionally, activated carbon may be used as carriers for catalysts. On account of its highly non-specific adsorptive properties, activated carbon may be the most widely used adsorbent. Further, statutory requirements as well as increasing environmental awareness are leading to an increasing demand for activated carbon.

Activated carbon is generally obtained by carbonization, such as by pyrolysis, smoldering, or coking, followed by the subsequent activation of suitable carbon-containing starting materials. Carbonaceous starting materials which lead to economically viable yields are preferred, since the weight losses caused by the removal of volatile constituents during carbonization and caused by burn-off during activation are considerable. The condition of the activated carbon produced – finely porous or coarser porous, strong or brittle etc. – depends on the carbon-containing starting material. Examples of standard carbonaceous starting materials include coconut shells, wood waste, peat, hard coal, pitches, but also particular plastics, such as for example sulfonated polymers, which play a major role inter alia in the production of activated carbon in the form of small granules or spheres.

Various forms of carbon may be used: powder coal, splint coal, granular coal, shaped coal, granule carbon, and spherical carbon. Granular coal, in particular spherical coal, is in very great demand for particular application areas, such as for many of the applications noted above. Activated carbon is usually produced in rotary tubular kilns (i.e. rotary tubular furnaces). These have, for example, a location for the raw material charge to be introduced at the start of the kiln and a location for the

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end product to be discharged at the end of the kiln.

For example, it is known to produce an activated carbon from an organic material with the simultaneous production of a reduced metal or metal oxide. This process heats organic material at a temperature of at least 200° C while generating combustible distilled gas from the organic material and activating the carbonized material by bringing it into contact with a material containing at least one metal compound at a temperature at which the metal compound is reduced by reaction with carbon. This process is achieved in a rotary kiln where the organic material is charged into one end of the rotary kiln and air or oxygen is charged into the opposite end of the rotary kiln. Another process activates lignite coke in a rotary tube after the addition of 25% aqueous potassium carbonate. These processes both require that the rotary kiln be operated at a temperature of typically 650-850° C and further require a residence time of 3-5 hours to activate coal, for example.

Another process involves a carbonaceous raw material impregnated with a chemical activating agent both of which are treated by controlling the rate of heat transfer to the particles via indirect heating of the activation furnace and simultaneously introducing a flow of independently controlled sweep gas at spaced intervals along the path of travel. Yet another process that is in use involves a method for the production of spherical activated carbon from powdered carbon material such as soot, bituminous coal, anthracite, charcoal and pitch as binder. A spherical activated carbon is produced by agglomeration, drying, charring and activation. Additionally, another process involves the production of spherical activated carbon from pitch by solvent agglomeration and activation in an ammonia atmosphere at from 550°-1,000° C and additional steam treatment. A further method involves a process for the production of spherical carbonaceous material and spherical activated carbon from pitch and amorphous coal particles with a viscosity modifier. These processes are expensive in terms of equipment and engineering, since the production of spherical starting materials requires additional process stages. The production of shaped activated carbon with very high adsorption capacity and BET (Brunauer, Emmett, and Teller method) surface area is limited by the reduction in hardness and abrasion resistance as the degree of activation increases, this being due to the nature of the process.

Additionally, the carbonization phases or step of these processes tends to produce amounts of acidic reaction products that tend to be extremely corrosive to

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the rotary kilns, which then imposes extremely high demands on the corrosion-resistance of the rotary tubular kiln material. Oftentimes, the rotary kilns may be comprised of different and separate compartments or stages to accommodate the corrosive process stage of carbonization being separated from the high-temperature stage of activation so as to prevent having to make a single rotary kiln out of expensive metals that resist the corrosiveness of the carbonization step.

Also, conventional processes use carbonaceous material feedstocks with a wide variety of sizes. For example, the feedstock for conventional processes may vary in size from 1 to 2,000 microns. During activation, a significant percentage of this feedstock is consumed. Another general problem associated with conventional processes is that the activation times are so great, that the processes are not generally responsive to minimal process changes. For example, if it takes 5 hours to activate a carbonaceous material with a conventional process and it is desired to change a characteristic of the activated carbonaceous material, small changes in the residence time is not going to produce such change in characteristics.

SUMMARY

In one embodiment, the system and method for activating carbonaceous material ("system for activating carbonaceous material") produces an activated carbonaceous material with greater efficiency and at a lower cost than conventional processes. Due to the size and purity of the carbonaceous material produced by any or all of the carbonaceous material feedstock production units, microwave drying unit, digestion unit, and drying unit of the present system for activating carbonaceous material, the carbonaceous material feedstock to an activation unit requires less energy and produces a more usable activated carbonaceous material for a plurality of applications. This efficiency is further achieved through the control of the temperature, time, and volume of oxidant (i.e., steam, carbon dioxide, and/or combinations thereof) with these processes and in the activation unit to produce an activated carbonaceous material of high quality with less energy input.

Moreover, the throughput increase of these units and processes of the system for activating carbonaceous material, the loss of carbonaceous material during the processes is substantially reduced from approximately 60% to approximately 30%. With the high costs of feedstocks, this significant decrease in loss provides additional benefits of the system for activating carbonaceous material. Further, the system for activating carbonaceous material may recover coal tars from the exhaust stream for

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recycling and may be used in the gas fired burners to heat a thermal unit, such as a rotary kiln of the system for activating carbonaceous material. Further, without being bound to any specific theories, it is believed that the carbonaceous material feedstock having been digested by the digestion unit of the present system for activating carbonaceous material further enables a shortened activation time through the activation unit of the present system for activating carbonaceous material.

Additionally, the feedstock from carbonaceous material feedstock production unit, microwave drying unit, digestion unit, and/or drying unit of the present system for activating carbonaceous material produces a uniform feedstock for activation unit, which further improves the activation efficiency of the process and reduces the residence time in the rotary kiln. These upstream units of the present system for activating carbonaceous material further provides a substantially less amount of carbonaceous material dust and fines, which further increases its activation efficiency. Further, the present system for activating carbonaceous material uses mechanical, chemical, and thermal processes in combination to provide an activated carbonaceous material that activates substantially faster than conventional processes. Because the present system for activating carbonaceous material is a faster and more efficient process for activating carbonaceous material, it is more responsive to short process changes. For example, to change the characteristics of an exemplary activated carbonaceous material with the present system for activating carbonaceous material, a slight change in the residence time may produce activated carbonaceous material with such revised characteristics. In one aspect, the carbonaceous material has a surface area of from about 200 m^2/g to about 1,500 m^2/g, with a typical range being from about 500 m^2/g to about 1,000 m^2/g. Further, carbonaceous material having smaller surface areas may be produced by using lower oxidant rates, lowered temperatures, shortened residence times, deeper bed depths, or any combination of these. Conversely, carbonaceous material having larger surface areas may be produced by using higher oxidant rates, higher temperatures, increased residence times, and shallower bed depths or any combination of these.

In one embodiment, the present system for activating carbonaceous material includes a carbonaceous material feedstock unit for producing a carbonaceous material of less than 5% mineral content; a digestion unit in communication with the carbonaceous material feedstock unit; an acid feedstock unit in communication with

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the digestion unit for providing an acid mixture solution; a separation unit in communication with the digestion unit for separating the digested carbonaceous material from the acid mixture solution; a dryer unit in communication with the separation unit for drying the digested carbonaceous material and separating the carbonaceous material; and a thermal unit for activating the carbonaceous material to produce activated carbonaceous material, the thermal unit having an inlet for receiving the carbonaceous material from the dryer unit and an outlet for exiting the activated carbonaceous material from thermal unit.

In another embodiment, the present system for activating carbonaceous material includes as material feedstock unit that includes: a first vibratory screen unit for sizing the carbonaceous material to a desired size; a density differential separation apparatus in communication with the first vibratory screen unit for producing a carbonaceous material of less than 5% mineral content; a digestion unit in communication with the carbonaceous material feedstock unit; an acid feedstock unit in communication with the digestion unit for providing an acid mixture solution to the first digestion unit including: a source of H_2O; a source of HF; a source of H_2SiF_6, wherein the HF, H_2SiF_6, and H_2O may be mixed together in predetermined ratios to form the acid mixture solution prior to being provided to the first digestion unit; a separation unit in communication with the digestion unit for separating the digested carbonaceous material from the acid mixture solution; a dryer unit in communication with the separation unit for drying the digested carbonaceous material and separating the carbonaceous material; and a thermal unit for activating the carbonaceous material to produce activated carbonaceous material, the thermal unit having an inlet for receiving the carbonaceous material from the dryer unit and an outlet for exiting the activated carbonaceous material from the thermal unit.

In yet another embodiment, the system for activating carbonaceous material may further include a conduit directly connecting the dryer unit with the inlet of the thermal unit. The thermal unit may further include a steam source located substantially adjacent to the inlet of the thermal unit for injecting steam into the internal chamber of the thermal unit. Additionally, the system for activating carbonaceous material may further include a halogenation unit located downstream of the outlet of the thermal unit for contacting the activated carbonaceous material with a halogenated compound. The heat source may be capable of operating the thermal unit at a temperature from about 400° C to about 1300° C. The system for

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activating carbonaceous material may further include a fractionation unit in communication with the thermal unit for fractionating coal tar from the carbonaceous material. The system for activating carbonaceous material may further include a recycle conduit located between the fractionation unit and the thermal unit for recycling the uncondensed coal tar as a fuel gas.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a schematic diagram of a carbonaceous material feedstock unit according to an embodiment of the present invention;

Figure 2 illustrates a schematic diagram of a microwave drying unit according to an embodiment of the present invention;

Figure 3 illustrates a schematic diagram of a digestion unit according to an embodiment of the present invention;

Figure 4 illustrates a schematic diagram of a fluidized bed dryer unit according to an embodiment of the present invention;

Figure 5 illustrates a schematic diagram of a packaging and product unit according to an embodiment of the present invention;

Figure 6 illustrates a schematic diagram of a vapor recovery unit according to an embodiment of the present invention;

Figure 7 illustrates a schematic diagram of a feedstock storage unit according to an embodiment of the present invention

Figure 8 illustrates a schematic diagram of an ultrasonic unit according to an embodiment of the present invention;

Figure 9 illustrates a schematic diagram of an ultrasonic unit according to another embodiment of the present invention;

Figure 10 illustrates a schematic diagram of an activation unit according to embodiment of the present invention;

Figure 11 illustrates a flow diagram for an exemplary process for refining carbonaceous material according to an embodiment of the present invention; and

Figure 12 illustrates a flow diagram for an exemplary process for activating carbonaceous material according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

In the drawings, like or similar elements are designated with identical reference numerals throughout the several views and figures thereof, and various

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depicted elements may not be drawn necessarily to scale.

The term “carbonaceous” means all materials that consist of substantial amounts of carbon. Without limitation the term includes coal, refined coal, activated carbon, carbon black, carbon products, solid crude oil, coal tar pitch, carbon fibers, tar, carbon, coke, graphite, and other carbon structures.

The term “digested carbonaceous material” means a carbonaceous material that has been subject to a cleaning or digesting process as herein described. In one aspect, the term means chemically cleaning the carbonaceous material by digesting the minerals embedded within the carbonaceous material. This term may further mean a carbonaceous material that has been chemically cleaned and may be noted as “chemically cleaned carbonaceous material.”

The term “macropore” typically means pores having a diameter size of greater than 50 nm. The term “micropore” typically means pores having a diameter size of smaller than 2 nm and the term “mesopore” typically means pores having a diameter size from about 2nm to about asymmetrical meander antenna 50 nm. The term “product” means all materials that are made from refined carbonaceous material, including without limitation: plastics, fibers, solvents, pharmaceuticals, carbon black, inks, activated carbon, carbon, tar, specialty minerals, boiler fuels, additives, gas cleanup, and the like.

Figure 1 illustrates an embodiment 100 of a carbonaceous material feedstock unit according to the present invention. In one embodiment, the carbonaceous material feedstock production unit 100 may be portable for relocating it at any location that produces a waste stream and/or settling pond stream containing carbonaceous material, such as preparation plants or washeries as is known to those skilled in the arts. Typically, a preparation plant is a plant that washes, sorts, sizes, cleans, and the like a source of carbonaceous material usually in proximity to a carbonaceous material mining operation, for example. Typically, these preparation plants produce smaller-sized carbonaceous material that is not processed further due to the cost of removing them from their carrier fluid stream, such as water. These smaller-sized carbonaceous particles required may be produced from washing the clays, carbonaceous material, and rocks off of the larger sized coal, which are generally separated out and discarded using various density related processes at a preparation plant. They are generally discarded because the size of the waste carbonaceous material is too small or not worth the expense to recover it

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from the preparation plant's process stream, thus this waste carbonaceous material flows with the waste water out to settling ponds where the waste carbonaceous material settles to the bottom of the settling pond and the waste water is later treated. In some instances, the percentage of carbonaceous material in these settling pond streams and/or settling ponds may be between 5% - 75% of the entire settling pond depending on the age of the settling pond and the efficiencies of the on-site processes. In one aspect, the system for refining carbonaceous material may recover the carbonaceous material from a preparation plant's process stream, such as a settling pond stream. In another aspect, the system for refining carbonaceous material may recover the carbonaceous material from an impoundment, such as a settling pond.

The carbonaceous material feedstock production unit 100 may be moved or located nearby a carbonaceous material washery, carbonaceous material processing plant, coal preparation plant, coal mining plant, settling impoundment, settling pond, and the like where it is connected via pipe 102 to a waste stream of a preparation plant or settling pond stream material with water added that contains the smaller-sized carbonaceous material. The pipe 102 is connected to a vibratory screen unit 104 that separates the larger-sized carbonaceous material pieces from the smaller-sized carbonaceous material. In one aspect, the vibratory screen unit 104 includes a series of descending screens of decreasing screen size. The vibratory screen units 104 may include gravity and/or density separation apparatuses, such as teeter beds, riffle tables, jigs, pulsing water beds, steady flow beds, and the like. Thus, the larger-sized carbonaceous material pieces are screened out at the upper screens while the smaller-sized carbonaceous material falls through to the lower parts of the vibratory screen unit 104. In one aspect, one of the intermediate screens may contain the desired size of carbonaceous material. Offsite process water is supplied through pipe 106 to the vibratory screen unit 104 for improved washing and processing at the vibratory screen unit 104.

In one embodiment, the smaller-sized particles and larger-sized particles that exceed a desirable predetermined size of carbonaceous material are removed from the vibratory screen unit 104 via pipes 108 and 110 and may be returned to the preparation plant, for example. Offsite process water may also accompany the undesirable particles exiting the vibratory screen unit 104. For ease of use, the pipes 102, 106, 108, and 110 may be flexible hoses, tubes, pipes, and the like for

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ease of connecting the carbonaceous material feedstock production unit 100 to the preparation plant. The desirable sized particles exit the vibratory screen unit 104 and flow via pipe 112 to a density differential separator 114. In one embodiment, the density differential separator 114 separates higher-density particles from lower-density particles. Typically, the lower-density particles will contain the desired carbonaceous material particles that will be processed as further described. The higher-density particles typically contain the material and particles that may not be used by the system for refining carbonaceous material.

The desirable-sized particles exit the density differential separator 114 and flow via pipe 122 to another vibratory screen unit 120. In one aspect, the vibratory screen unit 120 may additionally wash the particles and may further dry the carbonaceous material particles that enter the vibratory screen unit 120. Any sized particles that are not of a desired size may exit the vibratory screen unit 120 via pipe 122 and be returned to the preparation plant, for example. The washed and sized carbonaceous material may further be dried by forced air from a dryer 124. In one embodiment, the water content is preferably from about 7% to about 40% w/w, and more preferably from about 25% to about 35% w/w. As described more fully below, carbonaceous material having such a water content may be ideal for the later digestion processes and may eliminate the necessity and cost of re-wetting dried carbonaceous material. This may further save energy that would otherwise be expended to wet completely dry carbonaceous material that is typically supplied to refining plants. In one aspect, the water content may be further reduced at a preparation plant by use of a microwave drying unit and/or centrifuge to lower the expense of transporting the carbonaceous material to an off-site refining plant. In this aspect, the water content of the carbonaceous material may be approximately 7% w/w.

Once the carbonaceous material possesses water content is at a desired level, it may be transported by a conveyor or other appropriate device to an elevated height to be dropped into storage sacks, vessels, tanks, trucks, containers, and the like (storage containers 128). As described above, since the carbonaceous material feedstock production unit 100 may be movable or portable, the units described above may be mounted on a vehicle, such as a trailer 130. This enables the carbonaceous material feedstock production unit 100 to be moved from one site or preparation plant to another for supplying the later processes described herein with

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carbonaceous material of a desirable size and water or moisture content, while reducing the waste stream going to settling ponds, for example. In one embodiment, once the storage containers 128 are filled they may be loaded or moved to another vehicle (not shown) and may be transported to a microwave drying unit or digestion unit further described below. In one embodiment, the carbonaceous material feedstock production unit 100 may further include a centrifuge unit 132 for accepting a feed of carbonaceous material from the vibratory screen unit 120 for further reducing the moisture and/or water content of the carbonaceous material.

Preferably, carbonaceous material feedstock production unit 100 produces a carbonaceous material having a mineral content of less than 5%. In one aspect, carbonaceous material feedstock production unit 100 produces a carbonaceous material having a mineral content of less than 4%. In another aspect, carbonaceous material feedstock production unit 100 produces a carbonaceous material having a mineral content of less than 3%. In yet another aspect, carbonaceous material feedstock production unit 100 produces a carbonaceous material having a mineral content of less than 2%. In still yet another aspect, carbonaceous material feedstock production unit 100 produces a carbonaceous material having a mineral content of less than 1%.

Figure 2 illustrates an embodiment 200 of a microwave drying unit according to the present invention. In one embodiment, the system for refining carbonaceous material includes a microwave drying unit 200 and in another embodiment the system for refining carbonaceous material does not include a microwave drying unit 200. In this embodiment, storage containers 202 and 128 are emptied into a hopper 204 that feeds a conveyor 206 that passes through the microwave unit 208 for providing additional lowering of the water content of the carbonaceous material should it be desired. After exiting the microwave unit 208, the carbonaceous material may be transported via conveyor 212 to a hopper 214 for feeding to the next process unit. Hoppers 204 and 214 may be vibratory hoppers for unsettling clumped together carbonaceous material. In one embodiment, the microwave drying unit 200 may further include a centrifuge unit 216 for accepting a feed of carbonaceous material from the microwave unit 208 for further reducing the moisture and/or water content of the carbonaceous material. In another embodiment, additional centrifuge units may be used with the microwave unit 208, such as just before the microwave unit 208, for example

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Figure 3 illustrates an embodiment 300 of a digestion unit according to the present invention. Digestion unit 300 may include a conveyor 302 for transporting the cleaned and sized carbonaceous material to moisture balancing unit 346. The moisture balancing unit 346 may include a source of water and/or steam that controllably increases the moisture content of the cleaned and sized carbonaceous material. In cases where the moisture content of the carbonaceous material is reduced for transportation purposes, then the moisture balancing unit 346 may add moisture to the carbonaceous material. In one example, the moisture balancing unit 346 may produce carbonaceous material with a preferable moisture content of from about 7% to about 40% w/w, and more preferably a moisture content of from about 25% to about 35% w/w. After the moisture content has been adjusted or balanced in the moisture balancing unit 346, it may be fed to a conveyor 302, which transports the carbonaceous material to one or more digestion vessels 304, 308, and 310.

In one aspect, at the base of the conveyor 302 is a load cell 316 for weighing the carbonaceous material that enters the conveyor 302. Digestion unit 300 includes an acid mixture solution that is transported from an H_2SiF_6 adjustment tank 712 (Figure 7) via pipe 318. The acid mixture solution is fed into the digestion vessel 304, which includes a mixer 312 and a heater 314. The carbonaceous material is fed into the digestion vessel 304 and the digestion of the carbonaceous material is started. A valve 306 may be used to switch the carbonaceous material/acid mixture solution between the digestion vessels 304, 308, and 310. In one aspect, the digestion vessels 304, 308, and 310 may be gravity fed from one to another or pumped by pumps as described herein.

The carbonaceous material and acid mixture solution may then be fed into one of the digestion vessels 308 and 310 where the carbonaceous material is further digested. The digestion vessels 308 and 310 also include heaters 324 and 326, respectively, and mixers 322 and 326, respectively. The heaters 314, 324, and 326 are used to maintain the temperature of the digestion of the carbonaceous material in the digestion vessels 304, 308, and 310. The heaters may be steam fed heat exchangers as are commonly known in the art.

By having downstream digestion vessels 308 and 310, the carbonaceous material/acid solution mixture may be further digested while a new batch is being loaded into digestion vessel 304. Additionally, if a carbonaceous material/acid solution mixture is not in specification, it may be dumped to one of the digestion

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vessels 308 and 310 for further treating without holding up the digestion in the digestion vessel 304. Further, the carbonaceous material/acid mixture solution may be then moved or pumped to digestion vessel 310, which may be used to further the digestion of the carbonaceous material/acid mixture solution or may be used as a hold, stage, or surge vessel for feeding a centrifuge 328 via pipe 330, which may have a capacity or volume that is less than the digestion vessels 304, 308, and 310.

In one embodiment, the digestion vessels 304, 308, and 310 further include condensation loops or circuits 348 that may take any acid mixture solution that is vaporized in the digestion vessels 304, 308, and 310. The condensation circuits 348 may include condensation units, such as coolers, for condensing the vapor or gaseous acid mixture solution for storing in the present system for refining carbonaceous material. Separators, commonly known in the art, may further be used to separate the different components or compounds of the acid mixture solution. In another embodiment, catalyst beds may be used with the condensation circuits 348. In one aspect, the acid mixture solution may contain multiple acid compounds, such as HF and H_2SiF_6, that may be separated from each other by use of temperature controlled separators that separate the different compounds by temperature specific distillation. This separation may be controlled by controlling the temperature and ratio of the acid compounds within the separators. In addition, the metals digested out of the carbonaceous material may be precipitated at different pH levels and then filtered from the carbonaceous material/acid mixture solution.

In the above described embodiment, the present system for refining carbonaceous material may include multiple digestion vessels that are in series, one feeding the carbonaceous material/acid mixture solution to another downstream digestion vessel. In this embodiment, the carbonaceous material/acid mixture solution may be batched in a way to have a continuous flow downstream, which may be important for feeding a continuous centrifuge 328 via pipe 330, for example.

In another embodiment, the present system for refining carbonaceous material may include one digestion vessel by itself, such as digestion vessel 304. In this embodiment, no further downstream digestion vessels are fed the carbonaceous material/acid mixture solution and it is fed directly to a centrifuge 328, for example.

In yet another embodiment, the present system for refining carbonaceous material may include multiple digestion vessels that are in parallel that feed concurrently or simultaneously the carbonaceous material/acid mixture solution to

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the centrifuge 328, for example. In this embodiment, the digestion vessels 304, 308, and 310 are each individually fed the carbonaceous material/acid mixture solution from the conveyor 302.

Preferably, the acid mixture solution comprises HF and H_2SiF_6 in a range of proportions. In one example, the HF is present in a range preferably from about 2% to about 20% w/w, and more preferably from about 5% to about 15% w/w. The H_2SiF_6 is present in a range preferably from about 10% to about 58% w/w. Even more preferably, the HF is present in a range of from about 5% to about 12% w/w, and most preferably in the range of from about 8% to about 10% w/w and the H_2SiF_6 is present in a range more preferably from about 30% to about 38% w/w, and most preferably from about 22% to about 32% w/w. The balance of the mixture is water. So for example, an acid mixture solution that includes 10% HF and 35% H_2SiF_6 will have a H_2O content of 55% taking into account the moisture of the carbonaceous material being fed into the digestion vessels, in one aspect. Preferably, the acid mixture solution includes these mixed portions of HF and H_2SiF_6 prior to mixing them with the carbonaceous material.

In another embodiment, a fluorine acid solution can be prepared from a solution of H_2SiF_6 plus H_2O as the base acid to which anhydrous HF acid is added so that both of these reactive acids are in one solution. Some exemplary ranges of the acids are from about 5%-34% w/w H_2SiF_6, 32%-90% w/w H_2O, and 5%-34% w/w HF acid. In one aspect, a fluorine acid solution is prepared from a saturated solution of H_2SiF_6 in water and adding gaseous anhydrous HF acid. In another embodiment, SiF_4 may be reacted with H_2O to form H_2SiF_6.

In one embodiment, the digestion vessels 304, 308, and 310 may be operated at temperatures of from about 10 °C to about 125 °C and at a pressure of from about 0 kPa to about 105 kPa. In another embodiment, the temperature of the digestion vessels 304, 308, and 310 may be preferably in the range of from about 55 °C to about 85 °C, and more preferably in the range of from about 70 °C to about 85 °C.

In one embodiment, the carbonaceous material/acid mixture solution is agitated or stirred in the digestion vessels 304, 308, and 310 for preferably from about 20 to about 80 minutes, and more preferably from about 40 to about 60 minutes.

The digestion vessels 304, 308, and 310 may be made of a material that withstands the chemicals contained in them. For example, the digestion vessel 304

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may be made from a blend of plastic and carbon fiber composites or any structural material lined with any material that is impervious to the corrosive effects of the acid used.

The treated carbonaceous material has a specific gravity lower than the carbonaceous material/acid mixture solution, thus the treated carbonaceous material may float to the top of the carbonaceous material/acid mixture solution in the digestion vessels 304, 308, and 310 when the mixers 312, 322, and 324 are turned off. Unreacted iron sulfide and other un-dissolved heavy metal salts whose specific gravities are greater than the acid mixture solution may fall to the bottom of the digestion vessels 304, 308, and 310 if the agitation is stopped by turning off the mixers 312, 322, and 324. In one embodiment, the specific gravity of certain carbonaceous material, such as coal, is approximately 1.3 and the acid mixture solution is approximately 1.2 when entering the digestion vessel. After digestion, the carbonaceous material then typically has a specific gravity of 1.1 and the specific gravity of acid solution is 1.2 entering the centrifuge 328. In addition, during the separation process, the treated carbonaceous material acts as a filter to the metal fluorides and/or metal fluorosilicates that are contained in the acid mixture solution.

In one embodiment, the pipe 330 is connected to a pump 332 that pumps the carbonaceous material/acid mixture solution to the centrifuge 328. Preferably, the pump 332 pumps the carbonaceous material/acid mixture solution without degrading the particle size. In one aspect, the pump 332 is a peristaltic pump.

In one aspect, the centrifuge 328 may include several different stages. For example, it may spin at a speed sufficient to remove the acid mixture solution from the carbonaceous material in a first stage. In a second stage, water supplied from a de-ionized water supply 336 and/or a rinse water supply 334 may be used in washing the carbonaceous material. Preferably, this rinse water may be applied to the carbonaceous material while it is being spun inside of the centrifuge 328. The water used in this cycle may be heated before it is input into the centrifuge 328. For example, the water may be in a temperature preferably from about 30 °C to about 100 °C, and more preferably 75 °C to about 85 °C. Then, the centrifuge 328 may remove this wash water where it can be recycled after being filtered through a filtration apparatus in this second stage. The rinse water that is removed from the centrifuge 328 is sent for recycling via pipe 342 as described below. In another embodiment, the wash water removed from the centrifuge 328 may be sprayed on

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the carbonaceous material prior to it entering the digestion vessels 304, 308, and 310 in the moisture balancing unit 346 as the moisture content of the incoming carbonaceous material is lower than desired prior to digestion as described herein. The filtration apparatus removes some of the metal fluorides and metal chlorides, which may be sold to other markets, such as aluminum and steel plants.

Preferably, the third stage includes injecting steam into the centrifuge 328 during a spinning process. In one embodiment, the temperature within the centrifuge 328 is preferably from about 120 °C to about 400 °C and the quantity of steam that is applied to the carbonaceous material in the centrifuge 328 may be determined by several factors, including the size or carbonaceous material particles and the speed of drum inside the centrifuge 328 to prevent slumping of the carbonaceous material within the centrifuge 328. The steam helps in removing any residual fluorides. For example, the amount of steam applied to the carbonaceous material may be determined by the residual level of fluorine required in the finished carbonaceous material. For instance, an isotrope of HF, H_2SiF_6, and H_2O may vaporize preferably from about 105 °C to about 120 °C depending on the concentrations of the individual compounds. Thus, by providing steam into the centrifuge 328 the residual HF, H_2SiF_6, and H_2O are driven off of the carbonaceous material as a vapor and recovered later via pipe 342, for example, the steam process may also start the drying stage of the present system for refining carbonaceous material. In another example, there may be multiple centrifuges used in series and/or parallel to separate the stages.

The centrifuge 328 may further include scrapers or augers that remove the carbonaceous material from the centrifuge 328 by scraping or augering the carbonaceous material as it is spinning inside the centrifuge 328. Thus, the carbonaceous material exits the centrifuge 328; the carbonaceous material is then moved to a hopper 344 via a conveyor. In one aspect, it may be important not to use any conveyance means that will degredate the carbonaceous material to prevent the creation of smaller undesirable fines. The moisture content of the carbonaceous material at this point may be from about 4% to about 12% w/w.

Figure 4 illustrates an embodiment 400 of a drying unit according to the present invention. The drying unit 400 includes a dryer 402 that may further dry the carbonaceous material produced by the digestion unit 300. The carbonaceous material from the hopper 344 is fed into the dryer 402 where the carbonaceous

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material is subject to air flow of a desired velocity and temperature. After a residence time the carbonaceous material then exits the dryer 402 and is fed to a hopper 406 where it may be elevated to a final packaging and product unit 500 that may include a load cell or scale 504 for weighing the finished carbonaceous material that is placed in a storage container 502 as shown in Figure 5, or sent to bulk storage, where the almost pure and dried carbonaceous material is ready for the next stage, fuel, activation and the like.

In one embodiment, dryer 402 may be a fluidized bed that is generally a density dependent unit, such as a teeter bed, that has air flowing from the bottom to the top of the fluidized bed dryer that lifts the lighter carbonaceous material out the top of the fluidized bed dryer for transfer to a vessel, such as drum 410 by a cyclone and/or bag filter, such as cyclone 408. The carbonaceous materials particles are suspended in the air flow based on their density and are dried further by this process. The medium-sized carbonaceous material particles that do not flow out the top of the fluidized bed dryer are recovered at the bottom of the fluidized bed dryer for transfer on conveyor 404. The fluidized bed dryer includes a weir that controls the height of carbonaceous material inside the fluidized bed dryer. Conveyor 404 may be a vacuum and/or pneumatic conveyor as is known in the art. In one aspect, the smaller-sized carbonaceous material particles that exit the top of the fluidized bed dryer may be approximately 200 microns or smaller. To control the separation of the particle sizes through the fluidized bed dryer, the air flow may be adjusted. A higher air flow velocity through the fluidized bed dryer will produce larger-sized carbonaceous material particles exiting the top of the fluidized bed dryer, while a lower air flow velocity will produce smaller-sized carbonaceous material particles exiting the top of the fluidized bed dryer. In addition, the smaller-sized carbonaceous material particles may be fed into storage container, such as sacks and the like.

In another embodiment, the dryer 402 may be a number of designs so long as there is air flow and carbonaceous material movement, the temperature of the dryer 402 may be preferably in the range from about 100 °C to about 160 °C, more preferably from about 120 °C to about 140 °C, the temperature may be high enough to drive off most of the moisture and some of the tars in order to liberate the residual fluorine to a level close to the inherent value of the original carbonaceous material.

Figure 6 illustrates an embodiment 600 of a vapor recovery unit 600 according to the present invention. The process water produced by the system for refining

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carbonaceous material may be fed to a scrubber 602 where air is pulled through the scrubber 602 to remove any additional light volatile vapors from the process water. The air flow through the scrubber 602 is provided by blowers 608 which are fed to a stack 610. The stripped process water may be returned to the top of the scrubber 602 via pump 612. Additionally, the stripped process water may be fed to the moisture balancing unit 346 to be used as a feedstock for increasing the moisture content of the carbonaceous material within the moisture balancing unit 346.

Figure 7 illustrates an embodiment 700 of a feedstock storage unit according to the present invention. The feedstock storage unit 700 includes a de-ionized water storage tank 702 for holding de-ionized water that is used in the system for refining carbonaceous material. For example, de-ionized water is fed from de-ionized water storage tank 702 to centrifuge 328 via pipe 704. Feedstock storage unit 700 further includes a HF storage tank 706 that feeds HF acid via pipe 708 to a HF adjustment tank 710 and a H_2SiF_6 adjustment tank 712 may further include heaters to heat their respective acid mixture solutions after blending the acid mixture solution to a desirable strength. The H_2SiF_6 adjustment tank 712 may further be fed H_2SiF_6 in a more concentrated form that is stored in a H_2SiF_6 storage tank 714. Once the desired strength of acid mixture solution is achieved, then it is piped via pipe 716 to digestion vessel 304 for mixing with carbonaceous material. In addition, HF adjustment tank 710 may feed a reduced strength of HF to the centrifuge 328 via pipe 718. Also, feedstock storage unit 700 may further include a rinse water collection tank 722 that contains rinse water collected from the system for refining carbonaceous material. This rinse water may be fed to centrifuge 328 via pipe 720. Additional vessels 724 and 728 may be used to contain caustic compounds, such as bases, for neutralizing any acid spills or reducing the strengths of the acids of the system for refining carbonaceous material. Such bases may be fed to the digestion vessel 304 via pipe 726.

Figure 8 illustrates an embodiment 800 of an ultrasonic unit according to the present invention. In one embodiment, the digestion vessels 304, 308, and 310 may include a pipe 802 that takes a stream of the carbonaceous material/acid mixture solution and pumps it through the pipe 802 through a source of ultrasonic waves 804 for improved penetration of the acid mixture solution into the micropores and macropores of the carbonaceous material. In one aspect, the source of ultrasonic waves 804 may be a water bath that is subject to a source of such ultrasonic waves,

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thus imparting the ultrasonic waves through the pipe 802 for improved penetration of the acid mixture solution. In one embodiment, the wave signals are square to improve such penetrating and digesting action.

Figure 9 illustrates an embodiment 900 of an ultrasonic unit according to the present invention. In this embodiment, a source of ultrasonic waves 902 is placed upon the pipe 102 prior to entering the vibratory screen unit 104.

In one embodiment, the frequency of the source of ultrasonic waves 804 and 902 is from about 80 KHz to about 100 KHz. In one example, an opening of a macropore of carbonaceous material may be approximately 1 micron and it has been found that a frequency of 100 KHz source of ultrasonic waves 804 and 902 will cause the acid mixture solution to penetrate the macropore opening. Additionally, as the acid mixture solution is pumped into the macropores of the carbonaceous material, pressure is created within the macropore causing the acid mixture solution to be pumped out once the pressure becomes greater within the macropore than outside the macropore. This pumping action provides for improved penetration and digestion or removal of contaminants in the carbonaceous material. The source of ultrasonic waves 804 and 902 may be generated by ultrasonic transducers as well known in the art. In one aspect, these transducers may be in contact or communication with a water bath, which transfers the wave action to the water, which then transfers the wave action to the pipe, and so on, to provide the pumping action to the micropore and macropores of the carbonaceous material. This reduces the need for mechanical agitation and provides for improved digestion times. The frequency of the source of ultrasonic waves 804 and 902 causes cavitations, cavitation bubbles, and/or cavity bubbles within the acid mixture solution such that they are the size or smaller than the typical openings of the macropores of the carbonaceous material. In general, the higher the frequency the smaller the cavitation bubbles. If the cavitation bubbles are too large, they may tend to pulverize the carbonaceous material to smaller sizes that may not be desirable to the process. In one embodiment, source of ultrasonic waves 804 and 902 are capable of producing power from about 250 watts to about 16,000 watts with a frequency of from about 10 KHz to about 50 KHz. The ultrasonication may be performed at an increased pressure over ambient pressure using a feed pump and adjustable back-pressure valve next to the pipe where it is desired to operate.

Figure 10 illustrates an embodiment 1000 of an activation unit according to

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the present invention. In this embodiment, a thermal unit, such as rotary kiln 1002 is in communication with drying unit 400 via pipe or conduit 1014, in particular, in communication with dryer 402. Although a rotary kiln 1002 is shown and described, the thermal unit may be a direct-fired kiln, indirect-fired kiln, hearth kilns, multiple hearth kilns, and the like as is know to those skilled in the art. Rotary kiln 1002 includes an inlet 1016 preferably in communication with conduit 1014 and an outlet 1018 where the activated carbonaceous material is discharged for storage or transportation. In one aspect, the dried carbonaceous material is fed by direct loading from dryer 402 into rotary kiln 1002. Direct loading is preferable as it reduces the loss of heat in the dried carbonaceous material, thus reducing the amount of heat needed in the rotary kiln 1002 for activation. In one aspect, rotary kiln 1002 may be directly fired and in another it may be indirectly fired. Rotary kiln 1002 shown in Figure 10 is indirectly fired or heated by a heat source located outside of the shell of rotary kiln 1002.

Rotary kiln 1002 includes a shell 1004 and a plurality of moving elements 1006 for circulating and moving the carbonaceous material 1008 arranged in the interior of rotary kiln 1002. Moving elements 1006 may, for example, be metal circulation plates or turning plates as commonly known in the art. Moving elements 1006 located in the interior of rotary kiln 1002 are advantageously distributed over the interior of rotary kiln 1002, so that optimum circulation and movement of carbonaceous material 1008 is ensured in the operating state. Moving elements 1006 may, for example, be configured in paddle-form or plate-form, in order to ensure reliable movement and circulation of carbonaceous material 1008. According to one embodiment, moving elements 1006 run at least substantially in the radial direction of rotary kiln 1002, which ensures particularly intensive mixing of carbonaceous material 1008. Moving elements 1006 used may, for example, be metal sheets, in particular angled metal sheets (i.e. angled plates), which move carbonaceous material 1008 in the manner of a paddle. This is known per se to the person skilled in the art.

Rotary kiln 1002 and moving elements 1006 advantageously consist of material which is resistant to high temperature and corrosion, in particular of steel, since they may have to withstand temperature conditions of the activation phase during the production of activated carbonaceous material. Examples of suitable high-temperature-resistant steels which can be used to produce rotary kiln 1002

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and/or moving elements 1006 include high-alloy steels, i.e. steels containing more than 5% of alloying elements. Examples of such steels include high-alloy chromium and chromium/nickel steels, preferably with a chromium and/or nickel content of over 10%, in particular over 15%, particularly preferably over 20%, based on the alloy. Ferritic or ferritic-austenitic steels with good high-temperature properties may be preferably used as material for production of rotary kiln 1002 and/or moving elements 1006.

Moreover, rotary kiln 1002 may also have an inlet device 1010 and an outlet device 1012 for introducing and discharging gases and for allowing gases to pass through, for example for the introduction of inert gases for the activation phase during activated carbonaceous material production and for the further introduction of oxidation gases for the activation phase during activated carbon production. Inlet device 1010 and outlet device 1012 are shown such that they may provide a counter-current flow arrangement against the downwardly flowing carbonaceous material 1008, but in another embodiment, the locations or orientation of these devices may be such that they provide a flow pattern in the same direction as the carbonaceous material 1008. Additionally, inlet device 1010 may be a steam injection device to provide steam to the inside of rotary kiln 1002 to create and control the activation burn of the carbonaceous material 1008, for example. In one aspect, the steam may be of a rate of from about 0.25 pounds to about 4 pounds to 1 pound of carbon, more preferably about 3 pounds to 1 pound of carbon, and most preferably about 2 lbs to 1 lb of carbon. The steam may be injected at any point approximately from the inlet 1016 of the rotary kiln 1002.

Due to the novel size due to the carbonaceous material feedstock production unit 100 and chemical purity due to digestion of the carbonaceous material 1008 feedstock created by any or all of the carbonaceous material feedstock production units 100, microwave drying unit 200, digestion unit 300, and drying unit 400, the carbonaceous material 1008 that is fed into rotary kiln 1002, any or all three parameters of temperature, time, and volume of steam may be easily and efficiently controlled to produce an activated carbonaceous material that consumes less energy than found in conventional systems. Further, outlet device 1012 may recover vaporized coal tars from the carbonaceous material 1008 for further processing, recycling, and possible reuse in gas fired burners 1024. This may occur near inlet device 1010 of rotary kiln 1002 and this step may be referred to as carbonization in

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one aspect or embodiment. Outlet device 1012 may further include fractional condensation units for fractionating the exhaust stream for recovering the coal tars. Such fractionating may occur in a temperature range of from about 210-250° C. For example, the exhaust stream may be run through a cyclone maintained above 300° C to capture solids and then condense the stream at or around 220° C to capture the coal tars. They may then be run through a scrubber to remove and/or neutralize any acids. Further, they may be run into the combustion section of 1002 rotary kiln for thermal destruction of any volatile organic compounds and hazardous air pollutants present, as is known to those skilled in the art.

In another embodiment, more than one rotary kiln 1002 may be used in tandem for providing the activation process to the carbonaceous material. For example, two or three rotary kilns may be used together. Further, a conventional air lock may be employed in a well-known manner between the outlet 1018 and inlet 1016 of rotary kiln 1002 to isolate the internal atmosphere of each rotary kiln 1002 when more than one rotary kiln 1002 is employed, for example.

In one aspect, rotary kiln 1002 may be surrounded by an insulating jacket, not shown, and includes an array of independently controlled gas fired burners, illustrated and generally designated as heat source 1022, which are provided to generate the heat energy transferred through an air space between shell 1004 of rotary kiln 1002 and heat source 1022. While other conventional means may be used as an indirect heat source 1022, such as electric coils, coal, oil, and/or gas fired burners 1024 may be normally considered as the most economically practical source of heat energy in a commercial scale process.

Activation unit 100 may further include a temperature controller 1020 that controls heat source 1022. There are many commercially available, conventional temperature controllers of varying degrees of accuracy available to control the degree of heat energy supplied by the indirect heat source 1022 and operate in a manner well-known to those skilled in the art of industrial rotary kilns.

For purposes of the present system for activating carbonaceous material, the degree of accuracy of temperature controller 1020 chosen should be capable of maintaining the desired temperature profile of the bed of carbonaceous material 1008 traveling through rotary kiln 1002 to obtain useful results in accordance with the teachings of the present system for activating carbonaceous material. Within economically practical limits, reasonably precise control of heat source 1022

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provides a greater range of selectivity to affect the properties of the end product in a more reliable manner.

As mentioned above, temperature controller 1020 is operatively connected to heat source 1022 associated with activation unit 1000, and preferably includes suitably positioned temperature sensing devices associated with shell 1004 of rotary kiln 1002 to feed back temperature data to the controller circuitry of temperature controller 1020. Temperature controller 1020 may be set to vary the heat energy generated by gas fired burners 1024 through shell 1004 of rotary kiln 1002 and hence to the bed of carbonaceous material 1008 to provide a predetermined increasing temperature profile or heating ramp of the bed of carbonaceous material 1008 as it advances through rotary kiln 1002.

Preferably, devolatization and activation are generally carried out at temperatures in the range of 350-1,250° C, in particular in the range of 500-900° C, and more preferably in the range of 600-850° C. Generally, rotary kiln 1002 has a slope and rotational speed to provide a residence time for the carbonaceous material of from approximately 10 minutes to approximately 8 hours, preferably from about 30 minutes to about 6 hours, and more preferably from about 60 minutes to about 5 hours.

Once the carbonaceous material 1008 exits rotary kiln 1002 through outlet 1018 it may be cooled, stored, or transported for additional uses. The system for activating carbonaceous material produces a granular-sized carbonaceous material and not powdered-sized product as found with conventional processes that require a binder to achieve this with significant expenses. For example, activated carbonaceous material produced by the system for activating carbonaceous material may be used directly at this point for water filtration applications without further acid wash, as is generally required by other methods.

The present system for activating carbonaceous material preferably produces activated carbonaceous material with a size of from about 200 microns (“μm”) to about 2 millimeters (“mm”) for granular activated carbon and after pulverizing from about 200 μm to about 10 μm for powdered activated carbon. Additionally, activated carbonaceous material may be coated or infused with an additive, such as bromine, iodine, sulfur, or a number of other products depending on the specific application. For example, activated carbonaceous material may be infused or coated with bromine as a liquid or gas for mercury removal application in flue gas applications.

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In another example, activated carbonaceous material may be infused or coated with hard sulfur. In one aspect, the temperature of activated carbonaceous material may preferably be at or below 300° C prior to coating or infusing the activated carbonaceous material with an additive. In one aspect, the additives may be in a vapor phase during the coating or infusion process. In another aspect, the additives may be in a liquid phase during the coating or infusion process. For example, bromine may be applied at a rate of from about 1% to about 30% w/w to the activated carbon in a gas phase via a looped countercurrent flow apparatus as is known in the art.

In addition to the above, the carbonaceous material produced by the system for activating carbonaceous material may be micronized after the application of an additive, such as bromine, to less than 325 sieve size, which is typically 45 μm minus and a mean of around 10 μm for use in a flue gas scrubber to capture mercury, for example.

In addition to the aforementioned aspects and embodiments of the present system for activating carbonaceous material, the present invention further includes methods for refining carbonaceous material. Figure 11 illustrates an embodiment 1100 of a method for refining carbonaceous material. In step 1102, an acid mixture solution is prepared by mixing HF, H_2O, and H_2SiF_6 to a desired proportion. In this step, stored concentrated HF and H_2SiF_6 may be individually pumped to individual vessels where the concentration of each is reduced with water or a base, in one aspect. In another aspect, this step may include a different acid mixture with nitric acid, sulphuric acid, and/or a number of mineral acids as known to those skilled in the art. Then, these reduced concentrations of the HF and H_2SiF_6 may be combined into a vessel that then mixes and heats the mixture of HF, H_2SiF_6, and H_2O. In this step the exact amount of acid mixture solution is prepared for a specific amount of carbonaceous material to be digested.

In step 1104, the carbonaceous material is prepared by sizing a source of carbonaceous material, such as a preparation plant settling pond stream. This step further includes wetting the carbonaceous material with H_2O to a desired content, such as from about 20% to about 30% w/w. This step may further include the application of ultrasonic waves to the carbonaceous material prior to or during the sizing operation.

In step 1106, the carbonaceous material and acid mixture solution are

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combined in a digestion vessel which is temperature and pressure controlled. This step may further include transferring the carbonaceous material/acid mixture solution to a second digestion vessel for additional digestion time. This step may further include transferring the carbonaceous material/acid mixture solution to a third digestion vessel for addition digestion time. This step may further include the application of ultrasonic waves to the digestion vessel or to a loop or circuit pipe that takes a stream of the carbonaceous material/acid mixture solution out of the digestion vessel and then later inputs it back into the digestion vessel after the application of ultrasonic waves for improved digestion.

In step 1108, the carbonaceous material/acid mixture solution is transferred to a centrifuge for removal of the acid mixture solution. This step may further include spraying rinse water into the centrifuge for washing any residual acid mixture solution from the carbonaceous material. This may be followed by additional centrifuging until the carbonaceous material has a desirable moisture content. This step may also be performed with two or more centrifuges with the assistance of steam to transfer the material from one centrifuge to the next, for example.

In step 1110, the carbonaceous material may be further dried and separated based on densities to achieve the size of desirable product for a particular application or order. This step may include applying an air flow in a vertical vessel such that the less dense carbonaceous material is removed from the top of the dryer while the more dense carbonaceous material is retained in the dryer for removal to a storage vessel, such as a sack. In step 1112, the carbonaceous material is finished and weighed into final storage containers, such as sacks for their intended purpose. The process described herein is scale independent and can be used on a micro-scale, mesa-scale, and macro-scale.

Figure 12 illustrates an embodiment 1200 of a method for activating carbonaceous material. In step 1202, carbonaceous material is mechanically and chemically processed as disclosed herein. This step may produce a carbonaceous material that has preferable size, purity, and moisture content that is preferable to feeding into activation unit 1000. This step further includes processing the carbonaceous material with the carbonaceous material feedstock production unit 100, microwave drying unit 200, digestion unit 300, and drying unit 400 or a combination of similar machines and/or apparatuses such that the impurities are removed, the moisture content is of a preferred level, and the temperature of the

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carbonaceous material is elevated, thus reducing the amount of energy required at activation unit 1000 that for conventional processes.

In step 1204, the carbonaceous material is fed from drying unit 400 into rotary kiln 1002 via conduit 1014. Preferably, this step includes feeding digested carbonaceous material from drying unit 400 directly into rotary kiln 1002 so as to not lose any heat provided by the drying unit 400. This feed should be as direct and thermodynamically favorable as possible. By feeding carbonaceous material directly into inlet 1016 of rotary kiln 1002, the carbonaceous material is at an elevated temperature, thus less energy will be required to carbonize and activate the carbonaceous material in the rotary kiln 1002.

In step 1206, the carbonaceous material is activated. According to the present system for activating carbonaceous material, carbonaceous material is fed to rotary kiln 1002 that is pre-heated from about 600° C to about 850° C, for example. The amount of carbonaceous material fed into rotary kiln 1002 may preferably be from approximately 10% to approximately 30% of the volume of rotary kiln 1002. Rotary kiln 1002 may be subdivided into a carbonizing zone and activating zone, up to a filling volume of from about 5% to about 40%, and carbonized and activated continuously in an inert-gas flow with approximately 8-fold product turnover per kiln rotation and a product temperature profile in the carbonizing zone of from about 300° C to about 900° C, the residence time being from approximately 10 minutes to approximately 180 minutes, and a carbonaceous material temperature profile in the activating zone of from about 500° C to about 1,200° C, with a residence time of from about 30 minutes to about 180 minutes, with the addition of from 1 lb to 5 lb of steam to 1 lb of carbon in the activating zone, any distance from inlet 1016 of rotary kiln 1002.

In optional step 1208, activated carbonaceous material may be coated or infused with an additive. This step may be performed in a closed looped countercurrent flow device or apparatus, which may apply from about 5% to about 10% w/w of the preferred additive. In optional step 1210, the coal tar that is released from the carbonaceous material during the activation process may be fractionated. This step may be performed by using a temperature controlled vertical vein condenser at around 200 ° C to condense the coal tars yet keeping them in a fluid state so that they will drain from the present system for activating carbonaceous material into a holding vessel and clearing the condenser, for example.

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In optional step 1212, the coal tar that has not been fractionated may be recycled to be burned by gas fired burners 1024. The uncaptured vaporized coal tar is returned to the gas fired burners 1024 for further burning by gas fired burners 1024 and subsequent heating of rotary kiln 1002. In optional step 1214, activated carbonaceous material is finished, packaged, and/or stored to be used for further applications as described herein, for example.

There has been described a system for activating carbonaceous material. It should be understood that the particular embodiments described within this specification are for purposes of example and should not be construed to limit the invention. Further, it is evident that those skilled in the art may now make numerous uses and modifications of the specific embodiment described, without departing from the inventive concepts. For example, different temperatures, pressures, acid mixture solution compositions, and the like may be changed or altered to fit within the present system for activating carbonaceous material described herein or other without departing from the inventive concepts.

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CLAIMS

What is claimed:

1. A system for activating carbonaceous material comprising:
   a carbonaceous material feedstock unit for producing a carbonaceous material of less than 5% mineral content;
   a digestion unit in communication with the carbonaceous material feedstock unit;
   an acid feedstock unit in communication with the digestion unit for providing an acid mixture solution;
   a separation unit in communication with the digestion unit for separating the digested carbonaceous material from the acid mixture solution;
   a dryer unit in communication with the separation unit for drying the digested carbonaceous material and separating the carbonaceous material; and
   a thermal unit for activating the carbonaceous material to produce activated carbonaceous material, the thermal unit having an inlet for receiving the carbonaceous material from the dryer unit and an outlet for exiting the activated carbonaceous material from the thermal unit.

2. The system for activating carbonaceous material of claim 1, wherein the carbonaceous material feedstock unit produces a carbonaceous material of less than 4% mineral content.

3. The system for activating carbonaceous material of claim 1, wherein the carbonaceous material feedstock unit produces a carbonaceous material of less than 3% mineral content.

4. The system for activating carbonaceous material of claim 1, wherein the carbonaceous material feedstock unit produces a carbonaceous material of less than 2% mineral content.

5. The system for activating carbonaceous material of claim 1, wherein the carbonaceous material feedstock unit produces a carbonaceous material of less than 1% mineral content.

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6. The system for activating carbonaceous material of claim 1, wherein the thermal unit further comprises:
a source of at least one of carbon dioxide and steam located substantially adjacent to the inlet of the rotary kiln for injecting the at least one of carbon dioxide and steam to contact the carbonaceous material contained in the thermal unit.

7. The system for activating carbonaceous material of claim 1, wherein the thermal unit is selected from the group consisting of indirect-fired kilns, direct-fired kilns, hearth kilns, and multiple hearth kilns.

8. The system for activating carbonaceous material of claim 1, wherein the one or more heat sources are capable of operating the thermal unit at a temperature from about 350° C to about 1,250° C.

9. The system for activating carbonaceous material of claim 1, wherein the one or more heat sources are capable of operating the thermal unit at a temperature from about 500° C to about 900° C.

10. The system for activating carbonaceous material of claim 1, wherein the one or more heat sources are capable of operating the thermal unit at a temperature from about 600° C to about 850° C.

11. The system for activating carbonaceous material of claim 1, wherein the thermal unit provides a residence time of from about 30 minutes to about 8 hours for the carbonaceous material.

12. The system for activating carbonaceous material of claim 1, further comprising:
a fractionation unit in communication with the thermal unit for fractionating coal tar from the carbonaceous material.

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13. The system for activating carbonaceous material of claim 12, further comprising:

a recycle conduit located between the fractionation unit and the thermal unit for recycling the coal tar as a fuel gas.

14. A system for activating carbonaceous material comprising:

a carbonaceous material feedstock unit comprising:

a first vibratory screen unit for sizing the carbonaceous material to a desired size; a density differential separation apparatus in communication with the first vibratory screen unit for producing a carbonaceous material of less than 5% mineral content;

a digestion unit in communication with the carbonaceous material feedstock unit;

an acid feedstock unit in communication with the digestion unit for providing an acid mixture solution to the first digestion unit comprising:

a source of H_2O;

a source of HF;

a source of H_2SiF_6, wherein the HF, H_2SiF_6, and H_2O may be mixed together in predetermined ratios to form the acid mixture solution prior to being provided to the first digestion unit;

a separation unit in communication with the digestion unit for separating the digested carbonaceous material from the acid mixture solution;

a dryer unit in communication with the separation unit for drying the digested carbonaceous material and separating the carbonaceous material; and

a rotary kiln having a shell defining an internal chamber for activating the carbonaceous material to produce activated carbonaceous material, the rotary kiln having an inlet for receiving the carbonaceous material from the dryer unit and an outlet for exiting the activated carbonaceous material from the rotary kiln.

15. The system for activating carbonaceous material of claim 14, further comprising:

a conduit directly connecting the dryer unit with the inlet of the rotary kiln.

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16. The system for activating carbonaceous material of claim 14, wherein the rotary kiln further comprises:
a source of at least one of carbon dioxide and steam source located substantially adjacent to the inlet of the rotary kiln for injecting the at least one carbon dioxide and steam into the internal chamber of the rotary kiln.

17. The system for activating carbonaceous material of claim 14, further comprising:
a halogenation unit located downstream of the outlet of the rotary for contacting the activated carbonaceous material with a halogenated compound.

18. The system for activating carbonaceous material of claim 17, wherein the halogenation unit is a bromination unit for contacting the activated carbonaceous material with a brominated compound.

19. The system for activating carbonaceous material of claim 17, wherein the brominated compound is in a liquid phase.

20. The system for activating carbonaceous material of claim 14, wherein the heat source is capable of operating the rotary kiln at a temperature from about 500° C to about 900° C.

21. The system for activating carbonaceous material of claim 14, further comprising:
a fractionation unit in communication with the rotary kiln for fractionating coal tar from the carbonaceous material.

22. The system for activating carbonaceous material of claim 21, further comprising:
a recycle conduit located between the fractionation unit and the rotary kiln for recycling the coal tar as a fuel gas.

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23. A method for activating carbonaceous material comprising:
providing a digestion unit;
feeding an acid mixture solution into the digestion unit;
feeding a supply of pre-wetted carbonaceous material having a moisture content from about 15% to about 35% into the digestion unit to form a carbonaceous material/acid mixture solution;
digesting the carbonaceous material to remove contaminants, wherein the contaminants are soluble in the acid mixture solution;
feeding the digested carbonaceous material to a thermal unit; and
heating the digested carbonaceous material to a temperature of from about 350° C to about 1,250° C in the thermal unit to produce an activated carbonaceous material.

24. The method for activating carbonaceous material of claim 23, wherein the heating the digested carbonaceous material further comprises:
heating the digested carbonaceous material from about 30 minutes to about 8 hours.

25. The method for activating carbonaceous material of claim 23, wherein the heating the digested carbonaceous material further comprises:
contacting at least one of carbon dioxide and steam with the digested carbonaceous material.

26. The method for activating carbonaceous material of claim 23, wherein the feeding a supply of pre-wetted carbonaceous material further comprises:
removing a substantial amount of fines and powder from the supply of pre-wetted carbonaceous material.

27. The method for activating carbonaceous material of claim 23, wherein the heating the digested carbonaceous material further comprises:
fractionating an exhaust gas to produce a coal tar.

28. The method for activating carbonaceous material of claim 23, wherein the fractionating an exhaust gas to produce a coal tar further comprises:

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using the coal tar for the heating the digested carbonaceous material in the thermal unit.

29. The method for activating carbonaceous material of claim 23, further comprising:
coating the activated carbonaceous material with a halogenated compound.

30. The method for activating carbonaceous material of claim 29, wherein the halogenated compound is a brominated compound.

31. The method for activating carbonaceous material of claim 29, wherein the halogenated compound is in a liquid phase.

32. A method for activating carbonaceous material comprising:
providing a digestion unit;
feeding an acid mixture solution consisting of a mixture of H_2O, HF, and H_2SiF_6 into the digestion unit, wherein the HF, H_2SiF_6, and H_2O may be mixed together in predetermined ratios to form the acid mixture solution prior to being fed into the digestion unit;
feeding a supply of pre-wetted carbonaceous material into the digestion unit to form a carbonaceous material/acid mixture solution;
digesting the carbonaceous material to remove contaminants, wherein the contaminants are soluble in the acid mixture solution;
pumping the carbonaceous material/acid mixture solution from the digestion unit to a separation unit;
separating the digested carbonaceous material from the carbonaceous material/acid mixture solution;
subjecting the digested carbonaceous material to a desired velocity of a heated air flow, wherein the desired velocity of heated air flow separates the digested carbonaceous material based on density of the carbonaceous material, and wherein the desired velocity of heated air flow further dries the digested carbonaceous material;
feeding the digested carbonaceous material to a thermal unit; and

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heating the digested carbonaceous material in the thermal unit to produce an activated carbonaceous material.

33. The method for activating carbonaceous material of claim 32, wherein the heating the digested carbonaceous material further comprises:
heating the digested carbonaceous material to a temperature of from about 350° C to about 1,250° C.

34. The method for activating carbonaceous material of claim 32, wherein the heating the digested carbonaceous material further comprises:
heating the digested carbonaceous material from about 30 minutes to about 8 hours.

35. The method for activating carbonaceous material of claim 32, wherein the heating the digested carbonaceous material further comprises:
contacting at least one of carbon dioxide and steam with the digested carbonaceous material.

36. The method for activating carbonaceous material of claim 32, wherein the feeding a supply of pre-wetted carbonaceous material further comprises:
removing a substantial amount of fines and powder from the supply of pre-wetted carbonaceous material.

37. The method for activating carbonaceous material of claim 32, wherein the heating the digested carbonaceous material further comprises:
fractionating an exhaust gas to produce a coal tar.

38. The method for activating carbonaceous material of claim 32, wherein the fractionating an exhaust gas to produce a coal tar further comprises:
using the coal tar for the heating the digested carbonaceous material in the thermal unit.

39. The method for activating carbonaceous material of claim 32, further comprising:

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coating the activated carbonaceous material with a halogenated compound.

40. A system for activating carbonaceous material comprising:
means for providing a digestion unit;
means for feeding an acid mixture solution into the digestion unit;
means for feeding a supply of pre-wetted carbonaceous material into the digestion unit to form a carbonaceous material/acid mixture solution;
means for digesting the carbonaceous material to remove contaminants, wherein the contaminants are soluble in the acid mixture solution;
means for feeding the digested carbonaceous material to a thermal unit; and
means for heating the digested carbonaceous material in the thermal unit to produce an activated carbonaceous material.

41. The system for activating carbonaceous material of claim 40, wherein the means for heating the digested carbonaceous material further comprises:
means for heating the digested carbonaceous material to a temperature of from about 350° C to about 1,250° C.

42. The system for activating carbonaceous material of claim 40, wherein the means for heating the digested carbonaceous material further comprises:
means for heating the digested carbonaceous material from about 30 minutes to about 8 hours.

43. The system for activating carbonaceous material of claim 40, wherein the means for heating the digested carbonaceous material further comprises:
means for contacting one of carbon dioxide and steam with the digested carbonaceous material.

44. The system for activating carbonaceous material of claim 40, wherein the means for feeding a supply of pre-wetted carbonaceous material further comprises:
means for removing a substantial amount of fines and powder from the supply of pre-wetted carbonaceous material.

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45. The system for activating carbonaceous material of claim 40, wherein the means for heating the digested carbonaceous material further comprises:
means for fractionating an exhaust gas to produce a coal tar.

46. The system for activating carbonaceous material of claim 45, wherein the means for fractionating an exhaust gas to produce a coal tar further comprises:
means for using the coal tar for the heating the digested carbonaceous material in the thermal unit.

47. The system for activating carbonaceous material of claim 40, further comprising:
means for coating the activated carbonaceous material with a halogenated compound.

48. A system for activating carbonaceous material comprising:
means for providing a digestion unit;
means for feeding an acid mixture solution consisting of a mixture of H_2O, HF, and H_2SiF_6 into the digestion unit, wherein the HF, H_2SiF_6, and H_2O may be mixed together in predetermined ratios to form the acid mixture solution prior to being fed into the digestion unit;
means for feeding a supply of pre-wetted carbonaceous material into the digestion unit to form a carbonaceous material/acid mixture solution;
means for digesting the carbonaceous material to remove contaminants, wherein the contaminants are soluble in the acid mixture solution;
means for pumping the carbonaceous material/acid mixture solution from the digestion unit to a separation unit;
means for separating the digested carbonaceous material from the carbonaceous material/acid mixture solution;
means for subjecting the digested carbonaceous material to a desired velocity of a heated air flow, wherein the desired velocity of heated air flow separates the digested carbonaceous material based on density of the carbonaceous material, and wherein the desired velocity of heated air flow further dries the digested carbonaceous material;

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means for feeding the digested carbonaceous material to a thermal unit; and

means for heating the digested carbonaceous material in the thermal unit to produce an activated carbonaceous material.

49. The system for activating carbonaceous material of claim 48, wherein the means for heating the digested carbonaceous material further comprises:

means for heating the digested carbonaceous material to a temperature of from about 350° C to about 1,250° C.

50. The system for activating carbonaceous material of claim 48, wherein the means for heating the digested carbonaceous material further comprises:

means for heating the digested carbonaceous material from about 30 minutes to about 8 hours.

51. The system for activating carbonaceous material for activating carbonaceous material of claim 48, wherein the means for heating the digested carbonaceous material further comprises:

means for contacting at least one of carbon dioxide and steam with the digested carbonaceous material.

52. The system for activating carbonaceous material of claim 48, wherein the means for feeding a supply of pre-wetted carbonaceous material further comprises:

means for removing a substantial amount of fines and powder from the supply of pre-wetted carbonaceous material.

53. The system for activating carbonaceous material for activating carbonaceous material of claim 48, wherein the means for heating the digested carbonaceous material further comprises:

means for fractionating an exhaust gas to produce a coal tar.

54. The system for activating carbonaceous material for activating carbonaceous material of claim 48, wherein the means for fractionating an exhaust gas to produce a coal tar further comprises:

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means for using the coal tar for the heating the digested carbonaceous material in the thermal unit.

55. The system for activating carbonaceous material for activating carbonaceous material of claim 48, further comprising:

means for coating the activated carbonaceous material with an halogenated compound.

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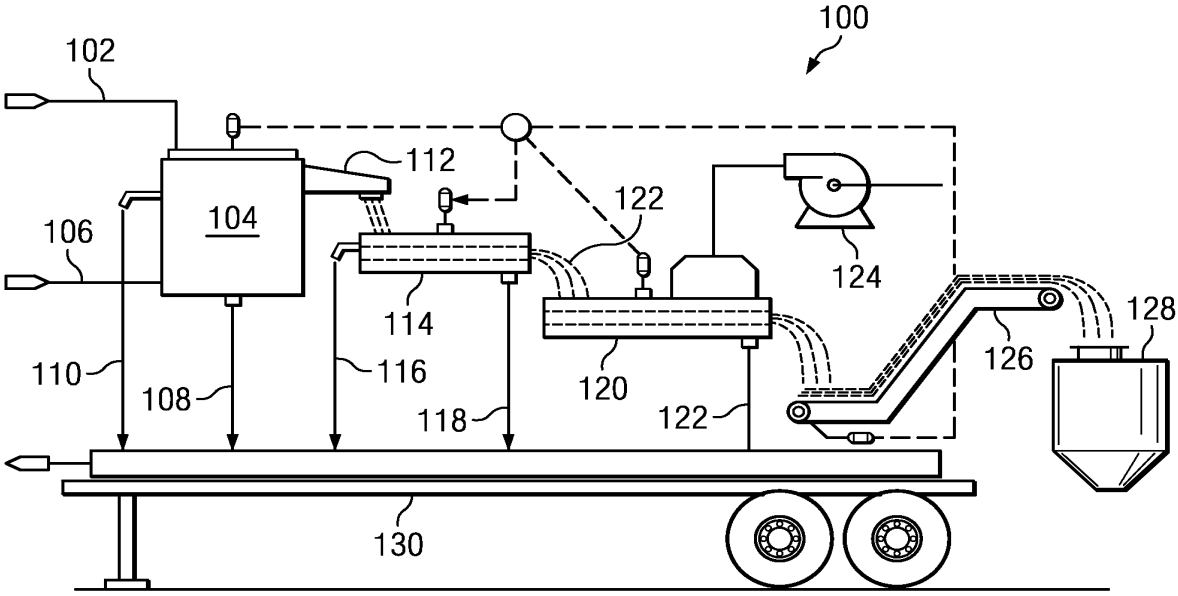

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FIG. 1

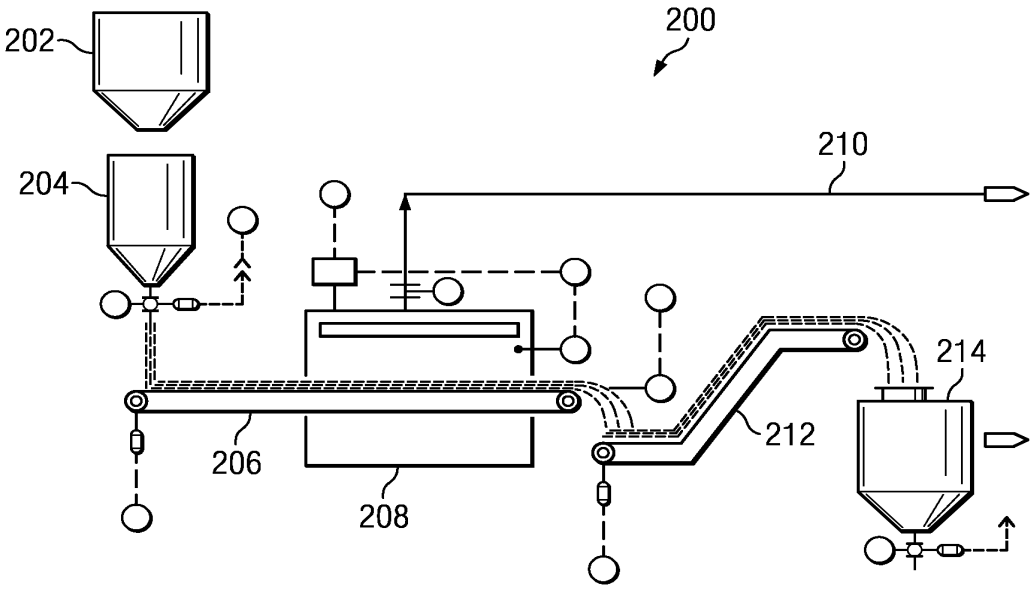

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FIG. 2

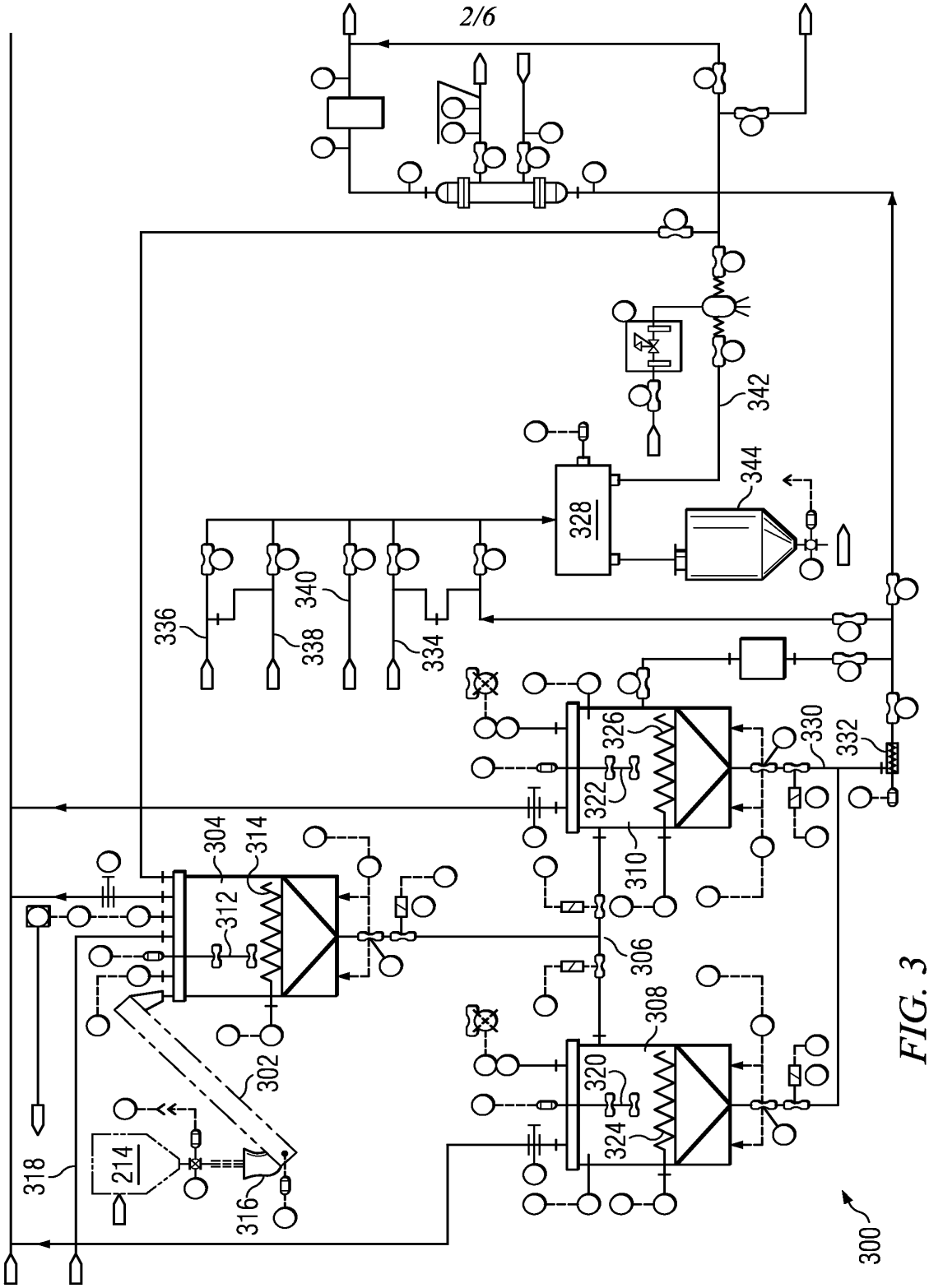

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FIG. 3

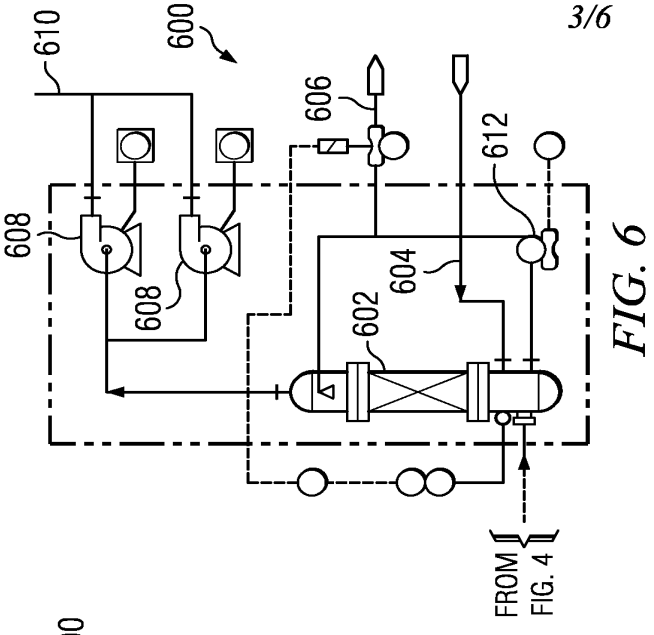


FIG. 6

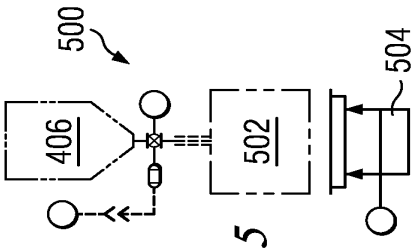


FIG. 5

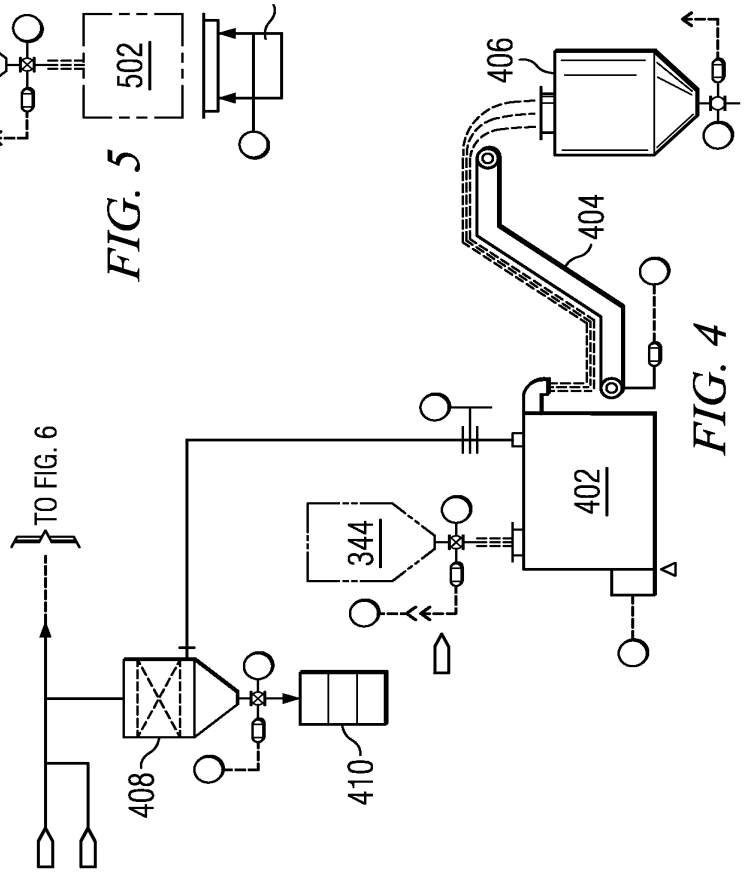


FIG. 4

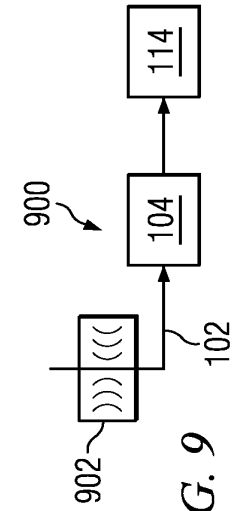


FIG. 9

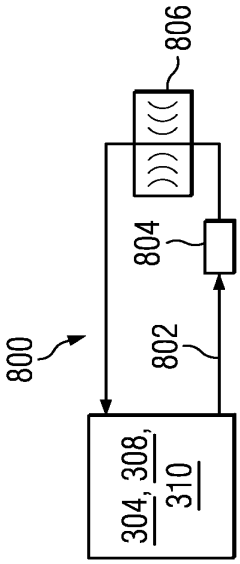


FIG. 8

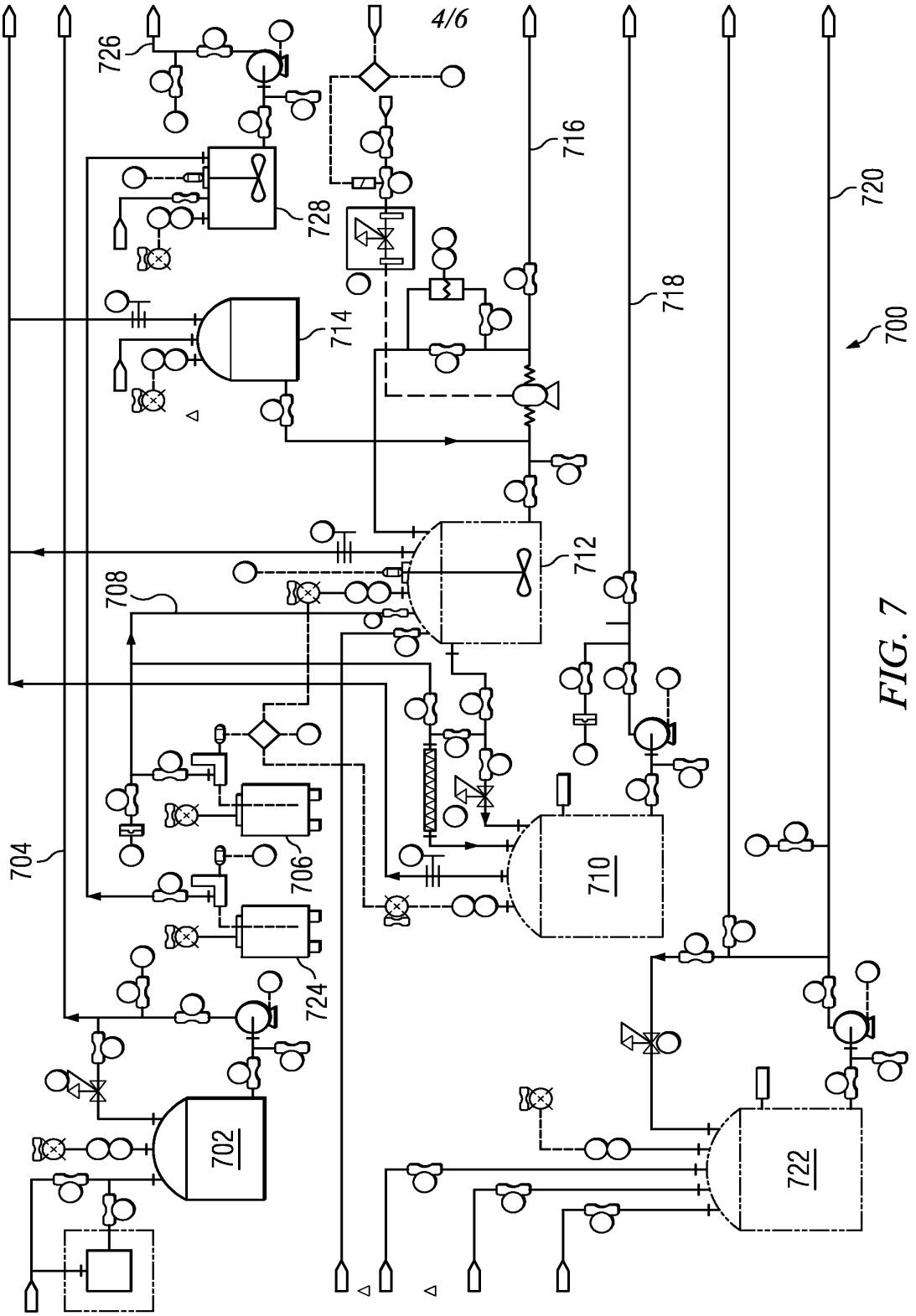


FIG. 7

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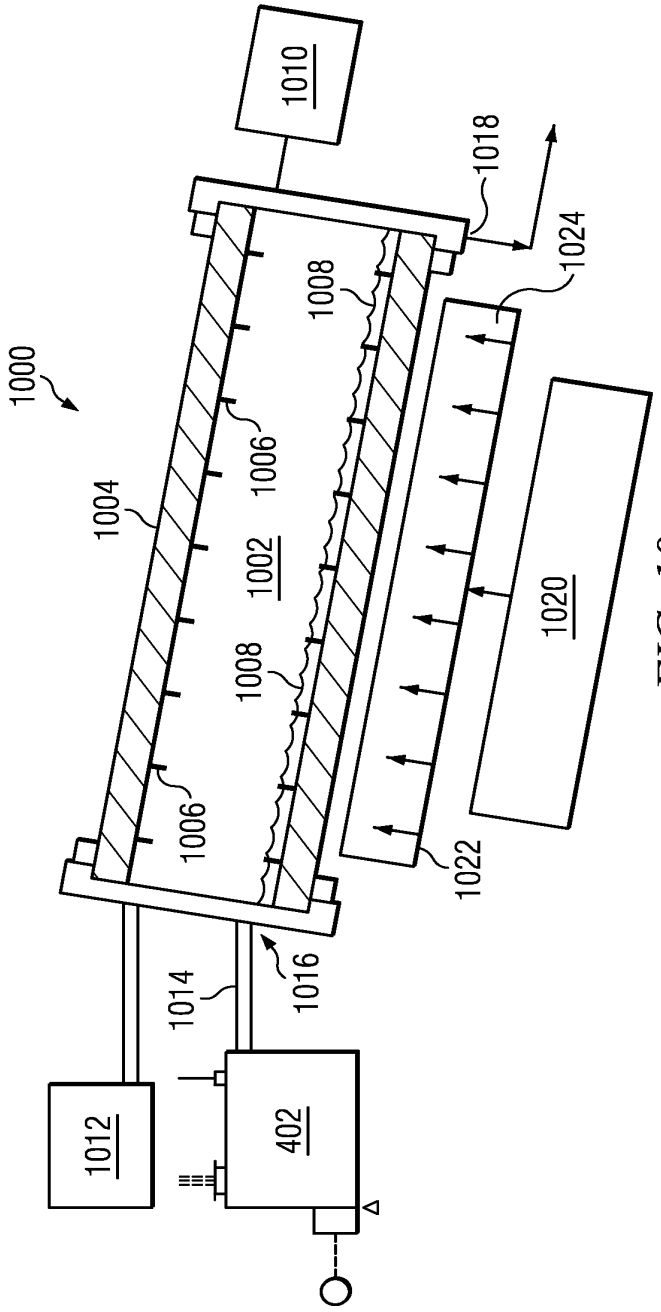

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FIG. 10

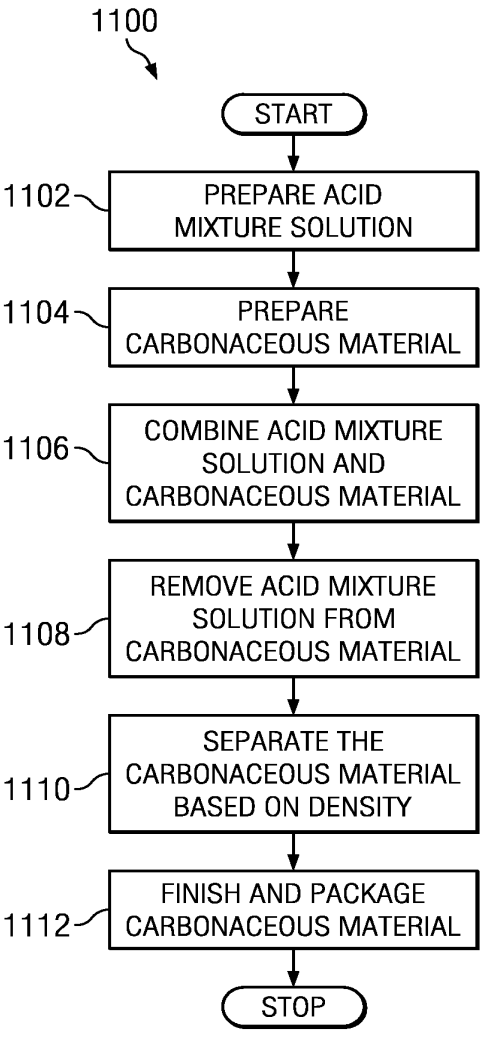

1100
START
1102
PREPARE ACID MIXTURE SOLUTION
1104
PREPARE CARBONACEOUS MATERIAL
1106
COMBINE ACID MIXTURE SOLUTION AND CARBONACEOUS MATERIAL
1108
REMOVE ACID MIXTURE SOLUTION FROM CARBONACEOUS MATERIAL
1110
SEPARATE THE CARBONACEOUS MATERIAL BASED ON DENSITY
1112
FINISH AND PACKAGE CARBONACEOUS MATERIAL
STOP

FIG. 11

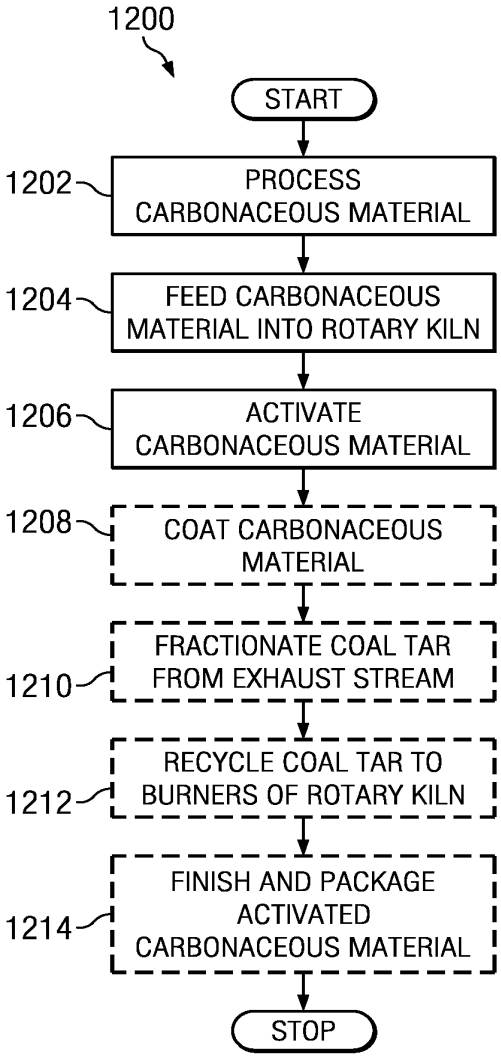

1200
START
1202
PROCESS CARBONACEOUS MATERIAL
1204
FEED CARBONACEOUS MATERIAL INTO ROTARY KILN
1206
ACTIVATE CARBONACEOUS MATERIAL
1208
COAT CARBONACEOUS MATERIAL
1210
FRACTIONATE COAL TAR FROM EXHAUST STREAM
1212
RECYCLE COAL TAR TO BURNERS OF ROTARY KILN
1214
FINISH AND PACKAGE ACTIVATED CARBONACEOUS MATERIAL
STOP

FIG. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/058150

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 157 314 A (MURTY HARI N [US]) 5 June 1979 (1979-06-05) example 1	23-28, 32-38
Y		29-31,39
X	US 1 867 750 A (NAUGLE JOHN J) 19 July 1932 (1932-07-19)	1-13,23
A	the whole document	12-22, 24-55
X	US 4 014 817 A (JOHNSON BRUCE C ET AL) 29 March 1977 (1977-03-29)	23-28
A	column 2, lines 16-21 column 3, line 61 - column 4, line 66; example 5	1-22, 29-55

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 January 2010	01/02/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marucci, Alessandra

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/058150

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 2003/181315 A1 (SUZUKI YASUHIRO [JP] ET AL) 25 September 2003 (2003-09-25) paragraphs [0012] - [0026], [0067]; example 1	23-25 1-22, 26-55
A	DE 37 43 248 C1 (RHEINISCHE BRAUNKOHLENW AG) 21 September 1989 (1989-09-21) the whole document	1-55
Y	US 2001/002387 A1 (TSUTSUMI YOSHIO [JP] ET AL) 31 May 2001 (2001-05-31) examples	29-31,39
P,X	WO 2009/089356 A (CARBONXT GROUP LTD [AU]; HARRIS RANDALL J [US]; WALES DAMIAN [US]) 16 July 2009 (2009-07-16) the whole document	1-16, 20-28, 32-38, 40-54

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/058150

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28 September 2010 (28.09.2010)

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61/246,398 28 September 2009 (28.09.2009) US
61/349,332 28 May 2010 (28.05.2010) US

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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Published:

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WO 2011/038415 A2

(54) **Title**: SORBENT FORMULATION FOR REMOVAL OF MERCURY FROM FLUE GAS

(57) **Abstract**: Methods and systems for reducing mercury emissions from fluid streams having a high concentration of sulfur oxide species are provided herein.

SORBENT FORMULATION FOR REMOVAL OF MERCURY FROM FLUE GAS

B. Cross-Reference to Related Applications:

[0001] This application claims benefit of priority to U.S. Provisional Patent Application No. 61/246,402 filed on September 28, 2009 entitled "Sulfur-Tolerant Sorbent Compositions For Mercury Removal From Flue Gas," U.S. Provisional Patent Application No. 61/246,398 filed on September 28, 2009 entitled "Novel Carbon Based Sorbents for High SO_3 Applications," and U.S. Provisional Patent Application No. 61/349,332 filed on May 28, 2010 entitled "Sulfur-Tolerant Sorbent Compositions For Mercury Removal From Flue Gas," the entire contents of which are hereby incorporated by reference.

C. Government Interests: Not applicable

D. Parties to a Joint Research Agreement: Not applicable

E. Incorporation by Reference of Material submitted on a Compact Disc: Not applicable

F. Background:

[0002] Mercury is a known environmental hazard and leads to health problems for both humans and non-human animal species. Approximately 50 tons per year are released into the atmosphere in the United States, and a significant fraction of the release comes from emissions from coal burning facilities such as electric utilities. To safeguard the health of the public and to protect the environment, the utility industry is continuing to develop, test, and implement systems to reduce the level of mercury emissions from its plants. In the combustion of carbonaceous materials, it is desirable to have a process wherein mercury and other undesirable compounds are captured and retained after the combustion phase so that they are not released into the atmosphere.

[0003] One of the most promising solutions for mercury removal from flue gas is Activated Carbon Injection (ACI). Activated carbon is a highly porous, non-toxic, readily available material that has a high affinity for mercury vapor. This technology is already established for use with municipal incinerators. Although the ACI technology is effective for mercury removal, the short contact time between the activated carbon and the flue gas stream results in an inefficient use of the full adsorption capacity of the activated carbon. Mercury is adsorbed while the carbon is conveyed in the flue gas stream along with fly ash from the boiler. The carbon and fly ash are then removed by a particulate capture device such as an Electrostatic Precipitator (ESP) or baghouse.

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[0004] In flue gas streams containing high concentrations of sulfur oxides, mercury removal by the injection of activated carbon is often compromised by the preferential adsorption and retention of the sulfur compounds such as sulfur trioxide, which are strongly adsorbed by carbon sorbents. The concentration of sulfur dioxide relative to mercury in a typical flue gas stream can be one million to one or higher, and the concentration of sulfur trioxide in such flue gas streams are typically one thousand to one. For example, high sulfur flue gas streams may contain from about 500 parts-per million per volume (ppmv) to about 2500 ppmv or more sulfur dioxide and from about 2 ppmv to about 20 ppmv or more sulfur trioxide. Water vapor in the flue gas further compounds the problem by combining with sulfur trioxide to form sulfuric acid in the pores of the carbon, effectively excluding the adsorption and removal of mercury. For utilities that burn bituminous coals or mixtures of bituminous coals with lower rank sub-bituminous coals, the presence of high levels of sulfur oxides, especially sulfur trioxide, can be a significant concern.

[0005] In addition to sulfur oxides that form during coal combustion, sulfur trioxide may also be produced inadvertently in selective catalytic reduction (SCR) processes downstream of the boiler for controlling NO_x emissions, or it may be added to the flue gas to enhance the performance of ESP devices used to capture the fly ash. Regardless of its origins, sulfur trioxide may have unintended consequences beyond its interference with mercury removal that affect the performance and profitability of the power plant. These consequences include corrosion of system components and unwanted increases in plume visibility and duration upon discharge from the stack.

[0006] To prevent the interference of sulfur oxides with mercury removal by the injected mercury sorbent, a number of prior art solutions have been proposed wherein gross reductions in total sulfur oxide levels are achieved in the gas phase. Nearly all of these solutions rely upon bulk injections of alkaline or other reactive agents into the flue gas to react chemically with the sulfur oxides, forming salt particulates in the gas phase which do not usually interfere with mercury adsorption by the sorbent. In some cases, the agent is injected as a dry solid (Dry Sorbent Injection (DSI)), while in other methods an aqueous solution of the agent is injected, which rapidly devolatizes at the temperature of injection to form a very fine, dry powder with even higher reactivity toward sulfur oxides in the duct. For example, trona, a naturally-occurring mixture of sodium carbonate and sodium bicarbonate, is a commercially-available material found to be effective in controlling sulfur oxides when injected into flue gas streams as a dry reactant.

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[0007] Other alkaline agents, such as calcium oxide (lime), calcium hydroxide (slaked lime), calcium carbonate (limestone), magnesium carbonate (dolomite), magnesium hydroxide, magnesium oxide, and sodium carbonate are also utilized to control sulfur oxide emissions. Solution injection of such agents is represented by Codan's SBS Injection™ technology, which uses an aqueous solution of the chemical reductants sodium bisulfite and sulfite, and is more selective and effective for sulfur trioxide removal. Alternatively, solutions of sodium carbonate, bicarbonate, or hydroxide or thiosulfate can also be used. However, all of these materials and methods suffer disadvantages in that relatively large amounts of the agent must be used for effective control and, more importantly, separate injection systems must be installed independent of mercury sorbent injection, adding cost and complexity to their application. In the case of alkali-based agents, a further disadvantage is found in the negative impact of such materials on the properties of the fly ash collected for subsequent sale to the cement and concrete industry. Although this disadvantage is avoided by using alkaline earth-based agents, these agents generally impart an unwanted increase in resistivity to the ESP, while the alkali-based agents usually have minimal impact on ESP operation.

[0008] Where alkaline or other SO_x reactive agents have been incorporated into the pore structure of the sorbents themselves, the intent has been uniformly the removal of the sulfur compounds and not the removal of mercury in the presence of such compounds. Numerous other examples of activated carbons and other sorbents that incorporate SO_x-reactive materials within the body of the sorbent have been reported, but none appear to advance the art of mercury removal since they are neither directed to that purpose nor are they likely to offer a preferred solution since major portions of the pore structure available for mercury adsorption are configured preferentially for sulfur oxide removal.

[0009] There is a need to provide dry sorbent compositions for mercury removal in flue gas streams containing high concentrations of sulfur oxides, especially sulfur trioxide, that do not depend on the independent injection of alkaline or other reactive agents elsewhere in the system for effective mercury removal, and are inherently effective in a single injection mode. Where such alkaline or reactive agents are used as part of the dry sorbent compositions, there is a further need to limit the impact of these agents on balance-of-plant operations by using only what may be necessary to enhance mercury removal locally at the point of sorbent injection, as well as to avoid incorporation within the body of the porous sorbent to afford increased opportunity for mercury removal. Where independent injection of said alkaline or reactive agents may yet be necessary, there is also a need to reduce the

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amount of such agents that might otherwise be used, consistent with effective mercury removal and marginal impacts on balance of plant issues.

G. Summary of the Invention:

[0010] Various embodiments are directed to a composition including a a porous absorptive material, a source of halogen and a source of nitrogen wherein said source of nitrogen has an oxidation state of -3 and said composition having a particle size of less than 12 μm. In some embodiments, the source of nitrogen may be selected from the group consisting of ammonium, ammonia, amines, amides, imines, quaternary ammonium and the like, and in other embodiments, the composition may have a mean particle diameter of less than about 7 μm. In still other embodiments, the at least one agent is ammonium bromide. The porous mercury adsorptive material may be any of a carbonaceous char, activated carbon, reactivated carbon, zeolite, silica, silica gel, alumina clay, or a combination thereof. In some embodiments, the porous mercury adsorptive material has a surface area of at least about 300 m^2/g, and in other embodiments, the porous mercury adsorptive material further comprises a hydrophobicity enhancement agent. In particular embodiments, composition may have a halide concentration of greater than 0.15 equivalents per 100 grams of the composition, and in certain embodiments, the at least one agent is from about 15 wt. % to about 70 wt. % of the composition, and particular embodiments, the composition may be a dry admixture.

[0011] Certain embodiments are directed to a sorbent for the removal of mercury from flue gas streams including a dry admixture of a porous mercury adsorptive material and at least one agent selected from the group consisting of ammonium halides, amine halides quaternary ammonium halides, and combinations thereof. In some embodiments, the dry admixture may have a mean particle diameter of less than about 12 μm. In other embodiments, the dry admixture may have a mean particle diameter of less than about 10 μm, and in still other embodiments, the dry admixture has a mean particle diameter of less than about 7 μm.

[0012] The porous mercury adsorptive material of embodiments may be a carbonaceous char, activated carbon, reactivated carbon, zeolite, silica, silica gel, alumina clay, or a combination thereof, and in some embodiments, the porous mercury adsorptive material may have a surface area of at least about 300 m^2/g. In certain embodiments, the porous mercury adsorptive material may further include a hydrophobicity enhancement agent including, but not limited to, elemental halogens fluorine salts, organo-fluorine compounds,

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fluorinated polymers, and combinations thereof. In other embodiments, the porous mercury adsorptive material may further include one or more oxidants such as, but not limited to, halogen salts, and in some embodiments, the oxidant may be greater than or equal to about 0.15 equivalents per 100 grams of the dry admixture.

[0013] In particular embodiments, the at least one agent may be ammonium bromide. In some embodiments, the at least one agent may be about 10 wt. % or greater of the dry admixture. In other embodiments, the at least one agent may be about 15 wt. % or greater of the dry admixture, and in still other embodiments, the at least one agent may be about 30 wt. % or greater of the total sorbent. In some embodiments, the at least one agent may be from about 15 wt. % to about 70 wt. % of the dry admixture. In other embodiments, the at least one agent may be from about 15 wt. % to about 50 wt. % of the dry admixture, and in still other embodiments, the at least one agent may be from about 20 wt. % to about 50 wt. % of the dry admixture. In certain embodiments, the at least one agent may be from about 20 wt. % to about 40 wt. % of the dry admixture. In further embodiments, the at least one agent may be greater than or equal to about 0.15 equivalents per 100 grams of the dry admixture.

[0014] Other embodiments are directed to methods for preparing a sorbent for the removal of mercury from flue gas streams including the steps of co-milling a dry porous mercury adsorptive material and at least one dry agent selected from the group consisting of ammonium halides, amine halides, and quaternary ammonium halides to form a dry admixture having a mean particle diameter of less than or equal to about 12 μm, and in particular embodiments, the porous mercury adsorptive material and at least one agent are not physically associated in the dry admixture. In some embodiments, co-milling may be performed until the dry admixture has a mean particle diameter of less than about 10 μm, and in other embodiments, co-milling may be performed until the dry admixture has a mean particle diameter of less than about 7 μm. The porous mercury adsorptive material and various agents may be any of those agents provided in the above embodiments, and the admixture may include any amount of the components as described above.

[0015] Still other embodiments include a method for removing mercury from flue gas streams containing sulfur trioxide (SO_3) including the steps of injecting into the flue gas stream a dry admixture of a porous mercury adsorptive material and at least one dry agent selected from the group consisting of ammonium halides, amine halides, and quaternary ammonium halides, wherein the dry admixture has a mean particle diameter of less than or

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equal to about 12 μm. In some embodiments, the dry porous mercury adsorptive material and the at least one dry agent may be combined to form a dry admixture prior to being injected into the flue gas stream, and in other embodiments, the dry porous mercury adsorptive material and the at least one dry agent may be injected in to the flue gas stream separately. The porous mercury adsorptive material and various agents may be any of those agents described in the above embodiments, and the admixture may include any amount of the components as described above.

H. Description of Drawings: Not applicable.

I. Detailed Description:

[0016] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0017] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a combustion chamber" is a reference to "one or more combustion chambers" and equivalents thereof known to those skilled in the art, and so forth.

[0018] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0019] Embodiments of the invention are directed to mercury sorbents having enhanced mercury removal capabilities in flue gas streams containing high concentrations of acid gases. In various embodiments, the mercury sorbent may include a mercury adsorptive material and a acid gas suppression agent. In some embodiments, the mercury adsorptive

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material may be an adsorptive material, such as, a carbonaceous char or activated carbon that has been treated with one or more additives that enhance the hydrophobicity of the adsorbent material, and in other embodiments, the mercury adsorptive material may be treated with a mercury adsorption enhancing additive. In certain embodiments, acid gas suppression agent may be any agent having an exceptionally high affinity, selectivity, and rapid kinetics for acid gases such as, for example, hydrochloric acid (HCl), hydrofluoric acid (HF), nitric oxide species (NO_x), or sulfur oxide species (SO_x). In certain embodiments, the sorbents of the invention may include a porous mercury sorbent and a SO_x suppression agent. Such sorbents may more effectively reduce the concentration of mercury in flue gas streams into which they are added over mercury adsorptive materials alone, in particular, when injected into flue gas streams containing high concentrations of sulfur oxide species.

[0020] In general, mercury adsorptive materials such as activated carbon remove carbon adsorb mercury with less efficiency in flue gas streams having high concentrations of acid gases and, in particular, sulfur oxide species, SO_x, such as, SO_3 and/or SO_2, and other acid gases. Sulfur trioxide, SO_3, is strongly adsorbed by activated carbon. Sulfur dioxide, SO_2, although less strongly adsorbed, can be oxidized to sulfur trioxide by oxygen in the flue gas in the presence of catalytic sites on the adsorbent surface. The overall effect of adsorption of these sulfur oxides precludes or strongly interferes with the adsorption of mercury from the flue gas.

[0021] The adsorption of sulfur oxide species may be further enhanced in the presence of water, which is commonly present in flue gas steams. Accordingly, increasing the inherent hydrophobicity of the adsorbent surface or making it less receptive to moisture adsorption can limit the formation and retention of sulfur species on the carbon surface, preserving more of the adsorption pore volume for mercury removal. Thus, various embodiments of the invention include hydrophobic mercury adsorptive materials. As used herein "hydrophobic" describes the forces driving a solute out of water (or other polar solvent) and the tendency for collection on surfaces or in non-polar solvents. In some embodiments, the hydrophobicity of the adsorbent may be enhanced to reduce SO_x adsorption to the adsorptive material, and in other embodiments, the porous regions of the adsorptive material may be treated such that the kinetics of mercury removal are enhanced relative to the kinetics of sulfur oxide removal.

[0022] The mercury adsorptive material of the sorbent composition of various embodiments may include any material having an affinity for mercury. For example, in some embodiments, the mercury adsorptive material may be a porous sorbent having an affinity for

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mercury including, but not limited to, activated carbon, reactivated carbon, zeolite, silica, silica gel, clay, and combinations thereof, and in particular embodiments, the mercury adsorptive material may be activated carbon.

[0023] The mercury adsorptive material may have any mean particle diameter (MPD). For example, in some embodiments, the MPD of the mercury adsorptive material may be from about 0.1 μm to about 100 μm, and in other embodiments, the MPD may be about 1 μm to about 30 μm. In still other embodiments, the MPD of the mercury adsorptive material may be less than about 15 μm, and in some particular embodiments, the MPD may be about 2 μm to about 10 μm, about 4 μm to about 8 μm, or about 5 μm or about 6 μm. In certain embodiments, the mercury adsorptive materials may have an MPD of less than about 12 μm, or in some embodiments, less than 7 μm, which may provide increased selectivity for mercury oxidation.

[0024] The mercury adsorptive materials of various embodiments may have an inherent hydrophobic character. For example, while activated carbon is inherently hydrophobic to the extent that it is wet more readily by organic solvents than by water, all activated carbons are not completely hydrophobic, and certain portions of the surface of activated carbons may exhibit partially hydrophilic characteristics. In some embodiments, the feedstock used to prepare the mercury adsorptive material may be selected from materials having fewer carbon-oxygen surface groups, which provide fewer active sites for carbon self-oxidation and fewer sites for oxidation of sulfur dioxide to sulfur trioxide. Such materials may be selected using, for example, a high peroxide index as described in U.S. Patent Nos. 6,238,641 and 6,514,906, which are hereby incorporated by reference in their entireties.

[0025] In other embodiments, the mercury adsorptive material may be treated to enhance the hydrophobicity of the adsorptive materials with, for example, one or more hydrophobicity enhancement agents that impede the adsorption and transport of water or other treatments of the sorbent that achieve similar results. Embodiments are not limited to the type of treated mercury adsorptive material or the means by which the mercury adsorptive material has been treated with a hydrophobicity enhancement agent. For example, in some embodiments, the mercury adsorptive material may be treated with an amount of one or more elemental halogen that can form a permanent bond with the surface. The elemental halogen may be any halogen such as fluorine (F), chlorine (Cl), or bromine (Br), and in certain embodiments, the elemental halogen may be fluorine (F). In other embodiments, the mercury adsorptive material may be treated with a hydrophobicity enhancement agent such as a

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fluorine salt, organo-fluorine compound, or fluorinated polymer, such as, TEFLON®. In such embodiments, treatment may be effectuated by grinding the mercury adsorptive material with the organo-fluorine compound or fluorinated polymer. In still other embodiments, carbon sorbents used as the mercury adsorptive material may be treated with mineral acids such as but not limited to, hydrochloric acid, nitric acid, boric acid, and sulfuric acid, under high temperature, *e.g.*, greater than about 400° C or greater than 600° C or greater than 800° C. The concentration of the acid is not critical to such treatments and concentrations as low as 1.0 percent by weight or less may be used. Without wishing to be bound by theory, such treatment may enhance hydrophobicity and decreased activity for the catalytic oxidation of sulfur dioxide to sulfuric acid in the presence of oxygen and water. Evidence of such treatments can be found in a high contact pH and a reduced tendency for the carbon alone to decompose hydrogen peroxide when compared to the same carbon without such treatments.

[0026] In still other embodiments, any of the adsorptive materials described above may be treated with one or more mercury removal agents or oxidizing agents that enhance mercury adsorption. For example, in some embodiments, the mercury removal agent may be a halogen salt including inorganic halogen salts, which for bromine may include bromides, bromates, and hypobromites, for iodine may include iodides, iodates, and hypoiodites, and for chlorine may be chlorides, chlorates, and hypochlorites. In certain embodiments, the inorganic halogen salt may be an alkali metal or an alkaline earth element containing halogen salt where the inorganic halogen salt is associated with an alkali metal such as lithium, sodium, and potassium or alkaline earth metal such as magnesium, and calcium counterion. Non-limiting examples of inorganic halogen salts including alkali metal and alkali earth metal counterions include calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and the like. In particular embodiments, the halogen salt may be a bromine salt, such as calcium bromide ($CaBr_2$). In such embodiments, the oxidant content may be near to or above about 0.15 equivalents per 100 grams of absorptive material, wherein one equivalent of oxidant is defined as the amount required to react with one mole of electrons in a redox reaction.

[0027] In various embodiments, treatment of the mercury adsorptive material with a halogen salt or other mercury removal agent may be effectuated by grinding the mercury adsorptive material with the halogen salt or other mercury removal agent. For example, in

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some embodiments, increased selectivity for mercury adsorption over sulfur trioxide adsorption may be provided by co-milling activated carbon with a halide salt to an MPD of less than about 10 μm or less than about 7 μm. Although not wishing to be bound by theory, the small MPD may improve the selectivity of mercury adsorption as the halide effectively oxidizes the mercury and the alkalinity interferes with the adsorption of the sulfur trioxide.

[0028] Certain embodiments of the invention include methods for treating an adsorptive material by grinding the adsorptive material with a halogen salt or other mercury removal agent and an organo-fluorine compound or fluorinated polymer. For example, in some embodiments, the mercury adsorptive material may be treated with both a halogen salt or other mercury removal agent and a solid hydrophobicity enhancement agent such as an organo-fluorine compound or a fluorinated polymer, and in such embodiments, the adsorptive material may be co-ground with both agents.

[0029] In some embodiments, mercury removal may be further enhanced by combining the adsorptive materials described above with one or more secondary agents having high affinity, high selectivity, and rapid kinetics for acid gas removal, which may be collectively referred to herein as "acid gas suppression agents" or "acid gas suppressors." In some embodiments, the acid gas agents may not be physically incorporated into and within the adsorptive material itself. Rather, the acid gas agents may be provided as a separate component of the mercury sorbent that is blended with the adsorptive agent; therefore, the maximum pore space for mercury reaction and adsorption can be maintained on the adsorptive material. In certain embodiments, the acid gas suppression agents may have high affinity, high selectivity, and rapid kinetics for sulfur reactive species such compositions are referred to herein as "SO_x suppression agents" or "SO_x suppressors." The resulting mercury sorbent thus includes an adsorptive material and one or more SO_x suppression agents. Any type of SO_x suppression agent known in the art may be used in the mercury sorbent of various embodiments. For example, the SO_x suppression agent may be an oxidizing agent, alkaline agent, dual-function agent having both alkalinity and oxidation capabilities, or adsorptive agent treated to specifically adsorb sulfur oxides.

[0030] In some embodiments, the acid gas or SO_x suppression agent may be an alkaline agent. Numerous alkaline agents are known in the art and currently used to remove sulfur oxide species from flue gas and any such alkaline agent may be used in the invention. For example, in various embodiments, the alkaline additive may be alkali oxides, alkaline earth oxides, hydroxides, carbonates, bicarbonates, phosphates, silicates, aluminates, and

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combinations thereof, and in certain embodiments, the alkaline additive may be calcium carbonate ($CaCO_3$; limestone), calcium oxide (CaO; lime), calcium hydroxide ($Ca(OH)_2$; slaked lime); magnesium carbonate ($MgCO_3$; dolomite), magnesium hydroxide ($Mg(OH)_2$), magnesium oxide (MgO), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), trisodium hydrogendicarbonate dihydrate ($Na_3H(CO_3)_2 \cdot 2H_2O$; trona), and combinations thereof. In various embodiments, the alkalinity agent may be provided at a concentration greater than or equal to about 0.15 equivalents per 100 grams of absorptive material, wherein one equivalent of the alkaline agent is defined as the amount required to produce one mole of hydroxyl ions or to react with one mole of hydrogen ions. In particular embodiments, such alkaline agents may have a relatively high surface area such as, for example, above 100 m^2/g for neat materials. High surface area materials may provide improved kinetics and capabilities for acid gas or SO_x mitigation while complementing halogen compounds and other added oxidants to provide oxidation of elemental mercury. Because alkaline agents are highly polar materials that may associate and bond with water, in various embodiments, alkaline agents may be combined with the primary mercury sorbent as a physical admixture and may not generally be present on the sorbent surface or contained within the sorbent pore structure.

[0031] In further embodiments, the acid gas or SO_x suppression agent is a dual-function agent having both acid gas adsorption capacity and mercury oxidation activity on the same agent. In some embodiments, the dual function agent may be a readily dissociable additive with an oxidizing component and alkaline component. Examples of such agents include a non-metal cation and a halide. In some embodiments, such compounds may include a halogen and a source of nitrogen having an oxidation state of -3. Various such nitrogen sources are known in the art and can include, for example, ammonium, ammonia, amines, amides, imines, quaternary ammonium, and the like. In certain embodiments, the agent may be, for example, ammonium halide, such as, ammonium iodide, ammonium bromide, or ammonium chloride, an amine halide, a quaternary ammonium halide, or an organo-halide and combinations thereof. These agents can be combined with a porous mercury adsorbent to provide the compositions and sorbents of the invention.

[0032] In such embodiments, an ammonium halide such as, for example, ammonium bromide (NH_4Br), can react with the sulfur oxides in the flue gas to form ammonium sulfate ($(NH_4)_2SO_4$) or ammonium sulfite ($(NH_4)_2SO_3$) and free bromine. The bromine liberated by this reaction is not substantially adsorbed by the activated carbon and is available to oxidize mercury in the flue gas, which is readily adsorbed by adsorptive material,

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although secondary oxidation pathways such as those afforded by the Deacon reaction may also be effective. Without wishing to be bound by theory, these dual-function additives may have higher vapor pressures and lower decomposition temperatures compared to alkali or alkaline earth metal halide salts that are commonly provided with mercury adsorbents, which are provided solely for oxidation of mercury. Thus, the dual-function additives may provide effective mercury oxidation together with improved kinetics for SO_x suppression and sulfur trioxide adsorption.

[0033] Acid gas or SO_x suppression agents having a dual-function agent may be prepared by any method known in the art. For example, in some embodiments, one or more ammonium halide, amine halide, or quaternary ammonium halide may be prepared independently and either combined with a mercury adsorptive agent or combined with an adsorptive material such as, for example, activated carbon, under conditions that do not allow the dual-function agent to impregnate and bind to the adsorptive agent. In other embodiments, an ammonium, amine, or quaternary ammonium containing compound may be combined with an adsorptive material simultaneously with an elemental halogen or decomposable halogen compound. In particular embodiments, the acid gas or SO_x suppression agent may include a dual-function agent having a surface area greater than about 50 m^2/g or greater than about 100 m^2/g for the neat materials. In particular embodiments, the dual-function agent may be provided at a concentration of greater than or equal to about 0.15 equivalents per 100 grams of absorptive material based on either the oxidant or alkalinity contributions. In various embodiments, the dual function agents such as ammonium halides, amine halides, or quaternary ammonium halides may be combined with the primary mercury sorbent as a dry physical admixture and may not generally be present on the sorbent surface or contained within the sorbent pore structure.

[0034] The acid gas or SO_x suppression agent is provided in the mercury sorbent of various embodiments to suppress acid gases, such as, hydrochloric acid, hydrofluoric acid, nitric oxide species, or sulfur dioxide and sulfur trioxide adsorption to the adsorptive material which would reduce the adsorption of mercury to the adsorptive material. The adsorptive material and the acid gas or SO_x suppression agent may be combined in any ratio which achieves suppression of acid gas and SO_x species while providing sufficient mercury removal. For example, in some embodiments, the adsorptive material to acid gas or SO_x suppression agent ratio may be from about 1:1, about 1:5, about 1:10, about 1:25, about 1:50, about 75:1, or about 1:100. In other embodiments, the adsorptive material to acid gas or SO_x suppression agent ratio may be from about 5:1, about 10:1, about 25:1, about 50:1, about

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75:1, or about 100:1. In other embodiments, the acid gas or SO_x suppression agent may make up about 10 wt. % or greater or about 15 wt. % or greater of the total sorbent, and in still other embodiments, the acid gas or SO_x suppression agent may make up about 30 wt. % or greater, 40 wt. % or greater, 50 wt. % or greater, 60 wt. % or greater, or 70 wt. % or greater of the total sorbent. In other embodiments, the dual function agents may be combined with other agents such as, for example, halide salts, halide metal salts, alkaline agents, and the like to prepare a composition or sorbent encompassed by the invention.

[0035] In particular embodiments, the sorbent may include a mercury adsorptive material such as activated carbon or treated activated carbon and an agent such as ammonium halide, amine halide, or quaternary ammonium halide, for example, ammonium bromide. In some such embodiments, the ammonium bromide may be provided about 10 wt. % or greater or about 15 wt. % or greater, about 20 wt. % or greater, about 25 wt. % or greater, about 30 wt. % or greater, about 40 wt. % or greater of the total sorbent. In other embodiments, the sorbent may include from about 10 wt. % to about 70 wt. %, about 10 wt. % to about 60 wt. %, or about 10 wt. % to about 50 wt. % SO_x suppression or about 15 wt. % to about 70 wt. %, about 15 wt. % to about 60 wt. %, or about 15 wt. % to about 50 wt. % SO_x suppression agent or about 20 wt. % to about 70 wt. %, about 20 wt. % to about 60 wt. %, or about 20 wt. % to about 50 wt. % SO_x suppression agent. Without wishing to be bound by theory, improved acid gas and SO_x suppression may allow for improved mercury adsorption by the mercury adsorptive agent, and increasing the concentration of the acid gas or SO_x suppression agent, and in particular a ammonium halide, amine halide, or quaternary ammonium halide such as, for example, ammonium bromide, may improve mercury adsorption beyond currently available adsorbents thereby providing a mercury adsorbent that includes, for example, low activated carbon content but that removes mercury from flue gas streams as effectively as high activated carbon content sorbents. Low activated carbon sorbents may provide improved stability when used in, for example, cement manufacturing.

[0036] The compositions of various embodiments described above may allow for a higher percentage of active halide and alkaline agents to be included in the injected sorbent. Mercury adsorbents that are impregnated with an additive by treating with an aqueous solution of the additive, for example, commercial brominated carbon sorbents, especially those impregnated with elemental bromine, can only retain a small percentage of the additive on the surface of the adsorbent, and impregnation tends to clog the pores of porous mercury adsorbents reducing the surface area available for mercury adsorption. In contrast, the percentage of active halide and acid gas or SO_x suppression agent in a dry mixture may be

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greater than about 10 wt. %, greater than about 15 wt. %, greater than about 20 wt. %, or greater than about 30 wt. % and up to about 50 wt. %, up to about 60 wt. %, or up to about 70 wt. % without exhibiting a reduction in mercury adsorption efficiency.

[0037] Moreover, the sorbents of various embodiments exhibit improved stability during manufacture, storage, and injection than currently available impregnated sorbents. For example, producing acid gas or SO_x suppression agents having a mean particle diameter of less than about 15 μm or 20 μm using any of the acid gas or SO_x suppression agents described herein is difficult. Moreover, all of the acid gas or SO_x suppression agents are somewhat hygroscopic, and ammonium halide, amine halide, or quaternary ammonium halide acid gas or SO_x suppression agents readily absorb water. Rapid moisture pickup causes substantial re-agglomeration making maintenance of acid gas or SO_x suppression agents at mean particle diameters of less than about 15 μm difficult. Without wishing to be bound by theory, re-agglomeration may be reduced as the result of the mercury adsorbent acting as separators and competing desiccants reducing the amount of moisture in the dry mixture and allowing long term storage and maintenance of acid gas or SO_x suppression agents with mean particle diameters of less than about 12 μm. Reduction in particles size may also provide more rapid and selective kinetics allowing improved synergistic effects.

[0038] In addition, at elemental bromine loadings above 10 wt % to 15 wt %, the equilibrium vapor phase concentrations under ambient conditions may rise above safe and acceptable threshold limit values (0.66 mg/m^3 TWA; 2.0 mg/m^3 STEL), creating problems in handling and use, and SO_x suppression agents such as ammonium halide, amine halide, or quaternary ammonium halide may provide fire retardant properties that reduce self heating and combustion associated with metal halide containing sorbents in which the metal cation can catalyze the oxidation of the carbon.

[0039] The adsorptive material and the SO_x suppression agent may be combined by any method. For example, in some embodiments, the adsorptive material and the SO_x suppression agent may be combined by blending or mixing the materials into a single mercury sorbent that can then be injected into a flue gas stream. In other embodiments, combining may occur during use such that the adsorptive material and the SO_x suppression agent may be held in different reservoirs and injected simultaneously into a flue gas stream.

[0040] In certain embodiments, the absorptive material and the SO_x suppression agent may be co-milled. For example, in various embodiments, a porous absorptive material and a acid gas or SO_x suppression agent may be combined and co-milled or sized to about the

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same particle size distribution which in some embodiments, may be a mean particle diameter of less than or equal to about 12 μm less than or equal to about 10 μm, or less than about 7 μm. Without wishing to be bound by theory, reducing the mean particle diameter of the sorbent, combined with localized acid gas or SO_x suppression added to the sorbent, but not contained within the sorbent pore structure, has been found to be surprisingly effective in facilitating rapid and selective mercury adsorption despite sulfur trioxide concentrations that are orders of magnitude higher than the mercury levels in the flue gas. This effect has been shown particularly effective when all of components of the sorbent are combined and co-milled or otherwise sized to a mean particle diameter of less than or equal to about 12 μm. Co-milling may be carried out by any means. For example, in various embodiments, the co-milling may be carried out using bowl mills, roller mills, ball mills, jet mills or other mills or any grinding device known to those skilled in the art for reducing the particle size of dry solids.

[0041] The sorbent of such embodiments may include any of the absorptive materials described above, any additive described above, and any acid gas or SO_x suppression agent described above. In certain embodiments, the absorptive material may be an activated carbon or reactivated carbon. In some embodiments, the additive provides rapid ancillary oxidation of elemental mercury in the gas stream such as, for example, a halide compound, and in particular embodiments, the halide compound may be less stable at elevated temperatures than alkali or alkaline-earth metal analogs. In certain embodiments, the SO_x suppression agent may be a dual function agent providing both oxidation and alkalinity such as, for example, ammonium halides, amine halides, and quaternary ammonium halides.

[0042] Further embodiments are directed to methods for removing mercury from flue gas by injecting a mercury adsorbent including a mercury adsorptive material and an acid gas or SO_x suppression agent into a flue gas stream. While such compositions may be particularly effective in flue gas streams having high SO_x, and in particular, high SO_3, concentrations, the sorbents described herein may be used to adsorb mercury in any flue gas streams regardless of the SO_3 concentration. For example, the sorbents of various embodiments may be used in flue gas streams having no or extremely low SO_3 content or flue gas streams containing high concentrations of other acid gases such as HCl, HF, or NO_x species. In some embodiments, the mercury adsorptive material and the acid gas or SO_x suppression agent may be combined prior to injection into the flue gas stream by, for example, mixing or blending, the mercury adsorptive material with the acid gas or SO_x

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suppression agent. In other embodiments, the mercury adsorptive material and the acid gas or SO_x suppression agent may be injected separately into the flue gas stream and combined in the flue gas stream itself. In such embodiments, the acid gas or SO_x suppression agent may adsorb sulfur oxide species such as sulfur trioxide and sulfur dioxide reducing the likelihood that such sulfur oxide species will adsorb to the mercury adsorptive agent. The increased availability for mercury adsorption of surface area on the mercury adsorptive agent may thus increase mercury adsorption.

EXAMPLES

[0043] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

EXAMPLE 1

[0044] Power Plant 1 - Three mercury sorbents were tested at a power plant burning a 25% PRB/ 75% CAPP coal mixture. Sorbent C was prepared by dry-mixing and co-grinding an activated carbon with about 15 wt. % bromide as ammonium bromide to an MPD of about 6 μm. Sorbent B was prepared by dry-mixing and co-grinding an activated carbon with about 15 wt% calcium as calcium oxide and about 5 wt. % bromide as ammonium bromide to an MPD of about 6 μm. These sorbents were compared to a commercial brominated carbon, Sorbent H, having an MPD not less than about 12 μm and containing no more than about 10 wt. % bromide as a bromide salt. The flue gas at this plant contained about 400 to about 600 ppmv sulfur dioxide and about 2 to about 10 ppmv sulfur trioxide at the SCR, selective catalytic reduction, outlet. When injected at the air pre-heater outlet at about 9 to about 9.5 lbs/MMacf the commercial sorbent, Sorbent H, achieved mercury removal levels of about 55% versus about 77% for Sorbent B and 85% for Sorbent C.

EXAMPLE 2

[0045] At Power Plant 2 burning 100% CAPP coal and generating greater than 10 ppmv of sulfur trioxide, Sorbent C, prepared as described in Example 1 was tested for mercury removal against Sorbent H, as described in Example 1. To achieve and maintain mercury removal levels around or above 90%, Sorbent H required injection rates of about 6 lbs/MMacf versus about 2 lbs/MMacf for Sorbent C.

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EXAMPLE 3

[0046] At Power Plant 3 where sulfur trioxide levels could be controlled and varied by the deliberate addition of such to the flue gas stream, several mercury removal sorbents were tested at different sulfur trioxide concentrations. Sorbent C was prepared by dry-mixing and co-grinding activated carbon with about 15 wt. % bromide as ammonium bromide to an MPD of about 6 μm. This sorbent was tested against Sorbent M, a commercial brominated carbon sorbent having an MPD not less than about 12 μm and containing not more than about 10 wt. % bromide as a bromide salt. Sorbent C was also tested against Sorbent N, another commercial brominated carbon sorbent believed to be prepared from a lignite-based activated carbon impregnated internally with about 3 to about 6 wt% bromide as sodium bromide and ground to an MPD of about 14 to about 16 μm.

[0047] With no sulfur trioxide in the flue gas, Sorbent C gave nearly 100% removal at a sorbent injection rate of 10 lbs/MMacf versus 85% and 76% removal for Sorbents M and N, respectively, at the same injection rate. At 10.3 ppmv sulfur trioxide and the same sorbent injection rate, Sorbent C gave about 94% mercury removal, while commercial brominated sorbents M and N declined to about 65% and 62%, respectively. At 20.3 ppmv of sulfur trioxide and an injection rate of 10 lbs/MMacf, Sorbent C achieved about 78% mercury removal, versus about 53% removal for both of the commercial brominated sorbents M and N. Adding 20 lbs/hr of trona at 25.3 ppmv sulfur trioxide reduced the Sorbent C injection rate to about 7 lbs/MMacf to maintain about 78% mercury removal, while about 8 lbs/MMacf were required for Sorbent M to maintain about 53% mercury removal. The sulfur trioxide levels reported in this example were all measured in front of the air preheater.

EXAMPLE 4

[0048] Power Plant 3 - Sorbent C, which includes about 15 wt. % bromine as ammonium bromide dry-mixed and co-ground with activated carbon to an MPD of about 6 μm, and Sorbent D, which includes about 36 wt. % bromine as ammonium bromide dry-mixed and co-ground with activated carbon to an MPD of about 6 μm, were tested against Sorbent N, a commercial brominated carbon sorbent believed to be made from a lignite activated carbon impregnated internally with about 3 to about 6 wt. % bromine as sodium bromide and ground to an MPD of about 14 to about 16 μm. At this coal-fired boiler, sulfur trioxide (SO_3) could be added to the flue gas in a controlled manner. At an SO_3 concentration of about 10 ppmv, injection rates for each sorbent were increased until 90% mercury removal had been achieved. For Sorbent N, between 50 and 60 lbs/min were required to meet the

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treatment objective, versus about 20 to about 25 lbs/min for Sorbent C and about 12 to about 15 lbs/min for Sorbent D, demonstrating the value in high SO_3 streams of both the higher alkalinity/halide content of the co-ground dual-function additive as well as smaller sorbent mean particle diameters. The sulfur trioxide levels reported in this example were all measured in front of the air preheater.

EXAMPLE 5

[0049] At Power Plant 3 - Sorbent C, containing about 15 wt. % bromide as ammonium bromide dry-mixed and co-milled with activated carbon to an MPD of about 6 μm, was tested in a flue gas stream containing about 9 ppmv sulfur trioxide. At an injection rate of about 24 pounds/ hour, Sorbent C achieved about 92% mercury removal compared to only about 79% removal at an injection rate of 40 pounds/ hour for Sorbent E, a sorbent comparable to Sorbent C in all respects but for a 15 wt. % bromine content provided by sodium bromide instead of ammonium bromide. This example illustrates the added utility for mercury removal afforded by the alkaline component of the dual-function ammonium bromide additive independent of other sorbent parameters.

EXAMPLE 6

[0050] At Power Plant 4 - Sorbent C, an activated carbon dry-mixed with about 15 wt. % bromine as ammonium bromide and co-ground to an MPD of about 6 μm, was tested at another power plant against Sorbent N, a commercial brominated carbon sorbent believed to made from a lignite activated carbon impregnated internally with about 3 to about 6 wt. % bromine as sodium bromide ground to an MPD of about 14 to about 16 μm. The flue gas of this boiler contained about 4 ppmv of sulfur trioxide.

[0051] When injected at the air pre-heater outlet at a rate of about 6 lbs/MMacf, Sorbent C achieved about 72% mercury removal versus about 42% for Sorbent N, showing the benefits of a smaller sorbent MPD combined with a higher sorbent content of a dual-functioning agent for mercury oxidation and SOx suppression.

EXAMPLE 7

[0052] At Power Plant 5 burning a high percentage of a low-sulfur South American coal with a lower percentage of a high-sulfur domestic coal, about 61% mercury removal was achieved using Sorbent C, including about 15 wt. % bromine as ammonium bromide dry-mixed and co-ground with activated carbon to an MPD of about 6 μm, and injected at the air pre-heater inlet at a rate of about 8 lbs/MMacf for a 70/30 blend, respectively, of the low and high sulfur content domestic coals. The SO_3 in the flue gas at the point of injection was

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measured to be about 8 to about 9 ppmv. Under the same conditions, Sorbent D, a sorbent comparable to Sorbent C but containing about 36 wt. % bromine as ammonium bromide, gave about 81% mercury removal under the same conditions, demonstrating the value of the higher localized alkalinity and halide levels afforded by higher levels of the dual-function additive.

EXAMPLE 8

[0053] Power Plant 5 - Three mercury sorbents were tested at Power Plant 5 fired with a coal blend of 20% PRB and 80% of another low-sulfur coal. The sulfur trioxide levels in the flue gas ranged from about 0.5 ppmv to non-detectable. Sorbent C was prepared by dry-mixing and co-grinding an activated carbon with about 15 wt. % bromide as ammonium bromide to an MPD of about 6 μm. Sorbent D was prepared similarly, but contained about 36 wt. % bromide as ammonium bromide. These sorbents were compared to Sorbent M, a commercial brominated carbon having an MPD not less than about 12 μm and a bromide content of not more than about 10 wt. % as a bromide salt. When injected at the air pre-heater inlet, about 8 lbs/MMacf were required to achieve about 90% mercury removal with Sorbent M, versus about 5.5. lbs/MMacf for sorbent C, and about 3 lbs/MMacf for Sorbent D. These data demonstrate the significant performance gains that can be obtained with bromide levels above about 10 wt. % and MPD reductions below about 12 μm, even in flue gas streams with little to no sulfur trioxide.

EXAMPLE 9

[0054] At Power Plant 6 containing 1 to 2 ppmv of SO_3 in the flue gas, Sorbent C, containing about 15 wt. % bromine as ammonium bromide dry-mixed and co-ground with activated carbon to an MPD of about 6 μm, was tested against Sorbent M, a commercially-available brominated carbon sorbent having an MPD not less than about 12 μm and containing not more than about 10 wt. % bromine as a bromide salt, and against Sorbent K, a commercially-available brominated carbon sorbent believed to be derived from a lignite or brown coal. When injected at the electrostatic precipitator (ESP) inlet, Sorbent K required an injection rate of about 9 lbs/MMacf to achieve 90% mercury removal, versus about 4.5 lbs/MMacf for Sorbent M and about 2 lbs/MMacf or less for Sorbent C.

EXAMPLE 10

[0055] Power Plant 7 - Five mercury sorbents were prepared by dry-mixing and co-grinding activated carbon with either 10 or 20 wt. % bromide as either ammonium or sodium

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bromide: Sorbent P contained about 10 wt. % bromide as ammonium bromide co-ground to about a 6 μm MPD; Sorbent Q contained about 10 wt. % bromide as ammonium bromide co-ground to about a 16 μm MPD; Sorbent S contained about 10 wt. % bromide as sodium bromide co-ground to about 16 μm MPD; Sorbent R contained about 20 wt% bromide as ammonium bromide co-ground to about a 16 μm MPD; and Sorbent T contained about 20% bromide as ammonium bromide co ground to about 6 μm. Sorbents P, R, Q, and S were tested for mercury removal at injection rates of about 100 lbs/hour under comparable conditions at a Power Plant 7 burning PRB coal and containing little sulfur trioxide in the flue gas.

[0056] Sorbents P, R, Q, and S achieved mercury removals of about 77%, 71%, 66%, and 53%, respectively. Sorbent R versus sorbent Q demonstrates the advantages of bromide levels above about 10 wt. % as ammonium bromide at a given MPD, while Sorbent P versus Sorbent Q demonstrates the advantages of an MPD below about 10 μm at a given bromide level. Sorbent Q versus Sorbent S demonstrates the advantages of using ammonium bromide over metal bromide salts, even in flue gas streams containing little sulfur trioxide.

[0057] In a second test at Power Plant 7, Sorbent T was compared to Sorbent P and Sorbent Q to determine the amount of sorbent required to remove 90% of the mercury. Sorbent T required approximately 270 lbs/hour, Sorbent P required approximately 320 lbs/hour, and Sorbent Q required over 420 lbs/hour to achieve 90% removal.

[0058] While presently preferred embodiments of the invention have been described, it is to be understood that the detailed embodiments are presented for elucidation and not limitation. The invention may be otherwise varied, modified or changed within the scope of the invention as defined in the appended claims.

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J. CLAIMS

What is claimed is:

1. A composition comprising particles having a mean diameter of less than about 12 μm, said particles including a porous absorptive material, a source of halo compounds, and a source of nitrogen, said source of nitrogen having a nitrogen at an oxidation state of -3.

2. The composition of claim 1, wherein said source of nitrogen is selected from the group consisting of ammonium, ammonia, amines, amides, imines, and quaternary ammonium.

3. The composition of claim 1, wherein the particles have a mean diameter of less than about 7 μm.

4. The composition of claim 1, wherein the source of halo compounds and said source of nitrogen being provided by a single agent.

5. The composition of claim 1, wherein the porous mercury adsorptive material is selected from the group consisting of carbonaceous char, activated carbon, reactivated carbon, zeolite, silica, silica gel, alumina clay, or a combination thereof.

6. The composition of claim 1, wherein the porous mercury adsorptive material has a surface area of at least about 300 m^2/g.

7. The composition of claim 1, wherein said composition has a halo compound concentration of greater than 0.15 equivalents per 100 grams of the composition.

8. The composition of claim 1, wherein the composition is a dry admixture.

9. The composition of claim 1, wherein the particles have a mean diameter of less than about 7 μm, and said single agent is selected from the group consisting of ammonium halides, amine halides, and quaternary ammonium halides.

10. The composition of claim 9, wherein said single agent is ammonium bromide at a concentration of 15 wt. % to about 70 wt. % of the composition.

11. A composition for the removal of mercury from flue gas streams comprising:

a porous mercury adsorptive material; and

at least one agent selected from the group consisting of ammonium halides, amine halides quaternary ammonium halides, and combinations thereof;

wherein the composition has a mean particle diameter of less than about 12 μm.

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12. The composition of claim 11, wherein the composition has a mean particle diameter of less than about 10 μm.

13. The composition of claim 11, wherein the composition has a mean particle diameter of less than about 7 μm.

14. The composition of claim 11, wherein the porous mercury adsorptive material is selected from the group consisting of carbonaceous char, activated carbon, reactivated carbon, zeolite, silica, silica gel, alumina clay, or a combination thereof.

15. The composition of claim 11, wherein the porous mercury adsorptive material has a surface area of at least about 300 m^2/g.

16. The composition of claim 11, wherein the porous mercury adsorptive material further comprises a hydrophobicity enhancement agent.

17. The composition of claim 16, wherein the hydrophobicity enhancement agent is selected from the group consisting of elemental halogens fluorine salts, organo-fluorine compounds, fluorinated polymers, and combinations thereof.

18. The composition of claim 11, wherein the porous mercury adsorptive material further comprises one or more oxidants.

19. The composition of claim 18, wherein the one or more oxidant is selected from halogen salts.

20. The composition of claim 18, wherein the oxidant comprises greater than or equal to about 0.15 equivalents per 100 grams of the composition.

21. The composition of claim 11, wherein the at least one agent is ammonium bromide.

22. The composition of claim 11, wherein the at least one agent is about 10 wt. % or greater of the composition.

23. The composition of claim 11, wherein the at least one agent is about 15 wt. % or greater of the composition.

24. The sorbent of claim 11, wherein the at least one agent is about 30 wt. % or greater of the composition.

25. The composition of claim 11, wherein the at least one agent is from about 15 wt. % to about 70 wt. % of the composition.

26. The composition of claim 11, wherein the at least one agent is from about 15 wt. % to about 50 wt. % of the composition.

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27. The composition of claim 11, wherein the at least one agent is from about 20 wt. % to about 50 wt. % of the composition.

28. The composition of claim 11, wherein the at least one agent is from about 20 wt. % to about 40 wt. % of the composition.

29. The composition of claim 11, wherein the composition is a dry admixture.

30. A method for preparing a sorbent for the removal of mercury from flue gas streams comprising co-milling a porous mercury adsorptive material and at least one agent selected from the group consisting of ammonium halides, amine halides, and quaternary ammonium halides to form an admixture having a mean particle diameter of less than or equal to about 12 μm.

31. The method of claim 30, wherein the porous mercury adsorptive material and at least one agent are not physically associated in the admixture.

32. The method of claim 30, wherein co-milling is performed until the admixture has a mean particle diameter of less than about 10 μm.

33. The method of claim 30, wherein co-milling is performed until the admixture has a mean particle diameter of less than about 7 μm.

34. The method of claim 30, wherein the porous mercury adsorptive material is selected from the group consisting of carbonaceous char, activated carbon, reactivated carbon, zeolite, silica, silica gel, alumina clay, or a combination thereof.

35. The method of claim 30, wherein the porous mercury adsorptive material has a surface area of at least about 300 m^2/g.

36. The method of claim 30, wherein the porous mercury adsorptive material further comprises a hydrophobicity enhancement agent.

37. The method of claim 30, wherein the porous mercury adsorptive material further comprises one or more oxidants.

38. The method of claim 37, wherein the one or more oxidant is selected from halogen salts.

39. The method of claim 37, wherein the oxidant comprises greater than or equal to about 0.15 equivalents per 100 grams of the admixture.

40. The method of claim 30, wherein the at least one agent is ammonium bromide.

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41. The method of claim 30, wherein the at least one agent is about 10 wt. % or greater of the admixture.

42. The method of claim 30, wherein the at least one agent is about 15 wt. % or greater of the admixture.

43. The method of claim 30, wherein the at least one agent is about 30 wt. % or greater of the sorbent.

44. The method of claim 30, wherein the at least one agent is from about 15 wt. % to about 70 wt. % of the admixture.

45. The method of claim 30, wherein the at least one agent is from about 15 wt. % to about 50 wt. % of the admixture.

46. The method of claim 30, wherein the at least one agent is from about 20 wt. % to about 50 wt. % of the admixture.

47. The method of claim 30, wherein the at least one agent is from about 20 wt. % to about 40 wt. % of the admixture.

48. The method of claim 30, wherein the at least one agent comprises greater than or equal to about 0.15 equivalents per 100 grams of the admixture.

49. A method for removing mercury from flue gas streams containing sulfur trioxide (SO_3) comprising injecting into the flue gas stream a dry admixture of a porous mercury adsorptive material and at least one dry agent selected from the group consisting of ammonium halides, amine halides, and quaternary ammonium halides, wherein the dry admixture has a mean particle diameter of less than or equal to about 12 μm.

50. The method of claim 49, wherein the dry porous mercury adsorptive material and the at least one dry agent are combined to form a dry admixture prior to being injected into the flue gas stream.

51. The method of claim 49, wherein the dry porous mercury adsorptive material and the at least one dry agent are injected in to the flue gas stream separately.

52. The method of claim 49, wherein the at least one dry agent is ammonium bromide.

53. The method of claim 49, wherein the at least one dry agent is about 10 wt. % or greater of the dry admixture.

54. The method of claim 49, wherein the at least one dry agent is about 15 wt. % or greater of the dry admixture.

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55. The method of claim 49, wherein the at least one dry agent is about 30 wt. % or greater of the dry admixture.

56. The method of claim 49, wherein the at least one dry agent is from about 15 wt. % to about 70 wt. % of the dry admixture.

57. The method of claim 49, wherein the at least one dry agent is from about 15 wt. % to about 50 wt. % of the dry admixture.

58. The method of claim 49, wherein the at least one dry agent is from about 20 wt. % to about 50 wt. % of the dry admixture.

59. The method of claim 49, wherein the at least one dry agent is from about 20 wt. % to about 40 wt. % of the dry admixture.

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(54) Title: METHODS FOR REMOVAL OF MERCURY FROM FLUE GAS

(57) Abstract: Methods and systems for reducing mercury emissions are provided herein.

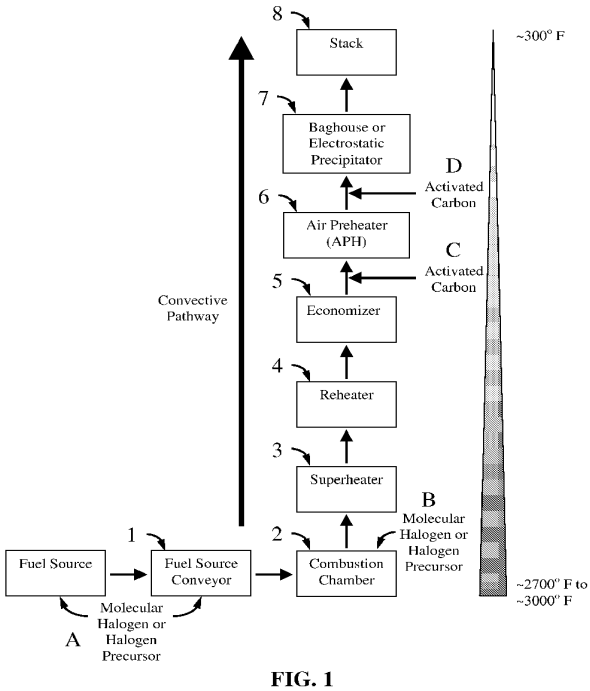


FIG. 1

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A. Title:

METHODS FOR REMOVAL OF MERCURY FROM FLUE GAS

B. Cross-Reference to Related Applications:

[0001] This application claims benefit of priority to U.S. Provisional Patent Application No. 61/321,696 filed on April 7, 2010 entitled "Methods for Removal of Mercury from Flue Gas," the entire contents of which are hereby incorporated by reference.

C. Government Interests: Not applicable

D. Parties to a Joint Research Agreement: Not applicable

E. Incorporation by Reference of Material submitted on a Compact Disc: Not applicable

F. Background: Not applicable

G. Summary of the Invention:

[0002] Various embodiments include a method for reducing heavy metal emissions including the steps of burning a heavy metal containing fuel in a combustion chamber, introducing molecular halogen or one or more halogen precursors into the combustion chamber or an exhaust stream resulting from combustion of the heavy metal containing fuel near the combustion chamber, and injecting activated carbon having a mean particle diameter of less than 15 μm into the exhaust stream. In some embodiments, the one or more halogen precursors may be calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, and potassium tri-iodide. In other embodiments, the halogen precursors can be calcium bromide, and in still other embodiments, the one or more halogen precursors may be a solid or powder, in an aqueous solution, or gaseous halogen. In certain embodiments, the molecular halogen or one or more halogen precursors can be introduced into the combustion chamber or an exhaust stream resulting from combustion of the heavy metal containing fuel near at a concentration and/or rate of addition sufficient to result in a concentration of halogen to produce a halogen to adsorptive material ratio of at least 0.7 moles of halogen per pound of adsorbent material, or about 0.7 moles/lb to about 5.7 moles/lb or about 0.8 moles/lb to about 3.1 moles/lb halogen to adsorbent material. In some embodiments, an aqueous solution of a halogen precursor having a concentration of about 50 % by weight can be introduced into the combustion chamber or an exhaust stream resulting from combustion of the heavy metal

containing fuel near the combustion chamber at a rate of less than 10 gallons per hour. In other embodiments, the halogen precursor may be introduced with the fuel source, injected into the combustion chamber, injected into the exhaust stream near the combustion chamber, or combinations thereof. In some embodiments, the activated carbon has a mean particle diameter of from about 2 μm to 10 μm. In other embodiments, the sorbent material can be injected into the exhaust stream at a rate of less than 5 pounds per million actual cubic feet (lbs/MMacf), less than about 4 lbs/MMacf, less than about 3 lbs/MMacf, or less than about 1 lbs/MMacf based on the total exhaust stream flow, and in particular embodiments, the sorbent material may be injected into the exhaust stream at a rate of less than 100 lbs/hr. In certain embodiments, the sorbent materials injected upstream of an air pre-heater (APH), and in particular embodiments, about 90% of the mercury in the fuel source may be removed. In some embodiments, the fuel source can be coal.

H. Description of Drawings:

[0003] For a fuller understanding of the nature and advantages of the present invention, reference should be made to the following detailed description taken in connection with the accompanying drawings, in which:

[0004] **FIG. 1** shows a flow chart showing elements of an exemplary coal fired power plant.

[0005] **FIG. 2** shows a chart comparing the percent removal of mercury versus the injection rate for activated carbon.

I. Detailed Description:

[0006] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0007] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a combustion chamber" is a reference to "one or more combustion chambers" and equivalents thereof known to those skilled in the art, and so forth.

[0008] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0009] As used herein, the term "sorbent material" is meant to encompass all know materials from any source capable of adsorbing mercury. For example, sorbent materials include, but are not limited to, activated carbon, natural and synthetic zeolite, silica, silica gel, alumina, and diatomaceous earths.

[0010] Mercury is a known environmental hazard and leads to health problems for both humans and non-human animal species. Approximately 50 tons per year are released into the atmosphere in the United States, and a significant fraction of the release comes from emissions from coal burning facilities such as electric utilities. To safeguard the health of the public and to protect the environment, the utility industry is continuing to develop, test, and implement systems to reduce the level of mercury emissions from its plants. In the combustion of carbonaceous materials, it is desirable to have a process wherein mercury and other undesirable compounds are captured and retained after the combustion phase so that they are not released into the atmosphere.

[0011] One of the most promising solutions for mercury removal from flue gas is Activated Carbon Injection (ACI). Activated carbon is a highly porous, non-toxic, readily available material that has a high affinity for mercury vapor. This technology is already established for use with municipal incinerators. Although the ACI technology is effective for mercury removal, the short contact time between the activated carbon and the flue gas stream results in an inefficient use of the full adsorption capacity of the activated carbon.

[0012] Various embodiments of the invention are directed to methods for removing heavy metals such as, for example, mercury, from a fluid stream produced as a result of combustion of a heavy metal containing fuel source by applying a molecular halogen or halogen precursor to the fuel source or introducing a molecular halogen or halogen precursor into a combustion chamber during combustion of the fuel source or introducing a molecular halogen or halogen precursor into an exhaust stream resulting from the combustion of the fuel source near the combustion chamber and injecting sorbent material into the exhaust stream,

i.e. flue gas, resulting from consumption of the fuel source. In such embodiments, the combination of applying the molecular halogen or halogen precursor to the fuel source or injecting the molecular halogen or halogen precursor into the combustion chamber and injection of sorbent material into the exhaust stream may result in substantial reduction in heavy metal emissions from the exhaust stream while significantly reducing the amount of both the molecular halogen or halogen precursor and the sorbent material used in such methods. In particular embodiments, mercury removal is improved over conventional methods. In some embodiments, greater than about 80% or greater than about 90% of the heavy metal can be removed from the exhaust stream based on the heavy metal content of the fuel source. Thus, the combination achieves similar or improved removal rates while reducing consumption of the molecular halogen or halogen precursor and sorbent material thereby reducing costs.

[0013] The methods and systems described above may implemented into any conventional system that involves combustion of a fuel source that includes heavy metals. Numerous systems and facilities that burn heavy metal-containing fuels are known and used in the art. For example, some embodiments provide compositions, methods, and systems for reducing emissions of heavy metals from incinerators, including solid waste incinerators. Other embodiments provide compositions, methods, and systems for reducing emissions of heavy metals such as mercury that arise from the combustion of heavy metal containing fossil fuels at, for example, power plants.

[0014] FIG. 1 provides a flow chart depicting relevant portions of an exemplary coal fired power plant. As indicated in FIG. 1, some such facilities may include a feeding mechanism such as a conveyor **1** for delivering fuel such as coal into a furnace or combustion chamber **2** where the fuel source is burned. The fuel fed into the furnace is burned in the presence of oxygen with typical flame temperatures in the combustion chamber of the furnace from about 2700° F to about 3000° F as indicated to the right of the flow chart. In operation, the fuel may be fed into the furnace at a rate suitable to achieve the output desired from the furnace the heat from which can be used to boil water for steam or provide direct heat that can be used to turn turbines that are eventually used to produce electricity (not pictured). From the furnace or combustion chamber **2**, ash, combustion gases, and air move downstream, away from the fireball, into a convective pathway, or exhaust stream, (large arrow to the left of the diagram) that can include various zones of decreasing temperature as indicated to the right. From the combustion chamber, the heated ash, combustion gases, and air can move through a superheater **3** and, in cases, a reheater **4** where, for example, water is

heated to provide steam which will eventually power a turbine that is used to generate electricity. The ash, combustion gases, and air can also pass through, for example, an economizer **5** where water fed into the superheater **3** and/or reheater **4** is preheated, and an air preheater **6** where air that is fed into the combustion chamber **2** is preheated. The combustion gases and ash may eventually pass through a baghouse or electrostatic precipitator **7** where particulate matter is collected. By this time, the temperature of the ash, combustion gases, and air is reduced to about 300° F before being emitted from the stack **8** and released into the atmosphere.

[0015] In some embodiments, the halogen source may be introduced during combustion by injecting molecular halogen or a halogen precursor **B** into the combustion chamber **2** or by applying the halogen source directly to the fuel source prior to combustion **A**. In other embodiments, the halogen may be found in the fuel source. For example, waste that includes plastics or rubbers may include halogen containing components that may release halogen ions or molecular halogens during incineration. In various embodiments, sorbent material may be injected into the exhaust stream anywhere along the convection pathway before emission of the ash, combustion gases, and air into the atmosphere, and in particular embodiments, sorbent material may be injected upstream of the baghouse or electrostatic precipitator **7**. In certain embodiments, sorbent material may be injected upstream **C** of the air preheater (APH) **6**, and in some embodiments, sorbent material may be injected into the exhaust stream downstream **D** of the APH **6**. In still other embodiments, sorbent material may be injected both upstream **C** of the APH **6** and downstream **D** of the APH **6**.

[0016] The molecular halogen or halogen precursor of various embodiments may be obtained from any source. For example, in some embodiments, molecular sources such as chlorine gas, bromine gas, or iodine gas can be injected into the exhaust stream near the combustion chamber alone or in combination with halogen precursor. In other embodiments, one or more halogen precursors may be applied to the fuel source, introduced into the combustion chamber, injected into the exhaust stream near the combustion chamber, or a combination thereof.

[0017] Numerous halogen precursors (halogen precursors) are known in the art and may be used in embodiments of the invention. In some embodiments, the halogen precursor may be a gaseous precursor such as, for example, hydrogen chloride, hydrogen bromide, or molecular chloride or bromide. The halogen precursor may be an organic or inorganic halogen-containing compound. For example, in some embodiments, the halogen precursor may be one or more inorganic halogen salts, which for bromine may include bromides,

bromates, and hypobromites, for iodine may include iodides, iodates, and hypoiodites, and for chlorine may be chlorides, chlorates, and hypochloriates. In certain embodiments, the inorganic halogen salt may be an alkali metal or an alkaline earth element containing halogen salt where the inorganic halogen salt is associated with an alkali metal such as lithium, sodium, and potassium or alkaline earth metal such as beryllium, magnesium, and calcium counterion. Non-limiting examples of inorganic halogen salts including alkali metal and alkali earth metal counterions include calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and the like. In other embodiments, the halogen may from an organic source, which contains a suitably high level of the halogen. Organic halogen precursors include, for example, methylene chloride, methylene bromide, methylene iodide, ethyl chloride, ethyl bromide, ethyl iodide, chloroform, bromoform, iodoform, carbonate tetrachloride, carbonate tetrabromide, carbonate tetraiodide, and the like.

[0018] In some embodiments, the halogen precursor may include one or more additional elements such as, for example, a calcium source, a magnesium source, a nitrate source, a nitrite source, or a combination thereof. Exemplary calcium and magnesium sources are well known in the art and may be useful to aid in the removal of sulfur in the flue gas that is released from the fuel source during combustion. In such embodiments, the calcium or magnesium source may include inorganic calcium such as, for example, calcium oxides, calcium hydroxides, calcium carbonate, calcium bicarbonate, calcium sulfate, calcium bisulfate, calcium nitrate, calcium nitrite, calcium acetate, calcium citrate, calcium phosphate, calcium hydrogen phosphate, and calcium minerals such as apatite and the like, or organic calcium compounds such as, for example, calcium salts of carboxylic acids or calcium alkoxylates or inorganic magnesium such as, for example, magnesium oxides, magnesium hydroxides, magnesium carbonate, magnesium bicarbonate, magnesium sulfate, magnesium bisulfate, magnesium nitrate, magnesium nitrite, magnesium acetate, magnesium citrate, magnesium phosphate, magnesium hydrogen phosphate, and magnesium minerals and the like, or organic magnesium compounds such as, for example, magnesium salts of carboxylic acids or magnesium alkoxylates. In certain embodiments, the calcium or magnesium source may be associated with the halide precursor such as, for example, calcium bromide, magnesium bromide, calcium chloride, magnesium chloride, calcium iodide, magnesium

iodide, and the like. Nitrate and nitrite sources are also well known in the art and any source of nitrate of nitrite can be formulated with halogen precursor.

[0019] The halogen precursor may be a solid such as a powder, a liquid, or a gas. For example, in some embodiments, the halogen precursor may be an aqueous solution that can be sprayed onto the fuel source such as coal before combustion or can be injected into the combustion chamber or exhaust stream near the combustion chamber. A liquid halogen precursor composition may be prepared at any suitable concentration. For example, in some embodiments, an aqueous solution of a halogen precursor such as, for example, calcium bromide or calcium chloride, may have a concentration of up to about 75%, and in other embodiments, the halogen precursor concentration in the aqueous solution may be up to about 60% by weight, 55% by weight, 50% by weight, 45% by weight, or 40% by weight or any concentration between these values.. In still other embodiments, an aqueous solution of a halogen precursor may include about 10% to about 75% by weight, about 20% to about 60% by weight, about 30% to about 55% by weight, or about 40% to about 55% by weight of the halogen precursor. Similarly, in other embodiments, dry, powdered halogen precursor may be applied to the coal at a concentration necessary to achieve a similar concentration of halogen in the flue gas stream.

[0020] In various embodiments, the molecular halogen or halogen precursor, which may be in solid, such as a powder, liquid, or a gaseous form, may be continuously supplied to the combustion chamber or provided incrementally during combustion. The rate of addition of the molecular halogen and halogen precursor may vary among embodiments and may depend, for example, on the rate of combustion of the fuel source, the origin of the fuel source, the amount of mercury in the fuel source, the adsorption of mercury, and the like. For example, in some embodiments, an about 40% to about 55% by weight aqueous solution of a halogen precursor such as, for example, calcium bromide or calcium chloride, may be introduced into a combustion chamber or injected into an exhaust stream near the combustion chamber at a rate of about 500 gallons/hr or less, and in other embodiments, an about 40% to about 55% by weight aqueous solution of the halogen precursor introduced into a combustion chamber or injected into an exhaust stream near the combustion chamber at a rate of about 400 gallons/hr or less, 300 gallons/hr or less, 200 gallons/hr or less, or 100 gallons/hr or less. In certain embodiments, an about 40% to about 55% by weight aqueous solution of the halogen precursor introduced into a combustion chamber or injected into an exhaust stream near the combustion chamber at a rate of less than 50 gallons/hr or less than 25 gallons/hr or less than 20 gallons/hr.

[0021] The feed rate of the molecular halogen or halogen precursor may vary among embodiments and may vary depending on, for example, the feed rate of the fuel source and/or the rate of consumption of the fuel source. For example, a combustion chamber burning about 330 tons/hr of a fuel source such as coal in six mills each burning about 55 tons/hr where about 10 gal/hr of a 50% by weight aqueous solution of calcium bromide ($CaBr_2$) is introduced into the combustion chamber during burning can result in about 125 ppm bromine added to the coal based on dry weight. Thus, in various embodiments, the concentration and/or feed rate the molecular halogen or halogen precursor may be modified based on the rate of consumption of the fuel source such that up to about 400 ppm (dry basis), up to about 500 ppm (dry basis) or up to about 700 ppm (dry basis) bromine may be added the fuel source. In some embodiments, about 50 ppm to about 500 ppm (dry basis), about 75 ppm to about 400 ppm (dry basis), about 100 ppm to about 300 ppm (dry basis), or about 125 ppm to about 200 ppm (dry basis) of bromine may be added to the fuel source.

[0022] In some embodiments, the methods and systems described herein may be utilized in a multi-stage furnace having for example, a primary and secondary combustion chambers, a rotary kiln, afterburning chambers, and any combinations thereof. In such embodiments, molecular halogen or halogen precursor in a solid or liquid form may be introduced into any one or any combination of the chambers of the furnace. For example, in some embodiments, the molecular halogen or halogen precursor may be introduced into one combustion chamber, and in other embodiments, the molecular halogen or halogen precursor may be introduced into a combination of combustion chambers. In still other embodiments, molecular halogen or halogen precursor may be introduced into one or more combustion chambers and into an exhaust stream after combustion.

[0023] In certain embodiments, the halogen precursor may be introduced into one or more combustion chambers and/or exhaust stream as an aqueous solution that is sprayed or injected into the chamber or exhaust stream. For example, in some embodiments, an aqueous solution of a halogen precursor may be sprayed or injected into a combustion gas stream downstream of a waste-heat boiler. In still other embodiments, an aqueous solution of the halogen precursor may be introduced into a recirculated substream such as, for example, a recirculated flue gas, recirculated ash, or recirculated fly ash. While embodiments are not limited by the zone where the molecular halogen or halogen precursor is introduced into the exhaust gas stream, the temperature in the injection zone should be sufficiently high to allow dissociation and/or oxidation of the elemental halogen from the halogen precursor. For

example, the temperature at the injection zone may be greater than about 1000° F, and in some embodiments, greater than about 1500° F.

[0024] Without wishing to be bound by theory, halogens from the molecular halogen or halogen precursor can oxidize with heavy metals released from the fuel source when it is burned in the combustion chamber. In general, oxidized heavy metals, such as mercuric halide species are adsorbable by alkaline solids in the exhaust stream such as fly ash, alkali fused acidic ash (*e.g.,* bituminous ash), dry flue gas desulfurization solids such as calcium oxide, calcium hydroxide or calcium carbonate, and removed from the flue gas by commonly used heavy metal control systems such as, for example, electrostatic precipitators, wet flue gas desulphurization systems, fabric filters, and baghouses. In certain embodiments, oxidized heavy metals may be adsorbed by activated carbon. Without wishing to be bound by theory, the rate at which a solution of a halogen precursor may be significantly reduced by combining the application of a halogen-containing composition with injection of sorbent material into the fluid stream of the combustion gases even when the mercury content of the fuel source is relatively high.

[0025] Activated carbon may be used in any embodiment. In such embodiments, the activated carbon may be obtained from any source and can be made from a variety of starting materials. For example, suitable materials for production of activated carbon include, but are not limited to, coals of various ranks such as anthracite, semianthracite, bituminous, subbituminous, brown coals, or lignites; nutshells, such as coconut shell; wood; vegetables such as rice hull or straw; residues or by-products from petroleum processing; and natural or synthetic polymeric materials. The carbonaceous material may be processed into carbon adsorbents by any conventional thermal or chemical method known in the art. The adsorbents will inherently impart different surface areas and pore volumes. Generally, for example, lignites can result in carbon having surface areas about 500-600 m^2/g and, typical fiber-based carbons areas are about 1200-1400 m^2/g. Certain wood-based carbons may have areas in the range of about 200 m^2/g, but tend to have a very large pore volume.

[0026] Surface area and pore volume of coal based carbon may also be made to allow for some control of surface area and pore volumes and pore size distributions. In some embodiments, the activated carbon adsorbent may have large surface area as measured by the Brunauer-Emmett-Teller ("BET") method, and may have a substantial micropore volume. As used herein, "micropore volume" is the total volume of pores having diameter less than about 2 nm. In some embodiments, suitable carbon adsorbents may have a BET surface areas greater than about 10 m^2/g or about 50 m^2/g, greater than about 200 m^2/g, or greater than

about 400 m^2/g. In other embodiments, the carbon adsorbent may have a micropore volume of greater than about 5 cm^3/100 g, and in still other embodiments, the adsorbent may have a micropore volume greater than about 20 cm^3/100 g.

[0027] Sorbent materials, such as activated carbon, of various sizes have been used to capture heavy metals in systems currently utilized, and any size sorbent material can be used in various embodiments. For example, in some embodiments, the sorbent material may have a mean particle diameter (MPD) of about 0.1 μm to about 100 μm, and in other embodiments, the MPD may be about 1 μm to about 30 μm. In still other embodiments, the MPD of the sorbent material may be less than about 15 μm, and in some particular embodiments, the MPD may be about 2 μm to about 10 μm, about 4 μm to about 8 μm, or about 5 μm or about 6 μm.

[0028] In some embodiments, the sorbent material may be treated with, for example, a halogen containing salt. For example, in various embodiments, the sorbent material may be impregnated with a bromine by, for example, immersing the sorbent material in a solution of a hydrogen bromide or a stream of elemental bromine gas for sufficient time to allow the bromine to impregnate the sorbent material. Various methods for impregnating the sorbent material and types of impregnated sorbent material are known and used in the art, and any such sorbent material may be used in embodiments.

[0029] The sorbent material may be injected into the exhaust stream anywhere along the convection pathway downstream of the combustion chamber and before the exhaust is emitted from the stack. The sorbent material of various embodiments may generally be injected downstream of a heavy metal control systems such as, for example, electrostatic precipitators, wet flue gas desulphurization systems, fabric filters, and baghouses or other ash or fly ash collection means where particulate matter can be collected and upstream of the combustion chamber. In certain embodiments, the sorbent material may be injected at any zone in the convection pathway having a temperature of less than about 700° F, less than about 500° F, less than about 400° F or less than about 350° F. For example, in some embodiments, sorbent material may be injected into an exhaust stream either upstream or downstream of an air pre-heater (APH), and in other embodiments, the sorbent material may be injected upstream of an air pre-heater (APH).

[0030] In some embodiments, the rate of injection of the sorbent material may depend upon the flow rate of the exhaust stream. For example, in a plant having a exhaust (flue) gas flow rate of about 2,000,000 actual cubic feet per minute (acfm) in which about 100 lbs/hr of

sorbent material is injected into exhaust stream in the ductwork of the plant, the rate of addition of sorbent material is about 0.8 pounds per million actual cubic feet (lbs/MMacf). Therefore, in various embodiments, the injection rate of the sorbent material may vary depending up on the flow rate of the exhaust gas in the ductwork. In such embodiments, the rate of addition of sorbent material based on the flow rate of the exhaust gas may be up to about 4 lbs/MMacf or up to about 5 lbs/MMacf. In other embodiments, the rate of addition of the sorbent material based on the flow rate of the exhaust gas may be from about 0.25 lbs/MMacf to about 5 lbs/MMacf, about 0.5 lbs/MMacf to about 4.0 lbs/MMacf, or about 0.75 lbs/MMacf to about 3.0 lbs/MMacf, and in particular embodiments, the rate of addition may be about 0.75 lbs/MMacf to about 1.5 lbs/MMacf.

[0031] Particular embodiments, for exemplary purposes, include methods and systems including the introduction of a halogen precursor, such as, calcium bromide, calcium chloride, sodium bromide, or sodium chloride, into a combustion chamber where a heavy metal containing fuel source is being burned, and injection of sorbent material having an MPD of less than about 15 μm into an exhaust stream upstream of a heavy metal and/or particulate control systems such as, for example, electrostatic precipitators, wet flue gas desulphurization systems, fabric filters, and baghouses or other ash or fly ash collection means where particulate matter can be collected. In some such embodiments, less than about 10 gallons/hour of the an aqueous halogen precursor may be introduced into the combustion chamber, and less than about 100 lbs/hour of sorbent material may be injected into the exhaust stream. As a result of such treatment, mercury emission from the plant employing such methods and systems may be reduced by greater than about 80% and in some embodiments, greater than 90%.

[0032] Further embodiments, include methods for reducing mercury emissions from flue gas in which the ratio of halogen to sorbent material provided is from about 0.7 to about 4.6 moles of halogen per pound of activated carbon, and in some embodiments, from about 0.8 to about 3.1 or about 1.2 to about 2.0 moles of halogen per pound of activated carbon. In such embodiments, the sorbent material may have an MPD of less than about 15 μm and, in certain embodiments, the sorbent material may have an MPD of less than about 10 μm. In still other embodiments, the sorbent material may have an MPD of about 6 μm or less. The halogen and sorbent material may be provided anywhere during the process. For example, in some embodiments, the halogen may be applied to the fuel source before combustion, and in other embodiments, the halogen may be introduced into the combustion chamber while the

fuel is burned. In still other embodiments, the halogen may be introduced into the flue gas stream either before or after the sorbent material. In further embodiments, the halogen may be provided with the activated carbon. For example, in some embodiments, the halogen may be injected into the flue gas stream separately with the activated carbon, and in other embodiments, the halogen may be applied to the sorbent material before it is introduced into the flue gas stream.

[0033] In embodiments in which the halogen is applied to the sorbent material before being injected into the flue gas stream, the ratio of halogen to sorbent material may be the same as the ratio of halogen to sorbent material when sorbent material is introduced separately. For example, in some exemplary embodiments, a halogen salt such as any of the halogen salts described above may be applied to an adsorbent material having an MPD of less than 15 μm, less than 12 μm, less than 10 μm in a ratio of from about 0.14 to about 1.0 pounds of halogen salt per pound of sorbent material to provide a composition that is from about 12 wt. % to about 50 wt. % halogen salt or about 15 wt. % to about 40 wt. % halogen salt. In another exemplary embodiment, a halogen salt such as calcium bromide ($CaBr_2$) or ammonium bromide (NH_4Br) may be applied to sorbent material having an MPD of about 6 μm at a ratio of about 0.43 pounds of halogen salt per pound of sorbent material or about 30 wt. % halogen salt, and the sorbent material/halogen salt combination may be introduced into the flue gas stream. These ratios can also be expressed as moles of halogen per pound of adsorbent material. For example, in some embodiments, the ratio of moles of halogen per pound of sorbent material may be from about 0.7 moles/lb to about 5.7 moles/lb, 0.8 moles/lb to about 3.1 moles/pound or any ratio there between, and in particular embodiments, the ratio of halogen per pound of sorbent material can be 2.0 moles/lb. In such embodiments, the halogen salt may be applied by conventional impregnation process or the halogen salt may be applied by mixing dry sorbent material with dry halogen salt. In other embodiments, the sorbent material can be impregnated using a gaseous halogen. In certain embodiments, such as those described above, the sorbent material may be activated carbon.

[0034] Coal fired power plants utilizing conventional methods for reducing mercury emissions where a halogen precursor is introduced into a combustion chamber and no sorbent material is injected into the exhaust generally inject halogen precursor at a rate of greater than 20 gallons/hour to reduce the mercury emission sufficiently. Coal fired power plants that utilize sorbent material injection without introducing a halogen precursor during combustion can inject greater than about 250 lbs/hour of sorbent material into the exhaust stream to

effectively reduce mercury emissions. In contrast, some embodiments of the invention provide mercury reduction of greater than about 80% or greater than 90% while using less than about 10 gallons/hour of a halogen precursor and less than 100 lbs/hour of an activated carbon, and in particular embodiments, less than 100 lbs/hour of sorbent material having a MPD of less than about 15 μm. This is a dramatic and surprising reduction in the amount of consumables necessary to effectively reduce mercury emissions to below regulatory levels. Such embodiments, therefore, provide substantial economic advantages over currently used methods for reducing mercury emission, while simultaneously reducing the amount of ash produced by plants that employ sorbent material injection and the amount of halogen precursor consumed.

[0035] In some embodiments, mercury levels can be monitored with conventional analytical equipment using industry standard detection and determination methods, and in such embodiments, monitoring can be conducted periodically, either manually or automatically. For example, mercury emissions can be monitored once an hour to ensure compliance with government regulations and to adjust the rate of halogen precursor introduction into the combustion chamber, the rate of sorbent material injection, or both. Mercury can be monitored in the convective stream at suitable locations. For example, in some embodiments, mercury released into the atmosphere can be monitored and measured on the clean side of a particulate control system.

EXAMPLES

[0036] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

EXAMPLE 1

A coal-fired power plant fitted with a system to add calcium bromide onto the coal prior to the combustion chamber and lances for injecting activated carbon into the ductwork of the power plant at various locations was utilized for testing. Coal burned at this facility was periodically tested for mercury content to ensure accuracy of mercury removal testing. Various powdered activated carbons (PACs) tested at this facility are provided in Table 1.

TABLE 1: Powdered Activated Carbon (PAC)

Identifier	Particle Size (MPD)	Brominated
Std	16 μm	No
Std Br	16 μm	Yes
PAC 6	6 μm	No
PAC 30	30 μm	No

Each of the PACs described in Table 1 was injected into the exhaust stream of the plant down stream of the APH at rate of about 100 lbs/hr or about 200 lbs/hr either with or without calcium bromide ($CaBr_2$) injection into the combustion chamber. The results are provided in Table 2 and are illustrated in FIG. 2.

TABLE 2: Injection Rate Raw Data

Symbol FIG. 2	Particle	CaBr	PAC Injection Rate (lbs/hr)	Removal (%)
■	Std.	0	100	48.2
	Std.	0	200	60.0
▲	None	1X	0	20.0
	Std.	1X	100	67.5
	Std.	1X	200	77.6
□	None	2X	0	33.4
	Std.	2X	200	83.3
Δ	None	3X	0	39.2
●	None	4X	0	37.1
	Std.	4X	200	88.0
○	Std.	8X	200	87.4
*	Std. Br	0	100	70.4
	Std. Br	0	200	82.7
	Std. Br	0	200	79.4
×	PAC 30	0	100	36.5
	PAC 30	0	200	48.4
◊	PAC 6	0	100	55.3
	PAC 6	0	200	67.6
♦	PAC 6	4X	100	87.4
	PAC 6	4X	200	92.7

[0037] As indicated in FIG. 1, $CaBr_2$ alone, PAC injection rate 0, resulted in less than about 50% mercury removal based on the mercury content of the coal consumed. The addition of PAC at 100 lbs/hr (PAC 30, PAC 16, PAC 6) resulted in similar reduction in mercury emission, about 50%, which varied slightly depending on the MPD of the PAC. The combination of $CaBr_2$ injection into the combustion chamber and PAC injection in the

exhaust stream (Std + 1x $CaBr_2$) showed improved reduction in mercury emission, as did the injection of brominated PAC (Std Br) into the exhaust stream. Notably, the combination of $CaBr_2$ injection into the combustion chamber and injection of a PAC having a smaller MPD into the exhaust stream (PAC 6 + 4x $CaBr_2$) resulted in nearly 90% reduction in mercury emissions, which represents almost 20% greater reduction in mercury emissions over brominated PAC (Std Br) and larger MPD PAC and $CaBr_2$ (Std. + 1x $CaBr_2$). Similarly, when the injection rate for PAC was increased to 200 lbs/hr, small MPD PAC outperformed brominated PAC (Std. Br) and larger MPD PAC and various injection rates of $CaBr_2$ (Std. 1x $CaBr_2$; Std. 2x $CaBr_2$; Std. 3x $CaBr_2$; Std. 4x $CaBr_2$; and Std. 8x $CaBr_2$).

EXAMPLE 2

[0038] Further testing was carried out to determine the injection rate for a given aqueous solution of $CaBr_2$ and PAC when the PAC is injected into the exhaust stream upstream of the APH (Post APH Injection) and downstream of the APH (Pre APH Injection) required to obtain 90% removal of mercury from plant emissions. The results are provided in Tables 3 and 4, respectively.

TABLE 3: Consumption at 90% mercury removal
POST APH INJECTION

Indentifier	$CaBr_2$ (gal/hr)	PAC (lbs/hr)	#/MMacf
Std.	20	300	2.5
PAC 6	20	150	1.2
Std. Br		420	3.4

TABLE 4: Consumption at 90% mercury removal
PRE APH INJECTION

Indentifier	$CaBr_2$ (gal/hr)	PAC (lbs/hr)	#/MMacf
Std.	18	125	1.0
PAC 6	6	60	0.5
Std. Br		320	2.6

Tables 3 and 4 show that a rate of $CaBr_2$ injection of 20 gal/hr and a PAC injection rate of 150 lbs/hr is sufficient to remove 90% of the mercury from the coal tested when small MPD PAC (PAC 6) is injected down stream of the APH whereas twice as much large MPD PAC (Std.) is required to achieve a similar result. When the PAC is injected upstream of the APH, 6 gal/hr of $CaBr_2$ and 60 lbs per hour of small MPD PAC (PAC 6) is necessary to remove 90% of the flue gas mercury at the same plant whereas 18 gla/hr of $CaBr_2$ and 125 lbs/hr of

standard MPD PAC (Std.) are required to achieve the same result. These data demonstrate that a decrease in carbon particle size, especially below about 12 μm or about 10 μm, creates its own synergistic effect in that, surprisingly, both less carbon and less halogen are needed for the same level of mercury removal, especially at levels around or above 90% mercury removal. The combined savings in both halogen and sorbent result in greatly improved economics as well as fewer balance-of-plant impacts such as reduced carbon in the fly ash, allowing more of the ash to retain commercial value as a concrete additive.

J. CLAIMS

1. A method for reducing heavy metal emissions comprising:

burning a heavy metal containing fuel in a combustion chamber;

introducing molecular halogen or one or more halogen precursors into the combustion chamber or an exhaust stream produced as a result of the burning of the heavy metal containing fuel; and

introducing a sorbent having a mean particle diameter of less than 15 μm into an exhaust stream resulting from burning of the heavy metal containing fuel in the combustion chamber;

wherein the halogen and sorbent material are introduced at a ratio of from about 0.7 to about 5.7 moles of halogen per pound (lb) of sorbent material.

2. The method of claim 1, wherein the halogen and sorbent material are introduced at a ratio of from about 0.8 to about 3.1 moles of halogen per pound (lb) of sorbent material.

3. The method of claim 1, wherein the halogen and sorbent material are introduced at a ratio of about 2.0 moles of halogen per pound (lb) of sorbent material.

4. The method of claim 1, wherein the sorbent material is activated carbon.

5. The method of claim 1, wherein the one or more halogen precursors are selected from the group consisting of calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, and potassium tri-iodide.

6. The method of claim 1, wherein the halogen precursor is selected from the group consisting of calcium bromide ($CaBr_2$), ammonium bromide (NH_4Br), and combinations thereof.

7. The method of claim 1, wherein the halogen precursor are in an aqueous solution.

8. The method of claim 1, wherein the halogen precursor is a solid.

9. The method of claim 1, wherein the halogen or halogen precursor is a gas.

10. The method of claim 1, wherein the halogen or halogen precursor is introduced into the exhaust stream having a temperature greater than about 1000° F.

11. The method of claim 1, wherein the sorbent material has a mean particle diameter (MPD) of from about 2 μm to 10 μm.

12. The method of claim 1, wherein the sorbent material is injected into the exhaust stream at a rate selected from the group consisting of less than about 5 pounds per million actual cubic (lbs/MMacf), less than about 4 lbs/MMacf, less than about 3, lbs/MMacf, and less than about 1 lbs/MMacf.

13. The method of claim 1, wherein the sorbent material is injected into the exhaust stream at a rate of less than 100 pounds/hr.

14. The method of claim 1, wherein the sorbent material is injected upstream of an air pre-heater (APH).

15. The method of claim 1, wherein about 90% of the mercury in the fuel source is removed.

16. The method of claim 1, wherein the fuel source is coal.

17. The method of claim 1, wherein the halogen or halogen precursor is introduced into the combustion chamber.

18. The method of claim 1, wherein the halogen precursor is applied to the fuel before the fuel is introduced into the combustion chamber.

19. The method of claim 1, wherein the halogen is applied to the sorbent material.

20. The method of claim 17, wherein the sorbent material has a mean particle diameter (MPD) of from about 2 μm to 10 μm.

21. The method of claim 17, wherein the halogen is provided to the sorbent material at a concentration of from about 0.7 moles of halogen per pound of sorbent material to about 5.7 moles of halogen per pound of sorbent material.

22. The method of claim 17, wherein the halogen is provided to the sorbent material at a concentration of from about 0.8 moles of halogen per pound of sorbent material to about 3.1 moles of halogen per pound of sorbent material.

23. The method of claim 17, wherein sorbent material has a mean particle diameter (MPD) of about 6 μm and the halogen is applied to the sorbent material to produce a final concentration of about 2.0 moles of halogen per pound of sorbent material.

24. The method of claim 17, wherein the sorbent material is activated carbon having a particle diameter (MPD) of about 6 μm and the halogen is applied to the activated carbon to produce a final concentration of about 2.0 moles of halogen per pound of sorbent material.

25. The method of claim 17, wherein the halogen is applied to the sorbent material by wet impregnation.

26. The method of claim 17, wherein the halogen is applied to the sorbent material by combining dry activated carbon with dry halogen salt.

27. The method of claim 26, wherein the halogen salt is selected from the group consisting of calcium bromide ($CaBr_2$), ammonium bromide (NH_4Br) and combinations thereof.

28. A flue gas sorbent comprising:

a sorbent material having a mean particle diameter (MPD) of less than about 15 μm; and

one or more halogens associated with the sorbent material at a ratio of from about 0.7 to about 5.7 moles of halogen per pound (lb) of sorbent material.

29. The flue gas sorbent of claim 28, wherein the one or more halogens are associated with the sorbent material at a ratio of from about 0.8 to about 3.1 moles of halogen per pound (lb) of sorbent material.

30. The flue gas sorbent of claim 28, wherein the one or more halogens are associated with the sorbent material at a ratio of about 2.0 moles of halogen per pound (lb) of sorbent material.

31. The flue gas sorbent of claim 28, wherein the sorbent material has a mean particle diameter (MPD) of from about 2 μm to 10 μm.

32. The flue gas sorbent of claim 28, wherein sorbent material has a mean particle diameter (MPD) of about 6 μm and the halogen is associated with the sorbent material at a final concentration of about 2.0 moles of halogen per pound of sorbent material.

33. The flue gas sorbent of claim 28, wherein the sorbent material is activated carbon having a particle diameter (MPD) of about 6 μm and the halogen is associated with the activated carbon at a final concentration of about 2.0 moles of halogen per pound of sorbent material.

34. The flue gas sorbent of claim 28, wherein the halogen is applied to the sorbent material by wet impregnation.

35. The flue gas sorbent of claim 28, wherein the halogen is applied to the sorbent material by combining dry activated carbon with dry halogen salt.

36. The flue gas sorbent of claim 35, wherein the halogen salt is selected from the group consisting of calcium bromide ($CaBr_2$), ammonium bromide (NH_4Br) and combinations thereof.

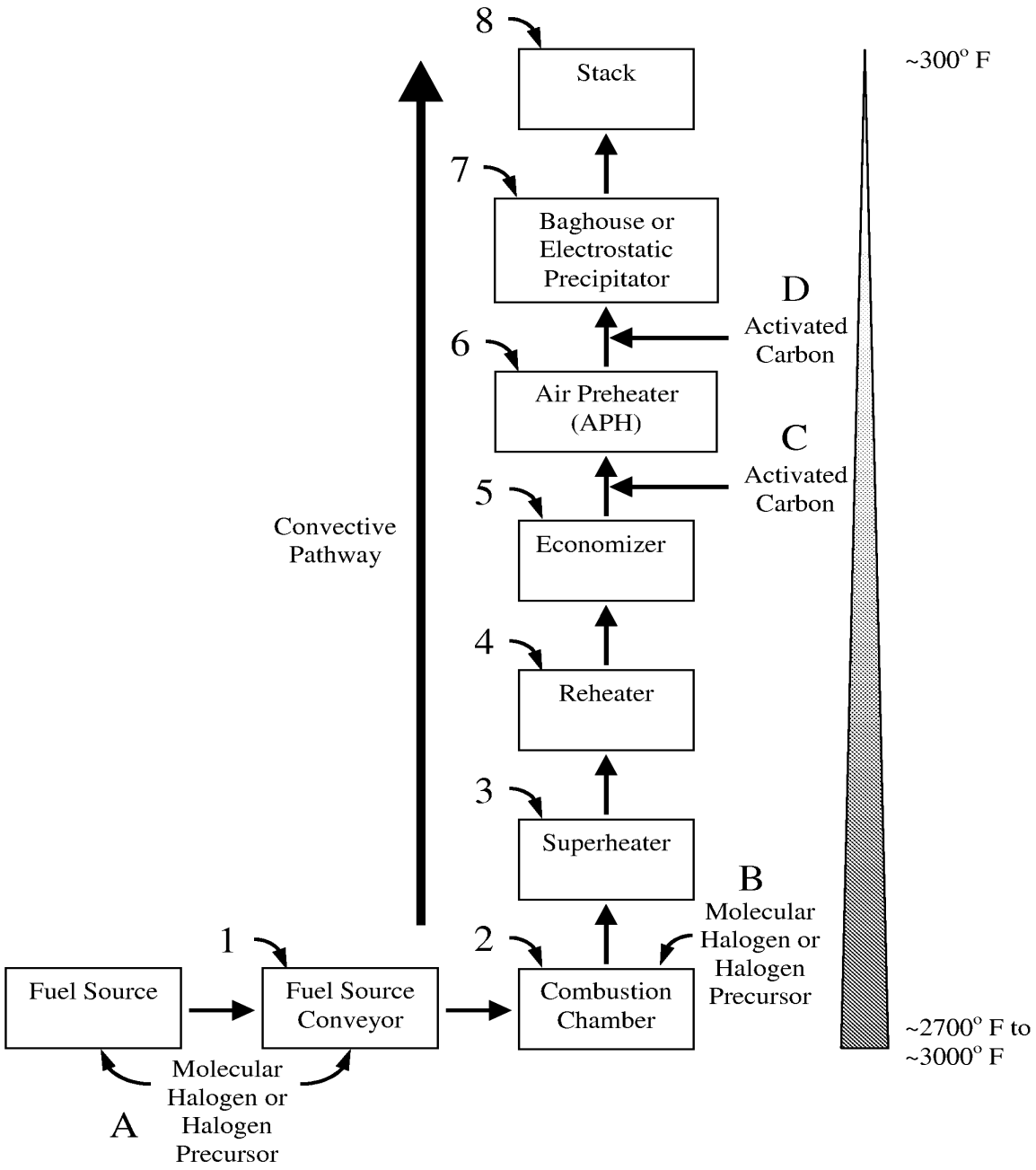

8
Stack
~300° F
7
Baghouse or Electrostatic Precipitator
D
Activated Carbon
6
Air Preheater (APH)
C
Activated Carbon
5
Economizer
Convective Pathway
4
Reheater
3
Superheater
B
Molecular Halogen or Halogen Precursor
1
2
Fuel Source
Fuel Source Conveyor
Combustion Chamber
~2700° F to ~3000° F
Molecular Halogen or Halogen Precursor
A

FIG. 1

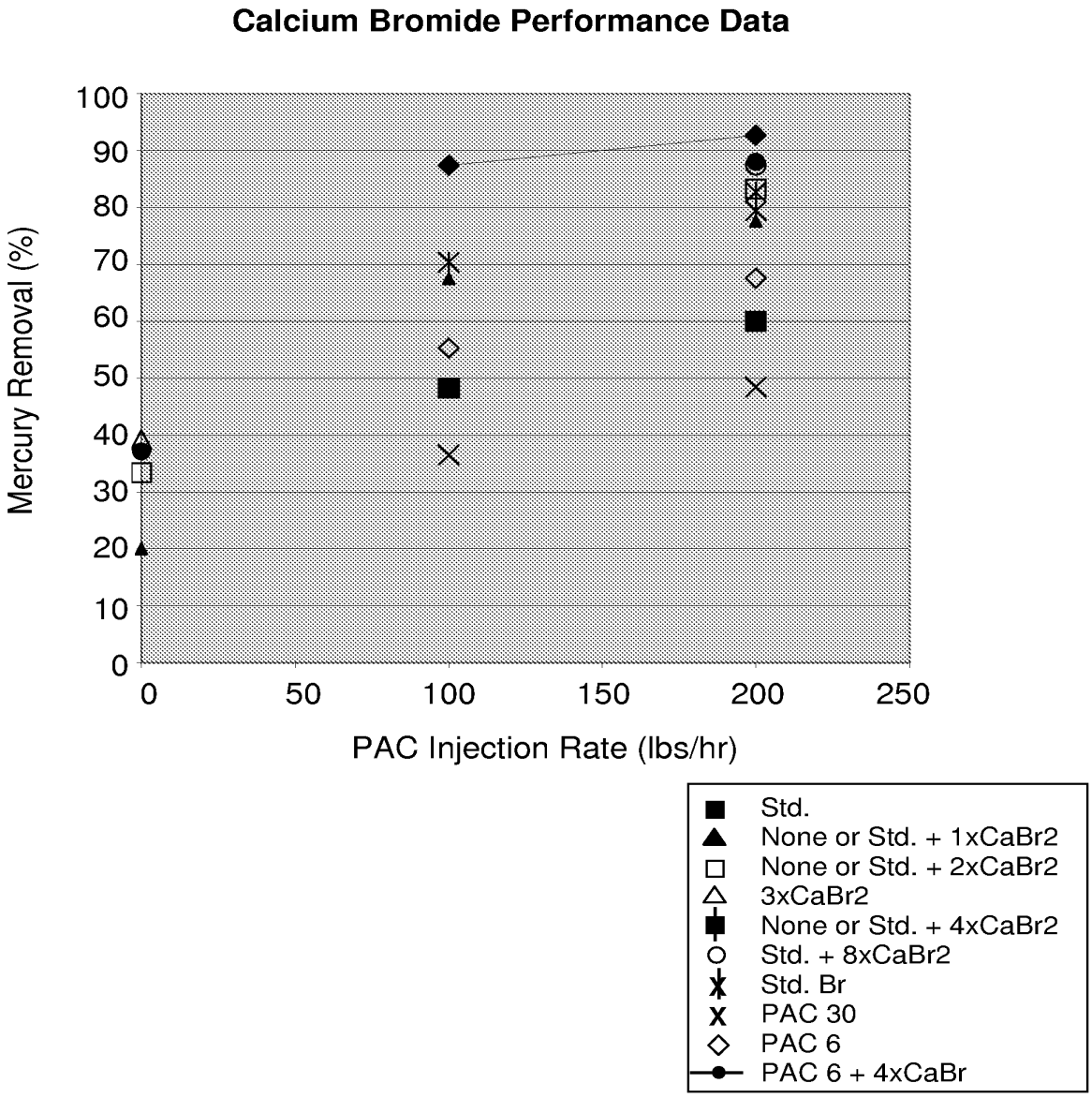

Calcium Bromide Performance Data
Mercury Removal (%)
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
PAC Injection Rate (lbs/hr)
Std.
None or Std. + 1xCaBr2
None or Std. + 2xCaBr2
3xCaBr2
None or Std. + 4xCaBr2
Std. + 8xCaBr2
Std. Br
PAC 30
PAC 6
PAC 6 + 4xCaBr

FIG. 2

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(54) **Title**: MULTI-FUNCTIONAL COMPOSITION OF MATTER FOR REMOVAL OF MERCURY FROM A FLUE GAS

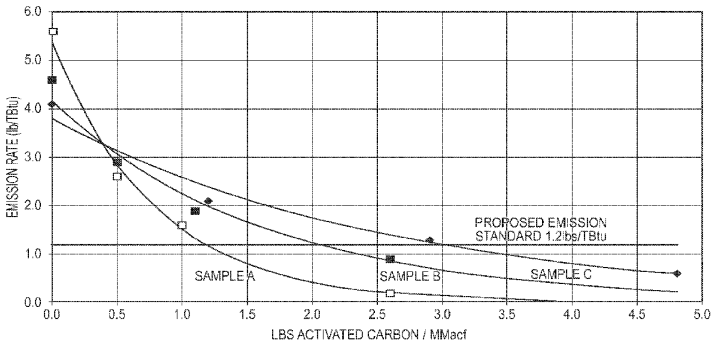


FIG.5

(57) **Abstract**: A multi-functional composition of matter that is useful for injection into a flue gas stream to rapidly and efficiently remove mercury from the flue gas stream. The multi-functional composition of matter may include a fixed carbon sorbent and minerals, halogens in the form of halide salts, to enhance (1) the oxidation reaction kinetics for the oxidation of mercury species and (2) the mass diffusion kinetics of the mercury species. The multi-functional composition of matter also does not have a significant detrimental impact on the ability of fly ash removed from the flue gas stream to be used with cementitious products such as concrete.

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MULTI-FUNCTIONAL COMPOSITION OF MATTER FOR REMOVAL OF MERCURY FROM A FLUE GAS

FIELD

[0001] This disclosure relates to the field of compositions for the rapid and efficient removal of mercury from a fluid stream such as a flue gas stream.

BACKGROUND

[0002] Mercury (Hg) is a highly toxic compound and exposure at appreciable levels can lead to adverse health effects for people of all ages, including harm to the brain, heart, kidneys, lungs, and immune system. Mercury is naturally occurring but is also emitted from various human activities, such as burning fossil fuels and other industrial processes. For example, in the United States about 40% of the mercury introduced into the environment comes from coal-fired power plants.

[0003] In the United States and Canada, federal and state/provincial regulations have been implemented or are being considered to reduce mercury emissions, particularly from coal-fired power plants, steel mills, cement kilns, waste incinerators and boilers, industrial coal-fired boilers, and other coal combusting facilities. For example, the United States Environmental Protection Agency (U.S. EPA) has promulgated Mercury Air Toxics Standards (MATS), which would among other things require coal-fired power plants to capture approximately 90% of their mercury emissions beginning in about 2016.

[0004] The leading technology for mercury control from coal-fired power plants is activated carbon injection. Activated carbon injection involves the injection of sorbents, particularly powder activated carbon, into flue gas emitted by the boiler of a power plant. Powder activated carbon is a porous carbonaceous material having a high surface area, which exposes significant amounts of beneficial chemically functional and catalytic reaction sites and which creates high adsorptive potential for many compounds, including capturing mercury from the flue gas. Activated carbon injection technology has shown the potential to control mercury emissions in most coal-fired power plants, even

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those plants that may achieve some mercury control through control devices designed for other pollutants, such as wet or dry scrubbers used to control sulfur dioxide and acid gases.

[0005] In addition to mercury, the boiler's flue gas stream carriers a variety of compounds, including particulate matter such as fly ash. Equipment such as an electrostatic precipitator (ESP) or a fabric filter bag house is used to remove such particulate matter, and the fly ash may be sold by the power plant operator to a concrete manufacturer as a substitute for Portland cement. Such sales are highly advantageous to the power plant operator as they create an additional revenue stream and eliminate the need to landfill the fly ash.

SUMMARY

[0006] According to the present disclosure, the capture and removal of mercury from a boiler flue gas through activated carbon injection can be characterized by three primary steps, which may occur sequentially or simultaneously: (1) contact of the injected sorbent with the mercury species, which is typically present in very dilute concentrations in the flue gas (*e.g.*, <100 parts per billion); (2) conversion of elemental mercury (*i.e.*, Hg^0), which is relatively inert and not easily adsorbed, into an oxidized mercury species (*e.g.*, Hg^+ and Hg^{+2}), which is more readily adsorbable and is significantly more soluble in an aqueous solubilizing medium such as water; and (3) the diffusion of the oxidized mercury species into pores where it is held tightly (*e.g.*, sequestered) without being released. The flue gas streams traverse the ductwork at very high velocities, such as in excess of 25 feet/second (*e.g.*, in excess of 7.6 meters/second). Therefore, once injected, the sorbent must rapidly accomplish these three steps to contact, oxidize and sequester the mercury. In some instances, the sorbent only has a residence time of 1 to 2 seconds in the flue gas. Conventional powder activated carbons and other similar sorbent products do not efficiently accomplish the three required steps within such constraints.

[0007] It would be advantageous to provide a novel composition of matter which overcomes the traditional limitations of conventional sorbents and can effectively act as

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a sorbent, catalyst, and solvent to efficiently and remove mercury from a flue gas stream, *e.g.*, to meet governmental regulations for mercury emissions. In this regard, various embodiments of a composition of matter that is multi-functional are provided. These multi-functional compositions of matter overcome the limitations of conventional sorbents in that they can be injected into a flue gas stream to efficiently and rapidly remove mercury from the flue gas stream, *e.g.*, to meet governmental regulations for mercury emissions.

[0008] The multi-functional composition of matter may comprise at least about 20 wt.% and not greater than about 75 wt.% fixed carbon, at least about 20 wt.% and not greater than about 50 wt.% minerals, at least about 1 wt.% and not greater than about 15 wt.% of a halogen, and at least about 3 wt.% and not greater than about 12 wt.% aqueous-based solubilizing medium. The multi-functional composition of matter may also have a median particle size of not greater than about 15 micron, a sum of micropore volume plus mesopore volume of at least about 0.2 cc/g, and a ratio of micropore volume to mesopore volume of at least about 0.7 and not greater than about 1.5.

[0009] Each power plant has unique factors (*e.g.*, power production capacity, coal feedstock, emissions control equipment, plant configurations, operating temperature and other conditions, *etc.*) that could cause mercury capture performance of the multi-functional composition of matter to vary from site to site. Thus, an informative way to compare the effectiveness of various compositions of matter to capture mercury is to conduct beta tests at a power plant to compare the mercury emissions while injecting the multi-functional composition versus injecting a standard commercially available product under similar conditions.

[0010] In one characterization, a multi-functional composition of matter, when injected in a beta test at a coal-fired power plant combusting high rank coal, will result in emissions of mercury of less than 1.2 lb Hg/TBtu at composition injection rates (in lbs/MMacf (one million actual cubic feet)) of at least approximately 30% less as compared to a standard commercially available powder activated carbon product identified herein as Comparative Sample C under comparable operating conditions. In

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yet another characterization, a multi-functional composition of matter, when injected in a beta test at a coal-fired power plant combusting high rank coal, will result in emissions of mercury of less than 1.2 lb Hg/TBtu at composition injection rates (in lbs/MMacf) of at least approximately 60% less as compared to a conventional powder activated carbon product identified herein as Comparative Sample C under comparable operating conditions.

[0011] In another characterization, a multi-functional composition of matter when injected in a beta test at a coal-fired power plant combusting high rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs/MMacf), the slope of the trendline with the highest R^2 value (*i.e.*, the correlation coefficient) at 1.2 lbs Hg/Tbtu will be more negative than about -0.6. In yet another characterization, a composition of matter when injected in a beta test at a coal-fired power plant combusting high rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs/MMacf), the slope of the trendline with the highest R^2 value at 1.2 lbs Hg/Tbtu will be more negative than about -1.5.

[0012] In another characterization, a multi-functional composition of matter, when injected in a beta test at a coal-fired power plant combusting low rank coal, will result in emissions of mercury of less than 4.0 lb Hg/TBtu at composition injection rates (in lbs/MMacf) of at least approximately 50% less as compared to a conventional powder activated carbon product identified herein as Comparative Sample D under comparable operating conditions.

[0013] In another characterization, a multi-functional composition of matter when injected in a beta test at a coal-fired power plant combusting low rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs/MMacf), the slope of the trendline with the highest R^2 value at 4.0 lbs Hg/Tbtu will be more negative than about -8.0.

[0014] In another characterization, the minerals of the multi-functional composition of matter are native to a feedstock that is used for the manufacture of the multi-functional composition of matter. In another characterization, the multi-functional composition of

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matter comprises of minerals from the group consisting of calcium-containing minerals, potassium-containing minerals, iron-containing minerals, silicon-containing minerals, silicate-containing minerals, sodium-containing minerals, tin-containing minerals, zinc-containing minerals, magnesium-containing minerals, alumino-silicate containing minerals and combinations thereof. In one particular characterization, the minerals comprise oxide minerals. In another characterization, the minerals comprise at least 1 wt.% iron-containing minerals.

[0015] In another characterization, the multi-functional composition of matter comprises at least about 3 wt.% and not greater than about 8 wt.% aqueous-based solubilizing medium.

[0016] In another characterization, the multi-functional composition of matter has a median particle size of not greater than about 12 micron. In yet another characterization, the multi-functional composition of matter has a median particle size of at least about 5 micron.

[0017] In another characterization, the multi-functional composition of matter has a Hardgrove Grindability Index of at least about 90. In yet another characterization, the multi-functional composition of matter has a Hardgrove Grindability Index of at least about 100.

[0018] In another characterization, the multi-functional composition of matter has a mercury particle density of at least about 0.5 g/cc and not greater than about 0.9 g/cc. In another characterization, the multi-functional composition of matter has an envelope particle density of at least about 0.3 g/cc and not greater than about 1.5 g/cc. In yet another characterization, the multi-functional composition of matter has an envelope particle density of at least about 0.5 g/cc and not greater than about 1.0 g/cc.

[0019] In another characterization, the sum of micropore volume plus mesopore volume of the multi-functional composition of matter is at least about 0.25 cc/g.

[0020] In another characterization, the porosity of the multi-functional composition of matter is controlled such that the mesopore volume of the multi-functional composition of matter is at least about 0.10 cc/g and is not greater than about 0.15 cc/g, the

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micropore volume of the multi-functional composition of matter is at least about 0.10 cc/g and is not greater than about 0.15 cc/g, and the ratio of micropore volume to mesopore volume is greater than about 0.9 and less than about 1.5.

[0021] In another characterization, the pH of the multi-functional composition of matter is greater than about 8 and is less than about 12.

[0022] In another characterization, when the multi-functional composition of matter is analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) at a magnification of 12,000 times over at least a 20 micron by 10 micron image area, the pixels attributed to the halogen exhibit a mean width of at least about 0.05 micron and not greater than about 2 micron, wherein the overall pixel area attributed to the halogen represents at least about 10% of the overall image area. In a further characterization, when the composition of matter is analyzed by Scanning Electron Microscopy and Energy Dispersive Spectrometry at a magnification of 12,000 times over at least a 20 micron by 15 micron image area, the pixels attributed to the halogen appear in at least 20% of the pixel area in any 10 micron by 10 micron scanning area.

[0023] Further, while activated carbon injection remains a viable and economical means for a power plant operator to reduce mercury emissions to meet government regulations, the added powder activated carbon may preclude the use of the fly ash extracted from the flue gas stream as a concrete additive, eliminating a potential revenue stream for the plant operator and requiring the plant operator to landfill the fly ash. Thus, it would also be advantageous to provide a composition of matter which can remove mercury from the flue gas stream, *e.g.*, to meet governmental regulations for mercury emissions, and which does not have a significant detrimental impact on the ability of the fly ash removed from the flue gas stream to be used with cementitious products such as concrete.

[0024] Thus, in one characterization, a multi-functional composition of matter may adsorb not greater than about 800 parts of air entrainment agent per million parts of composition of matter by mass during a foam stability test. In another characterization, the multi-functional composition of matter may adsorb not greater than about 750 parts of air entrainment agent per million parts of composition of matter by mass during a

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foam stability test. In yet another characterization, the multi-functional composition of matter may adsorb not greater than about 3 mg of air entrainment agent per 1 g of fixed carbon within the multi-functional composition of matter during a foam stability test when the foam is in a stable state. In a still further characterization, the multi-functional composition of matter is adapted to be blended with a cementitious composition including an air entrainment agent and water to form a cementitious blend, wherein the foam stability time of the cementitious blend is not greater than about 30 minutes.

DESCRIPTION OF THE DRAWINGS

[0025] **FIG. 1** schematically illustrates an example of the surface of a multi-functional composition of matter.

[0026] **FIG. 2** illustrates an image of colloidal bromide salt on the surface of a multi-functional composition of matter taken by Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry.

[0027] **FIG. 3** schematically illustrates a sample plant configuration and method for the capture and sequestration of mercury from a flue gas stream.

[0028] **FIG. 4** illustrates a flow sheet for the manufacture of a multi-functional composition of matter.

[0029] **FIG. 5** illustrates mercury capture performance of an approximate 200 MW coal-fired power plant burning a high rank coal (Powder River Basin coal) comparing two formulations of a multi-functional composition of matter with a commercially available sorbent.

[0030] **FIG. 6** illustrates mercury capture performance of an approximate 600 MW coal-fired power plant burning a low rank coal (North Dakota lignite coal) comparing a multi-functional composition of matter and a commercially available sorbent.

[0031] **FIG. 7** illustrates concrete foam stability test results comparing a sample of the multi-functional composition of matter to several comparative sorbent compositions.

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DETAILED DESCRIPTION

[0032] Various embodiments of a multi-functional composition of matter are provided that are particularly useful when injected into a fluid gas stream such as a flue gas stream (*e.g.*, from a coal-burning boiler or a waste energy boiler) to rapidly and efficiently capture and remove mercury from the flue gas stream. In this regard, the multi-functional composition of matter advantageously includes several different components that synergistically may (1) increase the probability of contact with mercury species in the flue gas, (2) decrease the time required for mercury oxidation and capture (*e.g.*, as a result of enhanced oxidation reaction kinetics and/or mass diffusional kinetics), and (3) advantageously reduce the total amount of material that must be injected to recover sufficient amounts of mercury to meet mercury removal criteria, such as applicable government regulations. Further, when the multi-functional composition of matter is removed from the flue gas stream after mercury capture (*e.g.*, in an electrostatic precipitator or fabric filter baghouse) along with fly ash from the boiler, the multi-functional composition of matter may be used with the fly ash as an acceptable substitute for cement in the manufacture of concrete or similar cementitious products.

[0033] In this regard, the multi-functional composition of matter may include a carbonaceous material (*e.g.*, fixed carbon), minerals, a halogen (*e.g.*, in the form of a halide salt), and an aqueous solubilization medium that together synergistically oxidize mercury and enhance the removal of mercury from a fluid stream, *e.g.*, from a flue gas stream. For example, the minerals and the halogen in the form of a halide salt (*e.g.*, a bromide salt) may enhance the oxidation of elemental mercury, and the aqueous solubilizing medium (*e.g.*, water) may solubilize the oxidized mercury and enhance mass diffusional kinetics. In addition, the multi-functional composition of matter may have various beneficial physical attributes such as a relatively small particle size and a well-controlled pore size distribution. As illustrated in **FIG. 1**, a multi-functional composition of matter containing a synergistic combination of minerals, halogen, and carbonaceous material having a small particle size and well-controlled pore size distribution provides a relatively large surface area on which kinetic mechanisms occur, and provides a sufficient capture mechanism to rapidly and efficiently sequester mercury from boiler flue gas.

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[0034] Referring to **FIG. 1**, the multi-functional composition of matter **100** may contain a porous carbonaceous material **102** (*e.g.*, fixed carbon) that is adapted to provide a large surface area in the appropriate pore size for the mercury oxidation and to sequester the oxidized mercury from the flue gas stream. The multi-functional composition of matter **100** may include at least about 10 weight percent of fixed carbon **102**, such as at least about 15 weight percent or even at least about 20 weight percent fixed carbon **102**. However, it is preferred that the fixed carbon content of the multi-functional composition of matter **100** not exceed about 75 weight percent, such as not greater than about 60 weight percent, or such as not greater than about 55 weight percent fixed carbon **102**. Due to a well-controlled pore structure and the presence of the other components in the multi-functional composition of matter **100**, a relatively low amount of fixed carbon **102** is required for mercury oxidation and sequestration (*e.g.*, a low amount of fixed carbon per unit volume of the flue gas stream as compared to typical sorbent compositions).

[0035] In one aspect, the multi-functional composition of matter **100** may have a relatively low average particle size *(e.g.*, median particle size, also known in the art as d_{50}), particularly as compared to typical sorbent compositions used for activated carbon injection. In this regard, the multi-functional composition of matter **100** may have a median particle size not greater than about 15 micron, such as not greater than about 12 micron. In another characterization, the multi-functional composition of matter **100** may have a median particle size of at least about 5 micron, such as at least about 6 micron or even at least about 8 micron. The d_{50} median particle size may be measured using techniques such as light scattering techniques *(e.g.*, using a Saturn DigiSizer II, available from Micromeritics Instrument Corporation, Norcross, GA). A relatively small median particle size, such as not greater than about 15 micron, means greater surface area per volume of the multi-functional composition. The increased surface area results in many benefits, including, but not limited to, increased exposure of the mercury to minerals and halogen, increased area available for reactions to occur, and thus overall improved reaction kinetics.

[0036] The multi-functional composition of matter **100** may also have a high pore volume and a well-controlled distribution of the pores **104**, particularly among the

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mesopores (*i.e.*, from 20 Å to 500 Å width) and the micropores (*i.e.*, not greater than 20 Å width). It has been found that a well-controlled distribution of micropores and mesopores is desirable for effective removal of mercury from the flue gas stream. In this regard, while not wishing to be bound by any theory, it is believed that the mesopores are the predominant structures for capture and transport of the oxidized mercury species to the micropores, whereas micropores are the predominate structures for sequestration of the oxidized mercury species.

[0037] In this regard, the sum of micropore volume plus mesopore volume of the multi-functional composition of matter **100** may be at least about 0.10 cc/g, such as at least 0.20 cc/g, and at least about 0.25 cc/g or even at least about 0.30 cc/g. The micropore volume of the multi-functional composition of matter may be at least about 0.10 cc/g, such as at least about 0.15 cc/g. Further, the mesopore volume of the multi-functional composition of matter **100** may be at least about 0.10 cc/g, such as at least about 0.15 cc/g. In one characterization, the ratio of micropore volume to mesopore volume may be at least about 0.7, such as at least about 0.9, and may be not greater than about 1.5. Such levels of micropore volume relative to mesopore volume advantageously enable efficient capture and sequestration of oxidized mercury species, such as $HgBr_2$, by the multi-functional composition of matter **100**. Pore volumes may be measured using gas adsorption techniques (*e.g.*, N_2 adsorption) using instruments such as a TriStar II Surface Area Analyzer (Micromeritics Instruments Corporation, Norcross, GA, USA).

[0038] The multi-functional composition of matter **100** may also be characterized by having a well-controlled particle density. Particle density is the mass of the particle over the volume of the particle (excluding pore volume of larger pores that do not contribute to adsorption), and is typically measured in g/cc. Particle density correlates to the surface area to volume ratio of the multi-functional composition of matter, which in turn affect mercury capture performance. Two methods of measuring particle density are described below.

[0039] Particle density can be measured by liquid mercury volume displacement, in which case the result is referred to as the mercury particle density. In this regard, the

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multi-functional composition of matter **100** may have a mercury particle density of at least about 0.5 g/cc, such as at least about 0.6 g/cc. Conversely, the mercury particle density of the multi-functional composition of matter may be not greater than about 0.9 g/cc, such as not greater than about 0.8 g/cc. Mercury particle density may be measured by the Micromeritics AccuPyc Pycnometer (Micromeritics Inc., Norcross, GA, USA).

[0040] Particle density can also be measured by sedimentary volume displacement, in which case the result is referred to as the envelope particle density. In this regard, the envelope particle density of the multi-functional composition of matter **100** may be at least about 0.5 g/cc, such as at least about 0.6 g/cc or at least about 0.7 g/cc. The envelope particle density of the multi-functional composition of matter **100** may be not greater than about 1.0 g/cc, such as not greater than about 0.9 g/cc. Envelope particle density may be measured using a Micromeritics GeoPyc Envelope Density Analyzer (Micrometrics, Inc., Norcross, GA, USA).

[0041] Another component of the multi-functional composition of matter **100** is minerals **106**. In one characterization, such minerals **106** may be native to the feedstock from which the carbonaceous material is formed (*e.g.*, by activation). In another characterization, some portion of the minerals **106** may be separately added to the multi-functional composition of matter, which requires additional expenses. While not wishing to be bound by any theory, it is believed that such minerals **106** may advantageously facilitate the oxidation of the elemental mercury in the flue gas stream. The presence of such minerals **106** may thereby enhance the kinetics of the mercury oxidation such that a reduced contact time with the flue gas stream is required to oxidize and remove sufficient amounts of mercury from the flue gas stream as compared to sorbents without such minerals.

[0042] The minerals **106** may advantageously be comprised of minerals including, but not limited to, aluminum-containing minerals, calcium-containing minerals, iron-containing minerals, silicon-containing minerals, silicate-containing minerals, sodium-containing minerals, potassium-containing minerals, zinc-containing minerals, tin-containing minerals, magnesium-containing minerals, and combinations thereof. The

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minerals may predominantly be oxide-based minerals, such as metal oxide minerals (*e.g.*, CaO, Fe_2O_3, Fe_3O_4, FeO, Al_2O_3), and silicates (*e.g.* Al_2SiO_5). In one characterization, the minerals **106** predominantly include metal oxides, particularly aluminum oxides and iron oxides. In another characterization, the minerals **106** include calcium-containing minerals, iron-containing minerals and alumino-silicates. These types of minerals are particularly well adapted to catalyze the oxidation reaction of the mercury. Iron-containing minerals are particularly well adapted to catalyze the oxidation reaction, and in one characterization, the minerals include at least 1 wt.% iron-containing minerals. The minerals **106** are intimately intertwined within the multi-functional composition of matter within a well controlled porous structure that facilitates the oxidation, capture and removal of mercury.

[0043] To provide sufficient reaction activity and rapid oxidation kinetics, the multi-functional composition of matter **100** may include at least about 20 weight percent of the minerals, such as at least 25 weight percent and even at least about 30 weight percent of the minerals. However, excessive amounts of the minerals **106** in the multi-functional composition of matter **100** may be detrimental to the capture of mercury. In this regard, the multi-functional composition of matter **100** may include not greater than about 50 weight percent of the minerals, such as not greater than about 45 weight percent. Advantageously, the multi-functional composition of matter may include not greater than about 40 weight percent of the minerals, such as not greater than about 35 weight percent. The total mineral content may be measured by a TGA701 Thermalgravitmetric Analyzer (LECO Corporation, St. Joseph, MI). The specific types and amount of particular minerals may be measured by the Niton XL3t X-Ray Fluorescence (XRF) Analyzer (Thermo Fisher Scientific Inc., Waltham, MA).

[0044] The multi-functional composition of matter **100** also includes an active halogen **108** such as a halide salt, *e.g.*, a bromide salt. Halogens by themselves are not known to be oxidants for mercury, but are a vital reaction participant in the oxidation of mercury. The multi-functional composition of matter **100** may include at least about one weight percent of the active halogen **108**, such as at least 2 weight percent. Significantly increased amounts of the halogen **108** may be detrimental to mercury capture and

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sequestration, and also can contribute to equipment corrosion and excessive bromine emissions in downstream liquid and gas streams, which may require further treatment processes. Therefore, the active halogen content of the multi-functional composition of matter may advantageously not exceed about 15 weight percent, such as not greater than about 10 weight percent.

[0045] It is an important aspect of the multi-functional composition of matter that the accessibility of the active halogen **108** (*e.g.*, Br or Br^-) is very high in order to facilitate mercury oxidation. In this regard, the halogen deposits may have primarily colloidal dimensions rather than granular dimensions. For example, these halogen deposits may have a mean width of at least about 0.5 micron and not greater than about 2.0 micron (in colloidal dimensions, as determined by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), as opposed to individual molecular dimensions). As stated above, the active halogen **108** is not by itself an oxidant but can participate as a reactant and therefore enhance the oxidation of mercury. In this regard, while not wishing to be bound by any theory, it is believed that the halogen **108** and the other features of the multi-functional composition of matter **100** synergistically enhance the oxidation of elemental mercury (Hg°) **110** to oxidized mercury (Hg^{2+}) **112**, particularly in the aqueous solubilization conditions (*e.g.*, high moisture flue gas conditions). It is believed that such a combination precludes the need to treat the multi-functional composition of matter with a more expensive and corrosive form of bromine (for example Br_2).

[0046] Thus, as illustrated in **FIG. 2**, the halogen may advantageously be dispersed throughout the multi-functional composition of matter in a colloidal fashion, particularly on the composition's surfaces which are in contact with the flue gas, *e.g.*, as determined by SEM with EDS. SEM images the composition while EDS enables the identification of the location of specific elements. Providing a highly dispersed halogen facilitates rapid reaction kinetics. This dispersion reflects a favorable approach to an application of halogens to the multi-functional composition of matter. The halogen is more effective when accessible and well-dispersed (*i.e.*, not in clumps or as a solid mix in the form of separate particles). In one characterization, when the multi-functional composition of

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matter is analyzed by SEM and EDS at a magnification of 12,000 times over at least a 20 micron by 10 micron image area, the pixels attributed to the halogen (*e.g.*, using EDS) exhibit a mean width of at least about 0.05 micron and not greater than about 2 micron, wherein the overall pixel area attributed to the halogen represents at least about 3% of this overall image area, for example at least about 10% of the overall image area, or even at least about 20% of the overall image area. In a further characterization as illustrated in **FIG. 2**, when the composition of matter is analyzed by SEM and EDS at a magnification of 12,000 times over at least a 20 micron by 15 micron image area, the pixels attributed to the halogen appear in at least 20% of the pixel area in any 10 micron by 10 micron scanning area.

[0047] In addition to the foregoing, the multi-functional composition of matter has additional beneficial surface chemistry characteristics. For example, flue gas is typically acidic. When sequestering metals like mercury in such an environment, it is advantageous to solubilize the metal prior to capture, which often requires specific ionic conditions. Thus, the multi-functional composition of matter may have a pH of the surface greater than 8 and not greater than about 12.

[0048] Moreover, and referring back to **FIG. 1**, the multi-functional composition of matter **100** may also include an amount of aqueous-based solubilizing medium such as water **116**. Such aqueous-based solubilizing medium can combat the acidity of the flue gas, enhance the mass diffusional kinetics of mercury oxidation and sequestration reactions by solubilizing oxidized mercury species within the pore structure, and prevent captured mercury from re-solubilizing and reentering the flue gas. In this regard, the multi-functional composition of matter may include at least about 2 weight percent of the solubilizing medium, such as at least about 3 weight percent or at least about 6 weight percent. However, the amount of solubilizing medium in the multi-functional composition of matter should be not greater than about 12 weight percent, such as not greater than about 10 weight percent to avoid adversely interfering with the mercury oxidation reaction(s) and consuming carbon adsorption capacity.

[0049] While not wishing to be bound by any particular theory, **FIG. 1** schematically illustrates the mechanisms that are believed to be responsible for the rapid oxidation

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and sequestration of mercury from a flue gas stream using the multi-functional compositions of matter disclosed herein. The fixed carbon **102** provides a large surface area for the elemental mercury **110** to react with the active halogen **108**, minerals **106**, and other components of the multi-functional composition of matter **100**. The minerals **106** that are in close proximity with other redox agents on or near the surface advantageously catalyze, oxidize, enhance, and/or otherwise facilitate the oxidation of the mercury and the formation of oxidized mercury species **112** such as Hg^{+2}, which can bond with the halogen to form such species **114**, for example $HgBr_2$. The presence of aqueous-based solubilizing medium on the multi-functional composition of matter (*e.g.*, water **116**) facilitates the redox activity, the transport of these mercury species **114** within the pore structure **104**, and the solubilization of these mercury species **114** within the pores **104** to sequester the mercury species **114** therein. As a result, the mercury oxidation kinetics and the mass diffusional kinetics are enhanced to enable the rapid and efficient oxidation and sequestration of mercury by the multi-functional composition of matter **100**.

[0050] The enhanced reaction and diffusional kinetics of the multi-functional composition of matter may enable coal-burning facilities (*e.g.*, a coal-fired power plant) to rapidly and efficiently capture mercury to meet regulatory limits on mercury emissions. For example, the U.S. EPA Mercury Air Toxic Standards (MATS) set mercury emission limits based on the amount of mercury per amount of power produced of 1.2 lb Hg/Tbtu for coal-fired power plants combusting high rank coals (*i.e.*, coals having >8,300 Btu/lb) and of 4.0 lb Hg/Tbtu for facilities combusting low rank coals (*i.e.*, coals having <=8,300 Btu/lb).

[0051] **FIG. 3** schematically illustrates a system and method for removal of mercury from a flue gas stream produced by a coal-burning power plant using activated carbon injection to contact the multi-functional composition of matter with the flue gas stream. The flue gas stream **301** exits a boiler **302** where coal has been combusted. As illustrated in **FIG. 3**, the flue gas stream **301** may then proceed to an air heater unit **304** where the temperature of the flue gas stream **301** is reduced. Thereafter, the flue gas stream **301** may be introduced to a separation unit **307** such as an electrostatic precipitator (ESP) or a fabric filter bag house which removes particulate matter from the

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flue gas, before exiting out a stack **308**. For example, a cold-side (*i.e.*, after the air heater unit) electrostatic precipitator can be used. It will be appreciated by those skilled in the art that the plant may include other devices not illustrated in **FIG. 3**, such as a selective catalytic reduction unit (SCR) and the like, and may have numerous other configurations. In order to capture mercury from the flue gas, the multi-functional composition of matter may be introduced to (*e.g.*, injected into) the flue gas stream **301** either before **303A** or after **303B** the air heater unit **304**, but before the separation unit **307** which will remove it from the flue gas.

[0052] The nature of the multi-functional composition of matter may advantageously enable a diminished amount of the multi-functional composition of matter to be injected into the flue gas stream to obtain high mercury removal rates as compared to typical sorbent compositions. The amount of multi-functional composition of matter required to remove mercury from the flue gas stream will vary depending upon the composition of the coal and process emission control steps. Therefore, it is advantageous to define a percent removal of mercury from the coal or fuel burned in the boiler, as percent removed in pounds of mercury per trillion BTU of fuel calorimetric heating value (lb Hg/Tbtu) from coal as measured at the plant stack **308** in accordance with US EPA MATS methodologies. The ability to capture high levels of mercury while injecting less sorbent material may advantageously reduce material cost to the power plant operator.

[0053] While the separation unit **307** may be selected from a number of devices, including an ESP or a fabric filter bag house, the multi-functional composition of matter disclosed herein is particularly useful for removing mercury from the flue gas stream **301** when an ESP is utilized as the separation unit **307**. For example, the separation unit **307** can be a cold-side ESP. While ESP units generally have a lower capital cost than a fabric filter bag house unit, fabric filter bag house units are often utilized to increase the contact time between the sorbent composition and the flue gas stream because the unit traps the sorbent and the flue gas continues to pass through the sorbent on the filter until the filter is rapped to remove the sorbent and other trapped materials. Such resident times are often deemed necessary to adequately capture mercury from the flue gas stream with temperatures of less than 350°F. However, utilizing the multi-functional composition of matter disclosed herein, which provides

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rapid kinetics for the oxidation reaction and mass diffusion of mercury species, even very short residence times (*e.g.*, the contact times) between the flue gas stream and the multi-functional composition of matter are sufficient to remove at least about 85% of the mercury from the flue gas stream, such as at least about 90% of the mercury. In this regard, the residence time may be not greater than about 5 seconds, such as not greater than about 3 seconds or even not greater than about 1 second while achieving such removal rates.

[0054] As stated previously, the separation unit **307** separates the multi-functional composition of matter from the flue gas stream, along with fly ash that is produced by combustion of coal in the boiler. This admixture **306** may be advantageously used in the manufacture of a cementitious material such as concrete by blending the admixture **306** with a cementitious composition including an air entrainment agent. In this regard, while not wishing to be bound by any theory, it is believed that due to the relatively small amount of fixed carbon in the multi-functional composition of matter, the multi-functional composition of matter adsorbs a diminished amount of air entrainment agent as compared to typical sorbent compositions. Thus, the multi-functional composition of matter recovered with fly ash may be blended with cementitious compositions to produce higher quality cement as compared to typical sorbent compositions.

[0055] Specifically, during the manufacture of concrete, air entrainment agents (*e.g.*, surfactants) are added to the mixture to entrain air into the concrete to form stable foam, which is necessary for concrete strength. Upon the introduction of the air entrainment agent, concrete manufacturers prefer that the foam stabilize over a relatively short period of time *e.g.*, within less than about 30 minutes. This short-time frame is particularly important for use in ready-mix concrete. However, most fly ash mixtures that contain conventional sorbents require both a high concentration of air entrainment agent due to the sorbent competing for the agent, and also result in the foam destabilizing over time.

[0056] In this regard, it is a particular advantage that the multi-functional composition of matter may adsorb not greater than 800 parts of air entrainment agent per million parts of multi-functional composition of matter such as not greater than 750 parts of air

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entrainment agent per million parts of multi-functional composition of matter by weight. Because the multi-functional composition of matter adsorbs a relatively low amount of air entrainment agent, more air entrainment agent is available to entrain air in the concrete mixture and the foam stabilization time is reduced to not greater than 30 minutes, such as not greater than 10 minutes. Further, due to the synergistic effect of the multi-functional composition of matter, a reduced amount of activated carbon may be injected into the flue gas stream to remove mercury as compared to typical sorbent compositions, resulting in a reduced amount of fixed carbon that is extracted with the admixture **306** from the separation device **307**.

[0057] **FIG. 4** is a flow sheet that illustrates an exemplary method for the manufacture of a multi-functional composition of matter in accordance with one embodiment. The manufacturing process begins with a carbonaceous feedstock **401** such as low-rank lignite coal with a relatively high content of natural deposits of native minerals. In the manufacturing process, the feedstock is subjected to an elevated temperature and one or more oxidizing gases under exothermic conditions for a period of time to sufficiently increase surface area, create porosity, alter surface chemistry, and expose and exfoliate native minerals previously contained within feedstock. The specific steps in the process include: (1) dehydration **402**, where the feedstock is heated to remove the free and bound water, typically occurring at temperatures ranging from 100°C to 150°C; (2) devolatilization **403**, where free and weakly bound volatile organic constituents are removed, typically occurring at temperatures above 150°C; (3) carbonization **404**, where non-carbon elements continue to be removed and elemental carbon is concentrated and transformed into random amorphous structures, typically occurring at temperatures of from about 350°C to about 800°C; and (4) activation **405**, where steam, air or other oxidizing agent(s) is added and pores are developed, typically occurring at temperatures above 800°C. The manufacturing process may be carried out, for example, in a multi-hearth or rotary furnace. The manufacturing process is not discrete and steps can overlap and use various temperatures, gases and residence times within the ranges of each step to promote desired surface chemistry and physical characteristics of the manufactured product.

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[0058] After activation **405**, the product may be subjected to a comminution step **406** to reduce the particle size *(e.g.*, reduce the median particle size) of the activated product. Comminution **406** may occur, for example, in a mill such as a roll mill, jet mill or other like process. Comminution **406** may be carried out for a time sufficient to reduce the median particle size of the thermally treated product to not greater than about 15 micron, such as not greater than about 12 micron.

[0059] Advantageously, the multi-functional composition of matter may have a relatively high Hardgrove Grindability Index (HGI), as measured by ASTM Method D409. The HGI was developed to empirically measure the relative difficulty of grinding coal to the particle size necessary for complete combustion in a coal boiler furnace. The use of HGI has been extended to grinding coal for other purposes such as iron-making, cement manufacture and chemical industries utilizing coal. Particulate materials of low value HGI are more difficult to grind than those with high values. Mill capacity also falls when grinding materials with a lower HGI. In this regard, the HGI of the multi-functional composition of matter may be at least about 80 such as at least about 90, at least about 100 or even at least about 110. The relatively high HGI enables the average particle size to be reduced with relatively low energy consumption. Further, the relatively soft materials of the multi-functional composition of matter will lead to reduced erosion (*e.g.*, attrition) of the comminuting equipment as compared to harder materials having a low HGI. While not wishing to be bound by any theory, it has been observed that utilizing lignite matter feedstock will lead to a relatively high HGI.

[0060] The halogen may be added to the product at any stage after the activation process. For example, as illustrated in **FIG. 4**, halogen may be introduced either before **407A** or after **407B** comminution. The halogen may be introduced as a dry or wet halide salt.

EXAMPLES

[0061] A beta test is a full-scale evaluation of the ability of an emission control technology at a coal-burning power plant to remove mercury from the flue gas. The first step is to establish baseline mercury emissions using a methodology certified by US EPA, specifically either Method 30A (Determination of Total Vapor Phase Mercury

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Emissions from Stationary Sources (Instrumental Analyzer Procedure)) or Method 30B (Determination of Total Vapor Phase Mercury Emissions From Coal-Fired Combustion Sources Using Carbon Sorbent Traps), each available in 40 CFR Part 60 Appendix A-8 to Part 60. Method 30A describes the use of a mercury continuous emission monitoring systems (Hg CEMs) (*e.g.*, manufactured by Thermo Fisher Scientific Inc. of Waltham, MA), while Method 30B describes testing using sorbent traps (*e.g.,* manufactured by Ohio Lumex Co. of Twinsburg, OH). If Method 30A is used, then mercury emissions are measured after a relatively steady-state of mercury emissions are achieved over at least a one-hour period based on a time-weighted average measurement. If Method 30B is used, mercury emissions are calculated based on (1) mercury captured in at least three pair of traps placed into the flue gas stream once the desired testing conditions are in a steady state, and (2) the average air emissions rate from the unit being tested, which can be measured at the stack. Method 30B specifies quality procedures for the sorbent traps.

[0062] Once the baseline is established, the sorbent is injected into the flue gas at the desired rate and the mercury emissions are measured once a steady state of mercury emissions is achieved, typically after about 15. This process is repeated for each sorbent at each desired injection rate under each desired operating condition. Typically, injection rates are varied beginning with a rate that is anticipated to not achieve EPA mercury emission limits (such as 0.5 lbs/MMacf or lower) to a rate that is expected to achieve or exceed the EPA mercury emission limits (such as 4.0 lbs/MMacf, 5.0 lbs/MMacf, or more). The amount of sorbent necessary to properly perform a beta test will depend on the desired injection rates, the conditions of the unit being tested and the EPA methodology used. Minimum testing requirements can be estimated based on the heat rate of the coal being burned (*e.g.*, BTU per MW), the MW of the unit, the actual volume flow of flue gas (*e.g.*, in cubic feet), and the estimated time required to properly complete testing.

[0063] Operating conditions for each injection scenario should be recorded, including, but not limited to, coal type, temperature, load, and emissions control equipment and configuration. Temperature of the flue gas should be less than 350°F and typically is between 275°F and 325°F. Testing should be conducted at full load of

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the unit, and additional testing at reduced loads can be performed if desired. In addition, if the unit uses various coal types in the combustion process then additional testing should be done with the various coals. The specific order and types of emission control devices should be recorded along with other operating conditions. The injection rate at the EPA MATS mercury emissions limit correlates approximately to the amount of sorbent that must be injected to achieve regulatory compliance under a given set of operating conditions.

[0064] Each power plant has unique power production capacity, coal feedstock, emissions control equipment, plant configurations, operating temperature and other conditions, and a variety of other factors. See above discussion of **FIG. 3**. Variability in these factors can cause mercury capture performance of the multi-functional composition of matter to vary from plant to plant. Thus, an informative way to compare the effectiveness of various compositions of matter to capture mercury is to compare the composition's mercury emissions rate (lb Hg/Tbtu) as a function of the amount of matter injected (lb/MMacf) with a standard commercially available product under similar conditions at each plant. Standard commercially available products include PowerPAC® Premium and PowerPAC® Premium Plus (ADA Carbon Solutions, LLC, Littleton, CO); DARCO® Hg-LH (Norit Americas Inc., Marshall, TX); FLUEPAC®-MC Plus (Calgon Corporation, Pittsburgh, PA); and B-PAC™ (Albermarle Corporation, Baton Rouge, LA).

[0065] In the event that the beta testing results in at least 4 data points (including the baseline), the data can be plotted and fitted with a trendline function of the best fit, as dictated by the highest R^2 value. The trendline is typically a non-linear function such as power, logarithmic, or an exponential function. The slope of this trendline at the regulatory compliance limit can be calculated as the tangent of the curve at that point. Such slope gives an indication of a sorbent's potential rate of mercury oxidation and potential for additional mercury removal. Particularly, sorbents with a steeper and more negative slope are believed to have enhanced reaction kinetics that can result in much greater rates of mercury capture. Results of 2 beta tests are presented below.

Example 1

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[0066] **Example 1** illustrates the ability of two samples of the multi-functional composition of matter disclosed herein to remove mercury in coal-fired power plants combusting a high rank coal as compared to a typical sorbent composition.

[0067] The first sample of the multi-functional composition of matter (Sample A) has a median particle size of about 8 micron. The second sample of the multi-functional composition of matter (Sample B) has a median particle size of about 12 micron. Samples A and B both have a mineral content of about 35 wt.%, a fixed carbon content of about 50 wt.%, a sum of mesopore volume plus micropore volume of about 0.25 cc/g, a total mesopore volume of about 0.12 cc/g, and a total micropore volume of about 0.13 cc/g. Both samples include about 5.5 wt.% bromide salt.

[0068] These samples are compared to a prior art sorbent material (Comparative Sample C), specifically a sorbent composition referred to as a PowerPac® Premium, (ADA Carbon Solutions, LLC, Littleton, CO). Comparative Sample C has a median particle size of about 25 micron, a fixed carbon content of about 50 wt.%, a mineral content of about 40 wt.%, a sum of the micropore volume plus mesopore volume of about 0.25 cc/g, a total mesopore volume of about 0.13 cc/g, and a total micropore volume of about 0.12 cc/g. Comparative Sample C includes about 4.5 wt.% bromide salt.

[0069] Each of Samples A, B and C is injected into a flue gas from an approximately 200 MW electric generating unit combusting a high rank coal (Powder River Basin coal). In all cases, the composition is injected upstream of an air heater unit and is extracted using a cold-side electrostatic precipitator. A CEMS measures mercury before composition injection and also in the stack to measure mercury removal efficacy of the compositions.

[0070] As illustrated in **FIG. 5**, which is a graph of mercury emission rates as a function of sorbent injection rate, Sample B achieves the US EPA compliance limit for high rank coals (1.2 lbs Hg/Tbtu) at approximately 33% less sorbent usage as compared to Comparative Sample C, and Sample A achieves the compliance limit at an injection rate of approximately 60% less sorbent usage as compared to Comparative Sample C. In other words, Comparative Sample C requires approximately more than

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about double the amount of Sample A to be injected in order to achieve the mercury compliance limit. In addition, the slopes of the mercury emission rate trendlines for Samples A and B at the compliance limit of 1.2 lbs Hg/Tbtu are about -1.7 and about -0.7, respectively, which are greater than about 2.5 and 2 times steeper than the slope for Comparative Sample C, respectively. Consequently, injection of additional amounts of the multi-functional composition of matter ultimately capture more mercury than comparable additional amounts of Sample C and would allow the facility to capture more mercury than that required by the regulatory limits.

Example 2

[0071] **Example 2** illustrates the ability of a sample of the multi-functional composition of matter disclosed herein to remove mercury in coal-fired power plants combusting a low rank coal as compared to a typical sorbent composition.

[0072] The sample of the multi-functional composition of matter in this Example 2 is the same as Sample A described in Example 1.

[0073] The prior art sorbent material (Comparative Sample D) in this Example 2 is a sorbent composition referred to as a PowerPac® Premium Plus (ADA Carbon Solutions, LLC, Littleton, CO). Comparative Sample D has a median particle size of about 25 micron, a fixed carbon content of about 50 wt.%, a native mineral content of about 40 wt.%, a sum of the micropore volume plus mesopore volume of about 0.25 cc/g, a total mesopore volume of about 0.12 cc/g, and a total micropore volume of about 0.13 cc/g. Comparative Sample D includes about 5.5 wt.% bromide salt.

[0074] Each of these compositions is injected into a flue gas from an approximate 600 MW electric generating unit combusting a low rank coal (North Dakota lignite coal). In each case, the composition is injected upstream of an air heater unit and is extracted using a cold-side electrostatic precipitator. A CEMS measures mercury before composition injection and also in the stack to measure mercury removal efficacy of the compositions.

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[0075] As illustrated in **FIG. 6**, which is a graph of mercury emission rates as a function of sorbent injection, Sample A achieves the US EPA MATS compliance limit for coal-fired power plants burning low rank coals (4 lbs Hg/Tbtu) at approximately over 60% less sorbent injected as compared to Comparative Sample D. In other words, Comparative Sample D required approximately more than about double the amount of Sample A to achieve the mercury compliance limit. In addition, Sample A has a slope of the trendline at the compliance limit of approximately -8, which is greater than about 2 times steeper than the slope for Comparative Sample D. Consequently, injection of additional amounts of multi-functional composition of matter at the compliance limit ultimately captures more mercury than comparable additional amounts of the currently available sorbent, and would allow the facility to capture more mercury than required by the regulatory limits.

Example 3

[0076] **Example 3** illustrates the potential of the multi-functional compositions of matter disclosed herein to be used in the manufacture of concrete. A sample of a multi-functional composition of matter (Sample A) is tested against two comparative samples (Comparative Sample E and Comparative Sample F), and a baseline which contains no sorbents or multi-functional compositions of matter. Samples A is described under Example 1. Comparative Samples E and F are both commercially available activated carbon products. Comparative Sample E has a median particle size of about 25 micron, a fixed carbon content of about 68 wt.%, a mineral content of about 19 wt.%, a sum of the micropore volume plus mesopore volume of about 0.4 cc/g, a total mesopore volume of about 0.25 cc/g, and a total micropore volume of about 0.14 cc/g. Comparative Sample F has a median particle size of about 18 micron, a fixed carbon content of about 72 wt.%, a mineral content of about 23 wt.%, a sum of the micropore volume plus mesopore volume of about 0.13 cc/g, a total mesopore volume of about 0.02 cc/g, and a total micropore volume of about 0.11 cc/g.

[0077] As used herein, the foam stability time is the amount of time until the initial foam is stable and requires no more air entrainment agent addition to remain stabilized.

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The foam stability time of concrete mixtures is measured for each of the foregoing samples. To perform the foam stability test, about 0.04 grams of each sample is mixed with about 3.96 grams of fly ash, about 16 grams of Portland cement, and 50 mL water. The baseline sample contains about 4 grams of fly ash, 16 grams of Portland cement, and 50 mL water. An air entrainment agent is added to the mixture until a stable layer of foam forms on the top surface (time = 0). The mixtures are checked at 10 to 30 minute time intervals to examine if the foam remains stable (*i.e.*, the foam bubbles remain after the prescribed duration). If the foam has destabilized, more air entrainment agent is added until the foam re-stabilizes. This test is a modification of a foam index test originally developed by V.H. Dodson of W.R. Grace & Co. (See V.H. Dodson, Foam Index Test, Concrete Admixtures, Structural Engineering Series, Van Nostrand Reinhold, New York, pp 140-143 (1990)).

[0078] As illustrated in **FIG. 7**, Comparative Sample F is very similar to the baseline sample. Sample A shows stabilization within about 10 to 30 minutes. Comparative Sample E does not stabilize even after 120 minutes.

[0079] While Comparative Sample F shows rapid stabilization, this is believed to be due in large part to the lack of mesoporosity and microporosity in the sorbent material. As a result, it is believed that Comparative Sample F, while not having a significant detrimental effect on the ability of the fly ash to be used as cement substitute, will not efficiently and rapidly remove mercury from a flue gas stream, and therefore, at best, very large quantities of this sorbent composition will need to be injected into the flue gas stream to meet applicable mercury removal regulations. In contrast, Sample A demonstrates both the ability to rapidly and efficiently remove and sequester mercury and to not having a significant detrimental effect on the ability of the fly ash to be used as cement substitute. Fly ash containing Comparative Sample E cannot be effectively used as a cement substitute due to the time required to achieve a stable foam.

[0080] While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention.

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What is Claimed is:

1. A multi-functional composition of matter, comprising at least about 20 wt.% and not greater than about 75 wt.% fixed carbon, at least about 20 wt.% and not greater than about 50 wt.% minerals, at least about 1 wt.% and not greater than about 15 wt.% of a halogen, and at least about 3 wt.% and not greater than about 12 wt.% aqueous-based solubilizing medium, wherein:

the multi-functional composition of matter has a median particle size of not greater than about 15 micron;

the multi-functional composition of matter has a sum of micropore volume plus mesopore volume that is at least about 0.2 cc/g; and

the ratio of micropore volume to mesopore volume is at least about 0.7 and is not greater than about 1.5.

2. A composition of matter that when injected in a beta test at a coal-fired power plant combusting high rank coal will result in emissions of mercury of less than 1.2 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 30% less as compared to Comparative Sample C under comparable operating conditions.

3. A composition of matter that when injected in a beta test at a coal-fired power plant combusting high rank coal will result in emissions of mercury of less than 1.2 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 60% less as compared to Comparative Sample C under comparable operating conditions.

4. A composition of matter that when injected in a beta test at a coal-fired power plant combusting high rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs /MMacf), the slope of the trendline with the highest R^2 value at 1.2 lbs Hg/Tbtu will be more negative than about -0.6.

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5. A composition of matter that when injected in a beta test at a coal-fired power plant combusting high rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs /MMacf), the slope of the trendline with the highest R^2 value at 1.2 lbs Hg/Tbtu will be more negative than about -1.5.

6. A composition of matter that when injected in a beta test at a coal-fired power plant combusting low rank coal will result in emissions of mercury of less than 4.0 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 50% less as compared to Comparative Sample D under comparable operating conditions.

7. A composition of matter that when injected in a beta test at a coal-fired power plant combusting low rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs /MMacf), the slope of the trendline with the highest R^2 value at 4.0 lbs Hg/Tbtu will be more negative than about -8.

8. The multi-functional composition of matter recited in Claim 1, wherein when injected at a coal-fired power plant combusting high rank coal will result in emissions of mercury of less than 1.2 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 30% less as compared to Comparative Sample C under comparable operating conditions.

9. The multi-functional composition of matter recited in Claim 1, wherein when injected at a coal-fired power plant combusting high rank coal will result in emissions of mercury of less than 1.2 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 60% less as compared to Comparative Sample C under comparable operating conditions.

10. The multi-functional composition of matter recited in Claim 1, wherein when injected in a beta test at a coal-fired power plant combusting high rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (in lbs/MMacf), the slope of the curve with the highest R^2 value at 1.2 lbs Hg/Tbtu will be more negative than about -0.6.

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11. The multi-functional composition of matter recited in Claim 1, when injected in a beta test at a coal-fired power plant combusting high rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (in lbs /MMacf), the slope of the curve with the highest R^2 at 1.2 lbs Hg/Tbtu will be more negative than about -1.5.

12. The multi-functional composition of matter recited in Claim 1, which when injected at a coal-fired power plant combusting low rank coal will result in emissions of mercury of less than 4.0 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 40% less as compared to Comparative Sample D under comparable operating conditions.

13. The multi-functional composition of matter recited in Claim 1, wherein when injected at a coal-fired power plant combusting low rank coal will result in emissions of mercury of less than 4.0 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least approximately 50% less as compared to Comparative Sample D under comparable operating conditions.

14. The multi-functional composition of matter recited in Claim 1, wherein when injected in a beta test at a coal-fired power plant combusting low rank coal and when the mercury emission rate (lb Hg/Tbtu) is plotted as a function of the composition injection rate (lbs matter/MMacf), the slope of the trendline with the highest R^2 value at 4.0 lbs Hg/Tbtu will be more negative than about -8.

15. The multi-functional composition of matter recited in Claim 1, wherein the minerals are native to a feedstock for the manufacture of the multi-functional composition of matter.

16. The multi-functional composition of matter recited in Claim 1, wherein the minerals are selected from the group consisting of calcium-containing minerals, potassium-containing minerals, iron-containing minerals, silicon-containing minerals, silicate-containing minerals, sodium-containing minerals, tin-containing minerals, zinc-containing minerals, magnesium-containing minerals, alumino-silicate containing minerals, and combinations thereof.

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17. The multi-functional composition of matter recited in Claim 1, wherein the minerals comprise oxide minerals.

18. The multi-functional composition of matter recited in Claim 1, wherein the minerals comprise at least 1 wt. % iron-containing minerals.

19. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter comprises at least about 3 wt.% and not greater than about 8 wt.% aqueous-based solubilizing medium.

20. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter has a median particle size of not greater than about 12 micron.

21. The multi-functional composition of matter recited Claim 1, wherein the multi-functional composition of matter has a median particle size of at least about 5 micron.

22. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter has a Hardgrove Grindability Index of at least about 90.

23. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter has a Hardgrove Grindability Index of at least about 100.

24. The multi-functional composition of matter as recited Claim 1, wherein the multi-functional composition of matter has a mercury particle density of at least about 0.5 g/cc and not greater than about 0.9 g/cc.

25. The multi-functional composition of matter as recited Claim 1, wherein the multi-functional composition of matter has an envelope particle density of at least about 0.3 g/mL and not greater than about 1.5 g/mL.

26. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter has an envelope particle density of at least about 0.5 g/cc and not greater than about 1.0 g/cc.

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27. The multi-functional composition of matter recited in Claim 1, wherein the sum of micropore volume plus mesopore volume of the multi-functional composition of matter is at least about 0.25 cc/g.

28. The multi-functional composition of matter recited in Claim 1, wherein:

the mesopore volume of the multi-functional composition of matter is at least about 0.10 cc/g and is not greater than about 0.15 cc/g;

the micropore volume of the multi-functional composition of matter is at least about 0.10 cc/g and is not greater than about 0.15 cc/g; and

the ratio of micropore volume to mesopore volume is greater than about 0.9 and less than about 1.5.

29. The multi-functional composition of matter recited in Claim 1, wherein the pH of the multi-functional composition of matter is greater than about 8 and is not greater than about 12.

30. The multi-functional composition of matter recited in Claim 1, wherein when the multi-functional composition of matter is analyzed by Scanning Electron Microscopy and Energy Dispersive Spectrometry at a magnification of 12,000 times over at least a 20 micron by 10 micron image area, the pixels attributed to the halogen exhibit a mean width of at least about 0.05 micron and not greater than about 2 micron, wherein the overall pixel area attributed to the halogen represents at least about 10% of the overall image area.

31. The multi-functional composition of matter recited in Claim 1, wherein when the composition of matter is analyzed by Scanning Electron Microscopy and Energy Dispersive Spectrometry at a magnification of 12,000 times over at least a 20 micron by 15 micron image area, the pixels attributed to the halogen appear in at least 20% of the pixel area in any 10 micron by 10 micron scanning area.

32. The multi-functional composition of matter recited in Claim 1, wherein when the halogen is in the form of a halide salt.

33. The multi-functional composition of matter recited in Claim 1, wherein when the halogen is in the form of a bromide salt.

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34. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter adsorbs not greater than about 800 parts of air entrainment agent per million parts of composition of matter by mass during the foam stability test.

35. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter adsorbs not greater than about 750 parts of air entrainment agent per million parts of composition of matter by mass during the foam stability test.

36. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter will adsorb not greater than about 3 mg of air entrainment agent per 1 g of fixed carbon within the multi-functional composition of matter during the foam stability test when the foam is in a stable state.

37. The multi-functional composition of matter recited in Claim 1, wherein the multi-functional composition of matter is adapted to be blended with a cementitious composition including an air entrainment agent and water to form a cementitious blend, wherein the foam stability time of the cementitious blend is not greater than about 30 minutes.

38. The multi-functional composition of matter recited in Claim 34, wherein the minerals are native to a feedstock for the manufacture of the multi-functional composition of matter.

39. The multi-functional composition of matter recited in Claim 34, wherein the minerals are selected from the group consisting of calcium-containing minerals, potassium-containing minerals, iron-containing minerals, silicon-containing minerals, silicate-containing minerals, sodium-containing minerals, tin-containing minerals, zinc-containing minerals, magnesium-containing minerals, alumino-silicate containing minerals, and combinations thereof.

40. The multi-functional composition of matter recited in Claim 34, wherein the minerals comprise oxide minerals.

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41. The multi-functional composition of matter recited in Claim 34, wherein the minerals comprise at least 1 wt. % iron-containing minerals.

42. The multi-functional composition of matter recited in Claim 34, wherein the multi-functional composition of matter comprises at least about 3 wt.% and not greater than about 8 wt.% aqueous-based solubilizing medium.

43. The multi-functional composition of matter recited in Claim 34, wherein the multi-functional composition of matter has a median particle size of not greater than about 12 micron.

44. The multi-functional composition of matter recited Claim 34, wherein the multi-functional composition of matter has a median particle size of at least about 5 micron.

45. The multi-functional composition of matter recited in Claim 34, wherein the multi-functional composition of matter has a Hardgrove Grindability Index of at least about 90.

46. The multi-functional composition of matter recited in Claim 34, wherein the multi-functional composition of matter has a Hardgrove Grindability Index of at least about 100.

47. The multi-functional composition of matter as recited Claim 34, wherein the multi-functional composition of matter has a mercury particle density of at least about 0.5 g/cc and not greater than about 0.9 g/cc.

48. The multi-functional composition of matter as recited Claim 34, wherein the multi-functional composition of matter has an envelope particle density of at least about 0.3 g/mL and not greater than about 1.5 g/mL.

49. The multi-functional composition of matter recited in Claim 34, wherein the multi-functional composition of matter has an envelope particle density of at least about 0.5 g/cc and not greater than about 1.0 g/cc.

50. The multi-functional composition of matter recited in Claim 34, wherein the sum of micropore volume plus mesopore volume of the multi-functional composition of matter is at least about 0.25 cc/g.

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51. The multi-functional composition of matter recited in Claim 34, wherein:

the mesopore volume of the multi-functional composition of matter is at least about 0.10 cc/g and is not greater than about 0.15 cc/g;

the micropore volume of the multi-functional composition of matter is at least about 0.10 cc/g and is not greater than about 0.15 cc/g; and

the ratio of micropore volume to mesopore volume is greater than about 0.9 and less than about 1.5.

52. The multi-functional composition of matter recited in Claim 34, wherein the pH of the multi-functional composition of matter is greater than about 8 and is less than about 12.

53. The multi-functional composition of matter recited in Claim 34, wherein when the multi-functional composition of matter is analyzed by Scanning Electron Microscopy and Energy Dispersive Spectrometry at a magnification of 12,000 times over at least a 20 micron by 10 micron image area, the pixels attributed to the halogen exhibit a mean width of at least about 0.05 micron and not greater than about 2 micron, wherein the overall pixel area attributed to the halogen represents at least about 10% of the overall image area.

54. The multi-functional composition of matter recited in Claim 34, wherein when the composition of matter is analyzed by Scanning Electron Microscopy and Energy Dispersive Spectrometry at a magnification of 12,000 times over at least a 20 micron by 15 micron image area, the pixels attributed to the halogen appear in at least 20% of the pixel area in any 10 micron by 10 micron scanning area.

55. The multi-functional composition of matter recited in Claim 34, wherein when the halogen is in the form of a halide salt.

56. The multi-functional composition of matter recited in Claim 34, wherein when the halogen is in the form of a bromide salt.

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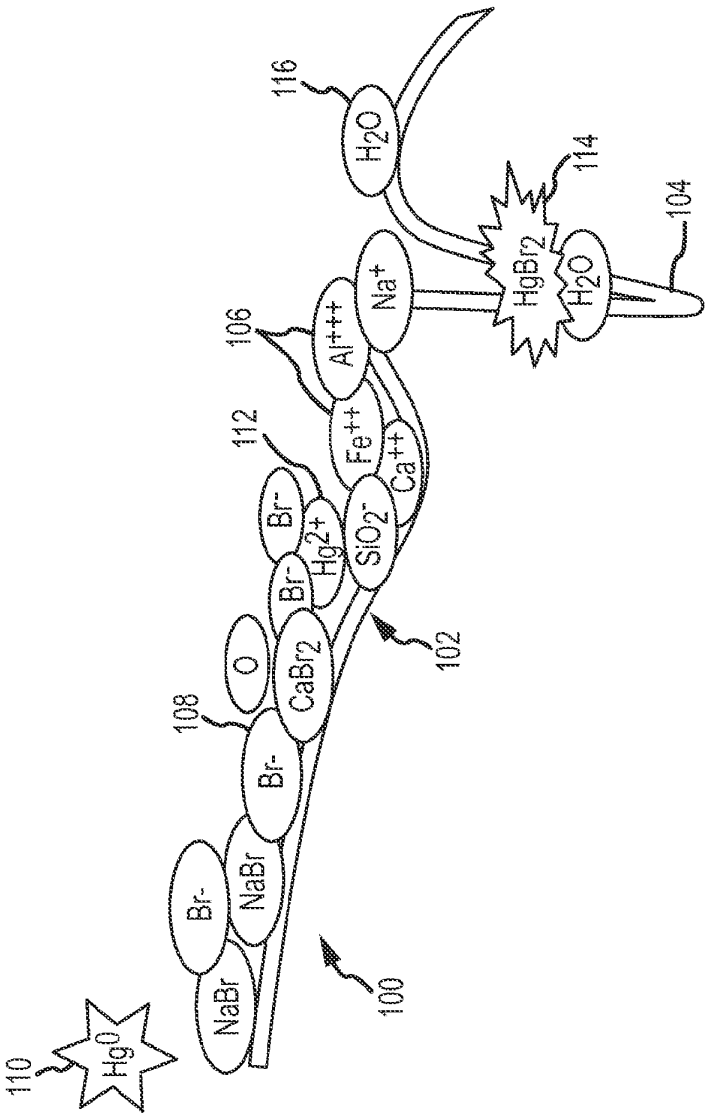

116
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114
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104
H_2O
106
Al^{+++}
Na^+
112
Fe^{++}
Ca^{++}
Br-
Hg^{2+}
SiO_2^-
Br
O
$CaBr_2$
102
108
Br-
NaBr
Br-
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100
110
Hg^0

FIG. 1



FIG.2

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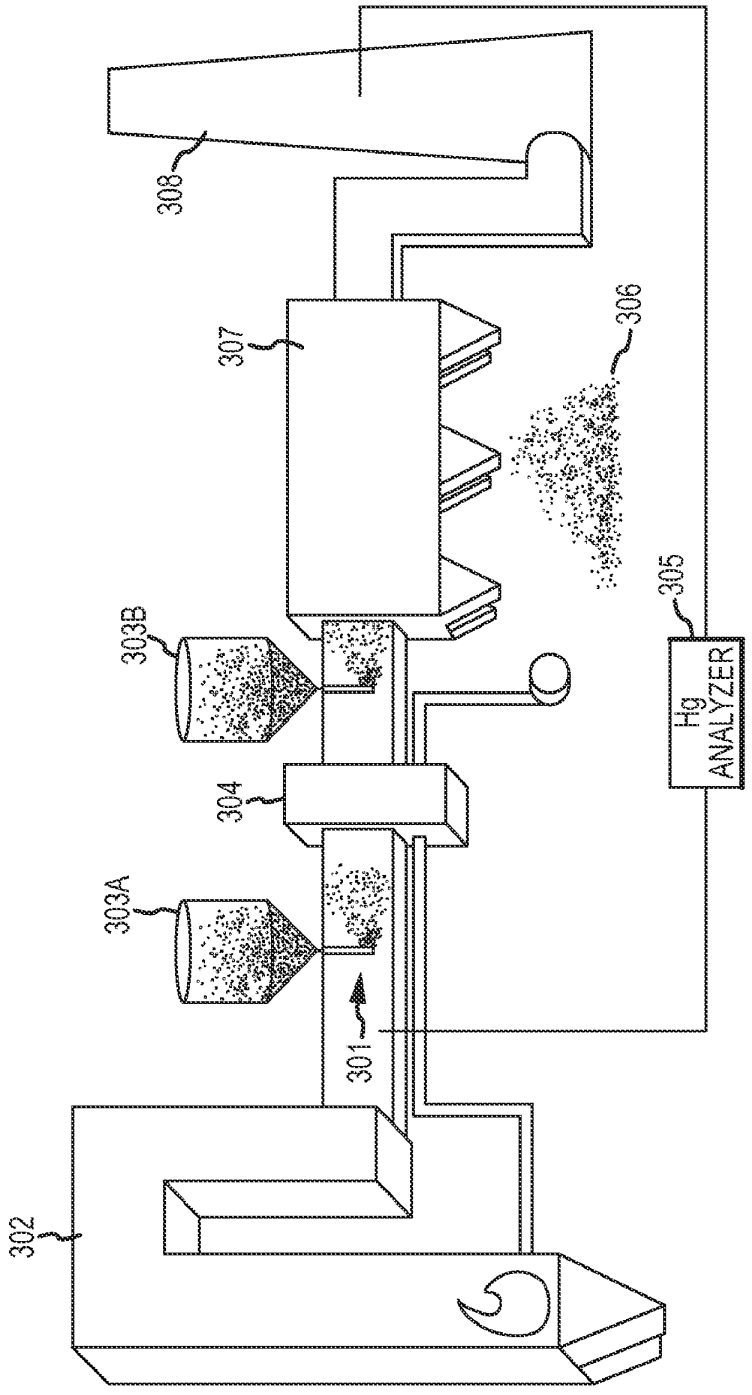


FIG.3

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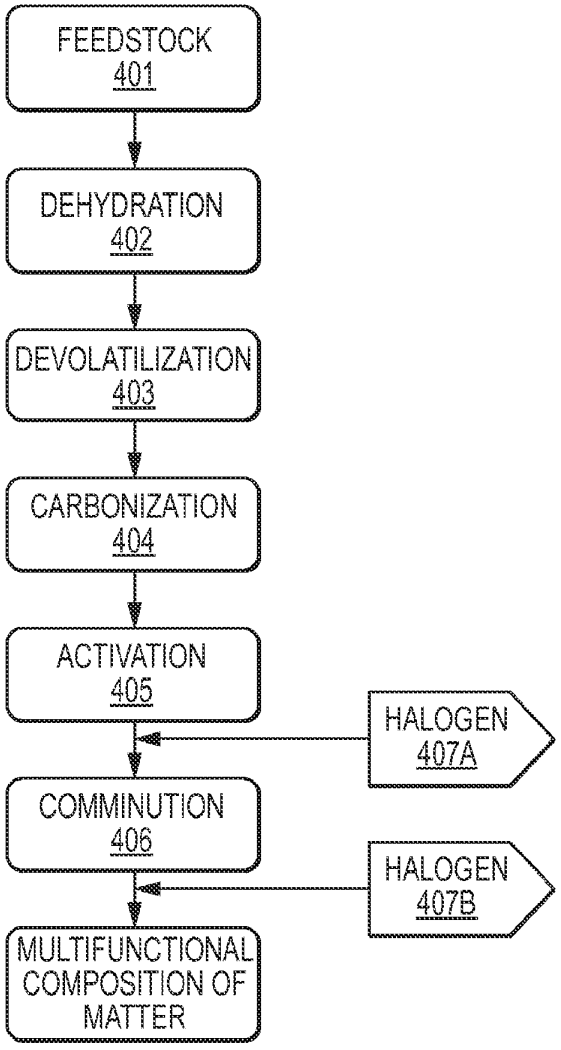


FIG.4

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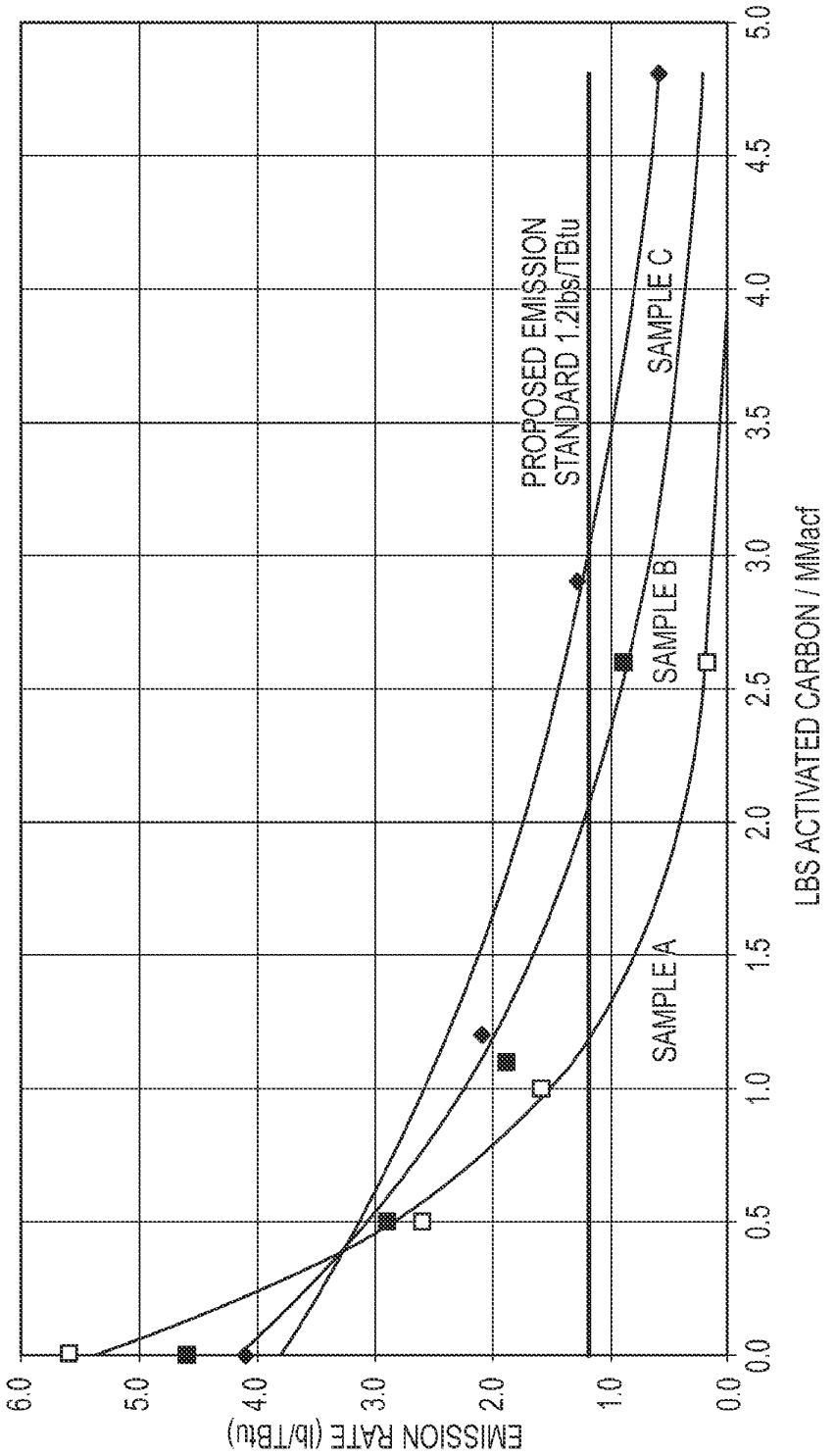


FIG.5

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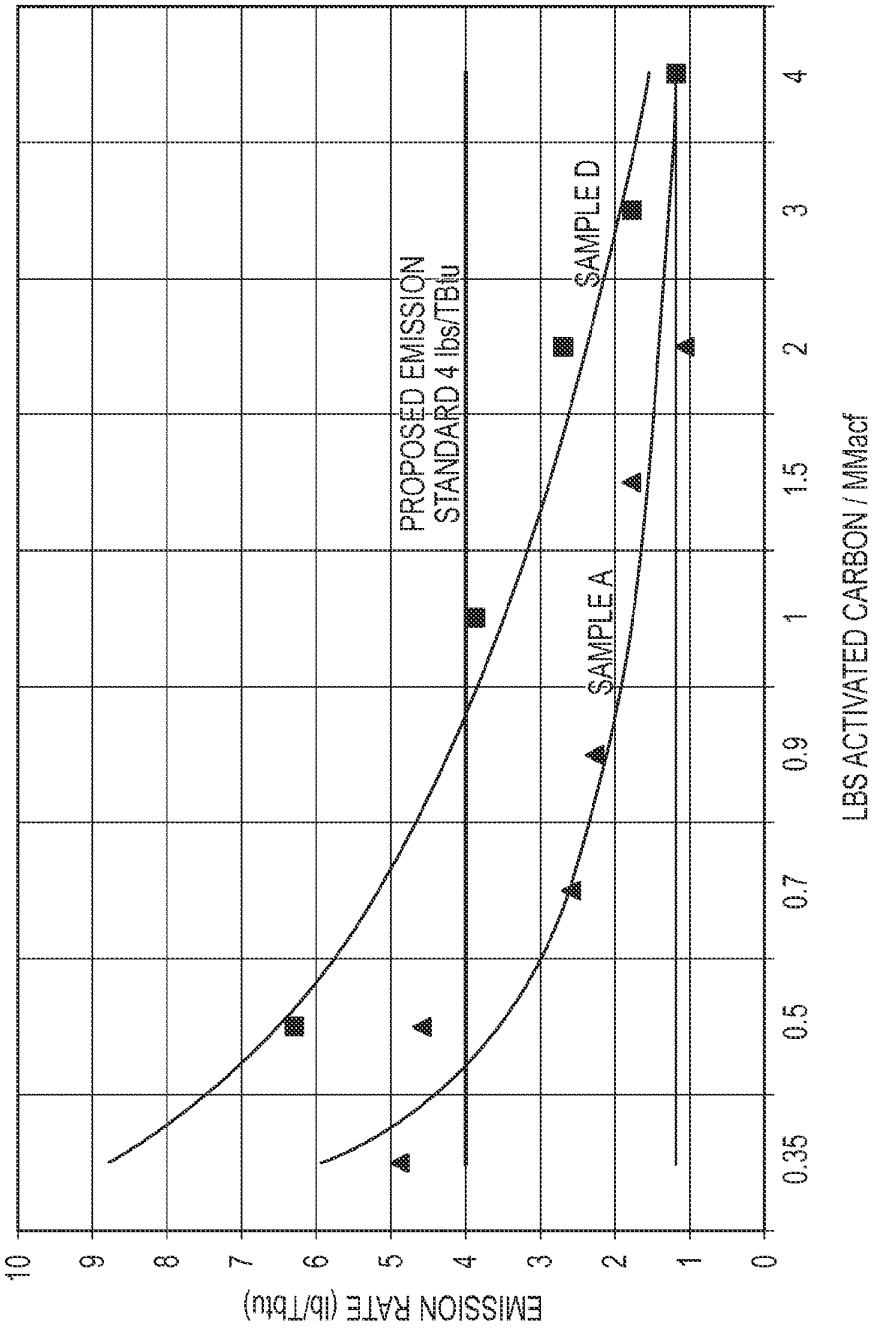


FIG.6

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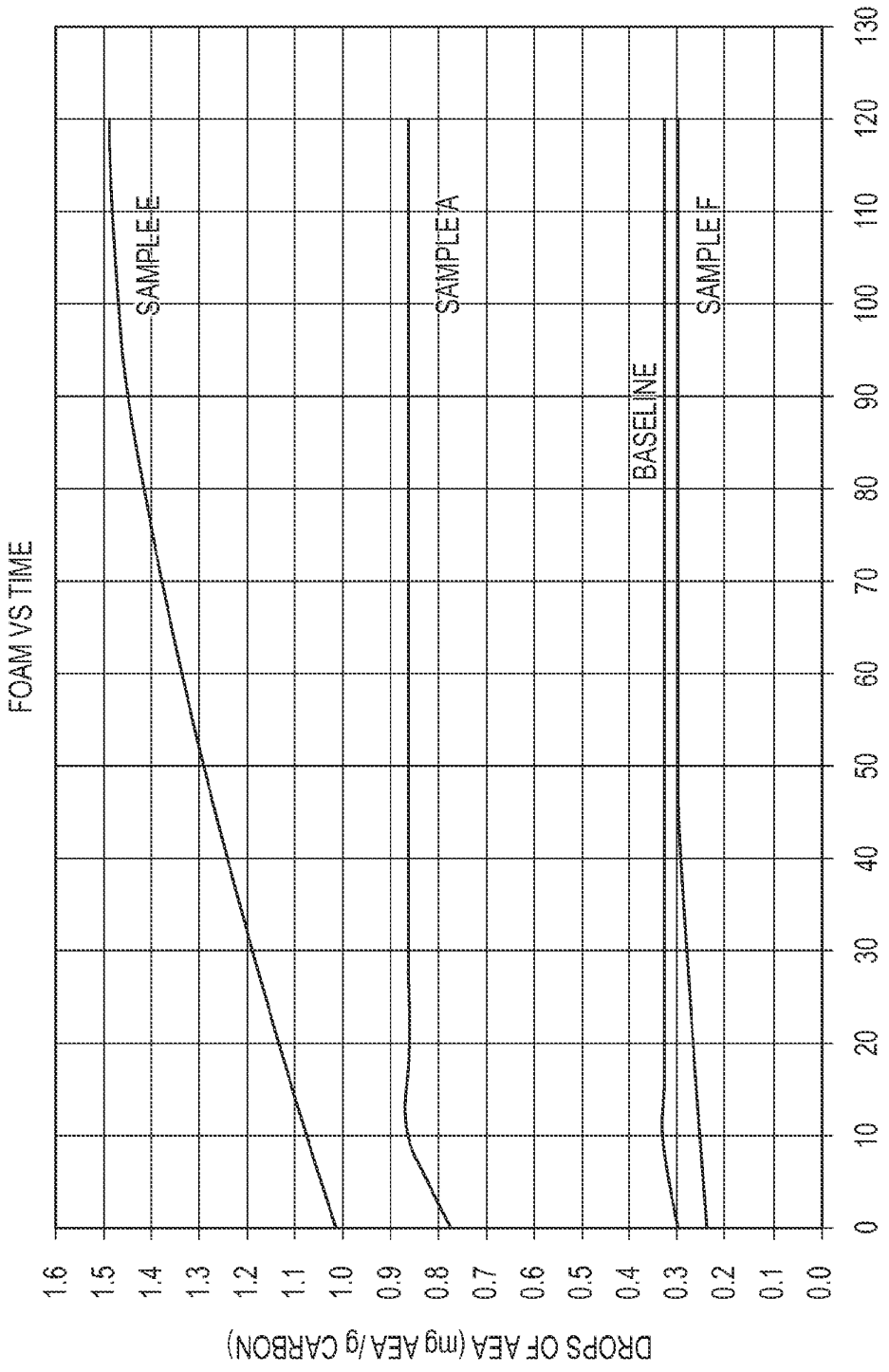


FIG.7

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/62253

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 53/34 (2013.01)
USPC - 423/210
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC - 423/210
IPC - B01D 53/34 (2013.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - all classes; NPL (key word limited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patent/Scholar
Search terms - Mercury, sorbent, "activated carbon", minerals, water, Vizcaino, Wong, Huston, Cannon, "residence time", flue, second, density, "g/cc", hardgrove, envelope

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y -- A	WO 2008/143831 A2 (Gadkaree et al.) 27 November 2008 (27.11.2008); para [0039], [0045], [0079], [00113], [00140], [00150] Table II	1, 8-29, 32-52, 55, 56 ---------- 30, 31, 53, and 54
Y -- A	US 2007/0265161 A1 (Gadkaree et al.) 15 November 2007 (15.11.2007); para [0028]; [0044]; claims 20 and 21	1, 8-29, 32-52, 55, 56 ---------- 30, 31, 53, and 54
Y -- A	US 4,976,848 A (Johnson) 11 December 1990 (11.12.1990); col. 1, ln 35-36; col. 5, ln. 38-43; col 8, ln 6-8; col 8, ln 35	1, 8-29, 32-52, 55, 56 ---------- 30, 31, 53, and 54
Y -- A	US 2006/0034743 A1 (Radway et al.) 16 February 2006 (16.02.2006); para [0019], [0020], and [0024]	22, 23, 45, 46 ---------- 30, 31, 53, and 54
Y -- A	US 2003/0206843 A1 (Nelson, Jr.) 06 November 2003 (06.11.2003); para [0018] and [0024]	34-36, 38-52, 55, and 56 ---------- 30, 31, 53, and 54
Y -- A	US 4,077,809 A (Plunguian et al.) 07 March 1978 (07.03.1978); col 2, ln 47-49; col 3, ln. 22-35; col 4, ln 44, Example 3	37 ---------- 30, 31, 53, and 54

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 February 2013 (02.02.2013)	25 FEB 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/62253

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1 and 8-56, directed to a multi-functional compsition of matter, comprising at least about 20 wt.% and not greater than about 75 wt.% fixed carbon, at least about 20 wt% and not greater than about 50wt.% minerals, at least about 1 wt.% and not greater than about 15 wt% of a halogen, and at least about 3 wt.% and not greater than about 12 wt.% aqueous-based solubilizing medium, wherein:
the multifunctional composition of matter has a median particle size of not greater than about 15 micron;
the multifunction composition of matter has a sum of micropore volume plus mesopore volume that is at least about 0.2 cc/g; and
the ratiof of micropore volume to mesopore volume is at least about 0.7 and is not greater than about 1.5.

See extra sheet below

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1 and 8-56

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

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Box No III Observations where unity of invention is lacking

Group II: Claims 2-7, directed to a composition of matter that when injected in a beta test at a coal fired power plant combusting high rank coal will result in emissions of mercury of less than 1.2 lbs/Tbtu at composition injection rates (in lbs/MMacf) of at least 30% less as compared to Comparative Sample C under comparable operating conditions.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group II does not require the percent composition for carbon, minerals, halogen and solubilizing medium, the micropore and mesopore ratio, or the particle size, as required by Group I.

Group I does not require mercury emission rates of less than 1.2 lbs/Tbtu at composition injection rates of at least approximately 30%less under comparable operating conditions, as required by Group II.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

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Espacenet

Bibliographic data: WO2014082076 (A1) — 2014-05-30

CONTROL OF MERCURY EMISSIONS

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Applicant(s): ECOLAB USA INC [US] ± (ECOLAB USA INC)

Classification: - international: ***B01D53/48; B01D53/64; B01D53/79; B01D53/83***
- cooperative: **B01D53/64; B01J20/22; B01J20/262; B01J20/264;** B01D2251/21; B01D2251/304; B01D2251/70; B01D2251/80; B01D2252/60; B01D2257/602; B01D2258/0283; B01J2220/44; F23J2215/60; F23J2219/40

Application number: WO2013US71978 20131126 Global Dossier

Priority number(s): US201261729823P 20121126 ; US201261729828P 20121126 ; US201261729837P 20121126

Also published as: CN104797324 (A) CN104797324 (B) EP2922615 (A1) EP2922615 (A4) US2014145111 (A1)

Abstract of WO2014082076 (A1)

Methods for controlling mercury emissions and/or reducing corrosion of equipment used in combustion processes are provided, and more particularly, methods for controlling mercury re-emissions from a wet flue gas desulfurizer and/or reducing corrosion of the wet flue gas desulfurizer.

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B01D 53/79 (2006.01) ***B01D 53/48*** (2006.01)

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(74) **Agent**: **SORENSEN, Andrew D.**; Ecolab USA Inc., 655 Lone Oak Drive, Eagan, Minnesota 55121 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2014/082076 A1

(54) **Title**: CONTROL OF MERCURY EMISSIONS

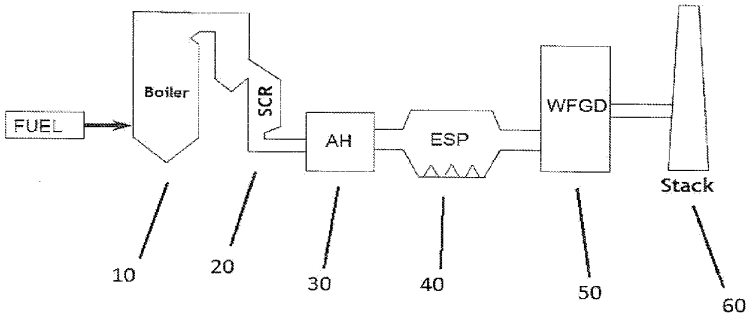


FIG. 1

(57) **Abstract**: Methods for controlling mercury emissions and/or reducing corrosion of equipment used in combustion processes are provided, and more particularly, methods for controlling mercury re-emissions from a wet flue gas desulfurizer and/or reducing corrosion of the wet flue gas desulfurizer.

CONTROL OF MERCURY EMISSIONS

TECHNICAL FIELD

[0001] The present disclosure relates generally to methods for controlling emissions of hazardous air pollutants, and more particularly, to methods for controlling mercury emissions from wet flue gas desulfurizers and/or controlling corrosion of scrubber equipment.

BACKGROUND

[0002] Many electricity generating units (EGUs) burn fossil fuels to produce electricity. The combustion process produces intense heat and flue gas, which contains hazardous air pollutants (e.g., Hg, CO_2, SO_2, SO_3, HCl). The flue gas is typically scrubbed prior to release into the atmosphere to reduce emissions of the pollutants. Wet flue gas desulfurizers (WFGDs) are one type of scrubber commonly used to reduce emissions. A WFGD contacts the combustion gas with an aqueous alkaline solution. This solution may be composed of magnesium compounds, sodium compounds, and slurries of lime or limestone to capture and neutralize acid gases, such as sulfur dioxide. The aqueous alkaline solution is commonly referred to as "WFGD liquor" or "scrubber liquor." In a forced oxidation system, oxygen may be introduced into the WFGD liquor to oxidize sulfite to sulfate. In many cases, this forms gypsum (calcium sulfate), as the final byproduct of scrubbing. Other systems may utilize inhibited or natural oxidation scrubbing, which results in sulfite salts or mixed sulfite/sulfate salts as byproduct.

[0003] Mercury entering EGUs as a contaminant of the fuel is released during combustion. Combustion gases exiting the boiler may contain mercury in three forms: particulate, oxidized, and elemental. Particulate mercury can be captured by particulate control devices such as electrostatic precipitators (ESPs) and fabric filters (FF). Oxidized mercury is water-soluble and as such, WFGDs can absorb the oxidized mercury from the combustion gas into the liquid phase. Elemental mercury, which is insoluble in water, is difficult to capture using existing air quality control devices.

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Accordingly, most elemental mercury control measures focus on converting elemental mercury into oxidized mercury. Mechanical methods such as fixed bed catalysts (e.g., SCRs), and chemical additives (e.g., calcium bromide, hydrogen bromide, ammonium chloride) have been developed that oxidize elemental mercury in the gas phase for subsequent capture with a WFGD. The captured mercury leaves the process via WFGD blow down.

[0004] As oxidized mercury is water soluble, WFGDs are theoretically capable of capturing nearly 100% of the oxidized mercury in a combustion gas. However, data collected by the Department of Energy (DOE) as well as numerous laboratory and commercial studies have shown lower capture efficiencies. The lower efficiencies are the result of reduction of oxidized mercury to elemental mercury (e.g., Hg^{2+} to Hg^{0}) within the WFGD scrubber liquor. For example, one reduction reaction involves the oxidation of sulfite by ionic mercury in the WFGD to provide sulfate and elemental mercury. The result is an increase across the WFGD of elemental mercury content in the scrubbed combustion gas, and thus a decrease in total mercury capture as measured from fossil fuel to stack. This reduction of oxidized mercury in the scrubber and subsequent release is known in the industry as mercury re-emission. The loss in WFGD mercury capture efficiency due to mercury re-emission will prevent some EGUs from meeting emissions requirements, necessitating installation of additional capital equipment.

[0005] There is a need in the art for improved methods of controlling mercury re-emission, which can supplement or replace current approaches of reducing hazardous air pollutant emissions.

SUMMARY

[0006] In one aspect, disclosed is a composition, comprising at least two components selected from a mercury re-emission additive; a free radical scavenger; and a polymer dispersant. The composition may comprise a mercury re-emission additive and a free radical scavenger. The composition may comprise a mercury re-emission additive and a polymer dispersant. The composition may comprise a free radical

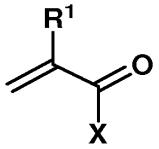
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scavenger and a polymer dispersant. The composition may comprise a mercury re-emission additive, a free radical scavenger, and a polymer dispersant.

[0007] The mercury re-emission additive may be a polymeric polydithiocarbamate compound.

[0008] The mercury re-emission control additive may be an ethylene dichloride ammonia polymer containing from 5 to 55 mole % of dithiocarbamate salt groups.

[0009] The mercury re-emission control additive may be a polymer derived from at least two monomers: acrylic-x and an alkylamine, wherein said acrylic-x has the following formula:



wherein X = OR, OH and salts thereof, or NHR^2 and wherein R^1 and R^2 is H or an alkyl or aryl group, wherein R is an alkyl or aryl group, wherein the molecular weight of said polymer is between 500 to 200,000, and wherein said polymer is modified to contain a functional group capable of scavenging one or more compositions containing one or more metals. The functional group capable of scavenging one or more compositions containing one or more metals may be a sulfur containing functional group.

[0010] The mercury re-emission control additive may be selected from the group consisting of: a polymeric polydithiocarbamate compound, sodium sulfide, sodium hydrosulfide, sodium bisulfide, a polysulfide, diethyldithiocarbamate or a sodium salt thereof, dimethyldithiocarbamate or a sodium salt thereof, a sodium polythiocarbonate, an inorganic polysulfide or blend, a sodium or calcium salt of 1,3,5-triazine-2,4,6(1H,3H,5H)-trithione, an activated carbon, 2,3-dimercaptopropanol, dimercaptosuccinic acid, 1,8-octanedithiol, 1,2-dithiolane-3-valeric acid, 2-methyl 1,3-dithiolane, mercaptoacetic acid or a sodium salt thereof, and a halogen-containing compound, or any combination thereof.

[0011] The free radical scavenger may be selected from the group consisting of: substituted phenols, derivatives of phenylenediamine, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), citric acid, tertiary butylhydroquinone (TBHQ),

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tocopherols, ascorbic acid, glutathione, lipoic acid, uric acid, and free radical scavenging enzymes, or any combination thereof.

[0012] The polymer dispersant may be selected from the group consisting of: polyacrylic acid, polyacrylates, polymaleic acid, maleic anhydride/ethyl acrylate/vinyl acrylate terpolymer and alkyl epoxy carboxylate, phosphinocarboxylic acids, and phosphonocarboxylic acids, or any combination thereof.

[0013] The polymer dispersant may be a polyacrylate or a phosphinosuccinate oligomer.

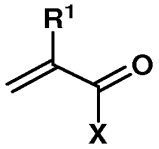
[0014] In another aspect, disclosed is a method of controlling mercury re-emission from a combustion process and/or reducing corrosion of equipment used in a combustion process, the method comprising applying to the combustion process at least two components selected from: a mercury re-emission additive; a free radical scavenger; and a polymer dispersant.

[0015] The components may be applied to a scrubber liquor of a wet flue gas desulpherizer (WFGD). The percent mercury re-emission from the scrubber liquor may be reduced to 10% or less. The percent mercury re-emission from the scrubber liquor may be reduced to 1% or less.

[0016] The mercury re-emission additive may be a polymeric polydithiocarbamate compound.

[0017] The mercury re-emission control additive may be an ethylene dichloride ammonia polymer containing from 5 to 55 mole % of dithiocarbamate salt groups.

[0018] The mercury re-emission control additive may be a polymer derived from at least two monomers: acrylic-x and an alkylamine, wherein said acrylic-x has the following formula:



wherein X = OR, OH and salts thereof, or NHR^2 and wherein R^1 and R^2 is H or an alkyl or aryl group, wherein R is an alkyl or aryl group, wherein the molecular weight of said polymer is between 500 to 200,000, and wherein said polymer is modified to contain a functional group capable of scavenging one or more compositions containing one or

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more metals. The functional group capable of scavenging one or more compositions containing one or more metals may be a sulfur containing functional group.

[0019] The mercury re-emission control additive may be selected from the group consisting of: a polymericpolydithiocarbamate compounds, sodium sulfide, sodium hydrosulfide, sodium bisulfide, a poly-sulfide, diethyldithiocarbamate or a sodium salt thereof, dimethyldithiocarbamate or a sodium salt thereof, a sodium polythiocarbonate, an inorganic polysulfide or blend, a sodium or calcium salt of 1,3,5-triazine-2,4,6(1H,3H,5H)-trithione, an activated carbon, 2,3-dimercaptopropanol, dimercaptosuccinic acid, 1,8-octanedithiol, 1,2-dithiolane-3-valeric acid, 2-methyl 1,3-dithiolane, mercaptoacetic acid or a sodium salt thereof, and a halogen-containing compound, or any combination thereof.

[0020] The free radical scavenger may be selected from the group consisting of: substituted phenols, derivatives of phenylenediamine, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), citric acid, tertiary butylhydroquinone (TBHQ), tocopherols, ascorbic acid, glutathione, lipoic acid, uric acid, and free radical scavenging enzymes, or any combination thereof.

[0021] The polymer dispersant may be selected from the group consisting of: polyacrylic acid, polyacrylates, polymaleic acid, maleic anhydride/ethyl acrylate/vinyl acrylate terpolymer and alkyl epoxy carboxylate, phosphinocarboxylic acids, and phosphonocarboxylic acids, or any combination thereof.

[0022] The polymer dispersant may be a polyacrylate or a phosphinosuccinate oligomer.

[0023] In another aspect, disclosed is a method of reducing mercury re-emission from a combustion process and/or reducing corrosion of equipment used in a combustion process. The method may include dispersing manganese species; inhibiting the formation of persulfate species; or complexing mercury and/or manganese. The method may include at least two of dispersing manganese species; inhibiting the formation of persulfate species; and complexing mercury and/or manganese.

[0024] The compositions, methods, and processes are further described herein.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1 depicts a diagram of a coal-fired power plant.

[0026] FIG. 2 depicts a diagram of a control strategy in a coal-fired power plant.

[0027] FIG. 3 depicts effect of oxidation-reduction potential on soluble manganese concentration.

[0028] FIG. 4 depicts effect of oxidation-reduction potential on soluble manganese concentration.

[0029] FIG. 5 depicts a correlation between oxidation-reduction potential and soluble manganese concentrations.

[0030] FIG. 6. depicts a correlation between soluble manganese and mercury re-emission.

DETAILED DESCRIPTION

[0031] Disclosed herein are compositions and methods for controlling mercury emissions from a scrubber process and/or reducing corrosion of scrubber equipment. The compositions and methods may include at least two components selected from a mercury re-emission additive, a free radical scavenger, and a polymer dispersant. The components may exhibit a synergistic effect for reducing mercury emissions and/or reducing corrosion.

[0032] The compositions and methods may control mercury emissions and/or corrosion by targeting one or more chemical species found in a combustion process, and in particular, species that lead to mercury re-emission and/or corrosion. Chemical species that can be targeted include, but are not limited to, persulfate species ($S_2O_8^{2-}$), manganese species (e.g., Mn^{4+}), mercury species (e.g., Hg^0), iron species, and free radical species (e.g., carbon dioxide anion radical). The disclosed compositions may target (e.g., bind to, inhibit formation of, or the like) one or more of these species, directly or indirectly.

[0033] The compositions provide several advantages over current technologies. In particular, the compositions can specifically target one or more species simultaneously, thereby providing reduced emissions and corrosion rates. The compositions can allow

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for specific components of the composition to focus on an intended target (e.g., mercury) without interference from another chemical species (e.g., manganese).

1. Definition of Terms

[0034] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control. Preferred methods and materials are described below, although methods and materials similar or equivalent to those described herein can be used in practice or testing of the present invention. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their entirety. The materials, methods, and examples disclosed herein are illustrative only and not intended to be limiting.

[0035] As used in the specification and the appended claims, the singular forms "a," "and" and "the" include plural references unless the context clearly dictates otherwise. The terms "comprise(s)," "include(s)," "having," "has," "can," "contain(s)," and variants thereof, as used herein, are intended to be open-ended transitional phrases, terms, or words that do not preclude the possibility of additional acts or structures. The present disclosure also contemplates other embodiments "comprising," "consisting of" and "consisting essentially of," the embodiments or elements presented herein, whether explicitly set forth or not.

[0036] The term "mercury re-emission," as used herein, refers to the phenomenon when water-soluble oxidized mercury (Hg^{2+}) undergoes chemical reduction to water-insoluble elemental mercury (Hg^0) in a wet flue gas desulfurization (WFGD) scrubber. It is believed the reduction occurs because of a reaction between mercury ions and sulfite ions present in the WFGD liquor. Because elemental mercury is insoluble in water, it exits the scrubber in the gas-phase. Thus the elemental mercury concentration in the flue gas exiting the scrubber is higher than the elemental mercury concentration entering the scrubber.

[0037] The term "percent mercury re-emission," as used herein, refers to:

$$\%\,\mathrm{Hg\ Re\text{-}emission} = \left(\frac{Hg^0_{outlet} - Hg^0_{inlet}}{Hg^T_{Inlet} - Hg^0_{Inlet}} \right) \times 100 \qquad \text{Equation A}$$

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where "outlet" refers to EGU stack gas mercury measurement, "inlet" refers to gas concentrations at the inlet to the WFGD, "0" refers to the concentration of elemental mercury in the gas, and "T" refers to the total concentration of mercury in the gas. The "outlet" measurement may refer to mercury gas measurements made at any location after the gas has exited the WFGD.

[0038] The term "percent mercury oxidation," as used herein, refers to:

$$\%\ \text{Hg Oxidation} = \left(\frac{Hg^{T}_{inlet} - Hg^{0}_{inlet}}{Hg^{T}_{Inlet}} \right) \times 100$$

Equation B

where the super- and sub-scripts have the same meaning as defined in Equation A above.

[0039] The term "percent mercury capture," as used herein, refers to:

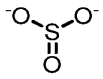
$$\%\ \text{Hg Capture} = \left(\frac{Hg^{T}_{Inlet} - Hg^{T}_{outlet}}{Hg^{T}_{Inlet}} \right) \times 100$$

Equation C

where the super- and sub-scripts have the same meaning as defined in Equation A above.

[0040] The term "oxidation-reduction potential," as used herein, refers to the summation of all the oxidation and reduction potentials in a given solution or scrubber liquor. As such, the oxidation-reduction potential varies depending on a liquor composition. Oxidation-reduction potential also depends on the fuel source of the electric generating unit, and operations of the wet flue gas desulfurizer (e.g., forced oxidation or natural, alkali source, purge rate).

[0041] The term "sulfite," as used herein, refers to SO_3^{2-}, and may have the structure shown below.



sulfite

[0042] The term "sulfite radical," as used herein, refers to $SO_3^{\bullet -}$, and may have the structure shown below.

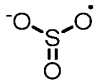
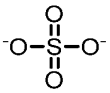


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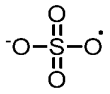
sulfite radical

[0043] The term "sulfate," as used herein, refers to SO_4^{2-}, and may have the structure shown below.



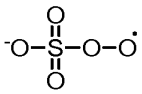
sulfate

[0044] The term "sulfate radical," as used herein, refers to $SO_4^{\bullet-}$, and may have the structure shown below.



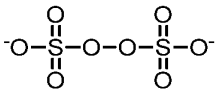
sulfate radical

[0045] The term "peroxymonosulfate radical," as used herein, refers to $SO_5^{\bullet-}$, and may have the structure shown below.



peroxymonosulfate radical

[0046] The term "persulfate," as used herein, refers to $S_2O_8^{2-}$, and may have the structure shown below.



persulfate

[0047] The term "carbon dioxide," as used herein, refers to CO_2, and may have the structure shown below.

O=C=O

carbon dioxide

[0048] The term "carbon dioxide anion radical," as used herein, refers to $CO_2^{\bullet-}$, and may have the structure shown below.



carbon dioxide anion radical

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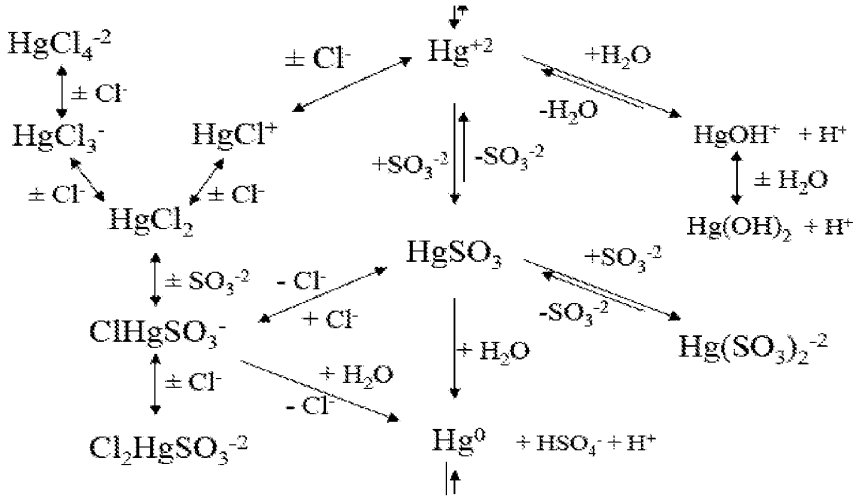
2. Targets for Reducing Mercury Re-emission and/or Corrosion

[0049] WFGD scrubber liquors contain multiple chemical species intended to react or interact with hazardous pollutants in order to prevent emission of the pollutants into the atmosphere. Within the liquor, a multitude of chemical reactions occur (e.g., oxidation/reductions), producing a variety of chemical species. Some of the reactions are favorable for reducing emissions, whereas others may result in mercury re-emission and/or corrosion, for example.

[0050] It has been discovered that several of these chemical species in a combustion gas and/or in a scrubber liquor can be targeted, directly or indirectly, to reduce mercury re-emissions and/or corrosion processes. In particular, persulfate species, transition metal species, and free radical species can be targeted to control mercury re-emission and /or corrosion processes.

[0051] In addition, various mercury species can be directly targeted to reduce mercury re-emission, such as those shown in Scheme 1. Other chemical species that may be present and can optionally be targeted include, but are not limited to, chloride, bromide, fluoride, HSO_3^-, $CaSO_4$, SeO_3^{2-}, organic acids, Mn^{2+}, Fe^{3+}, and other species.

Scheme 1



a. Persulfate Species

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[0052] Persulfate species present in WFGD scrubber liquors may be responsible for mercury re-emission. Persulfate species may also contribute to corrosion of scrubber equipment by increasing scrubber liquor oxidation-reduction potential, which leads to transition metal precipitation onto scrubber surfaces and galvanic corrosion.

[0053] Persulfate species ($S_2O_8^{2-}$) formation can be targeted to reduce mercury re-emissions and/or corrosion processes. In particular, constituents that lead to persulfate formation in WFGD scrubber liquors can be targeted to prevent formation of persulfate. The downstream activity of persulfate and species resulting from persulfate reaction, can also be targeted to reduce mercury re-emissions and/or corrosion processes. In particular, free radical species resulting from persulfate activity can be targeted to reduce mercury re-emissions and/or corrosion processes.

[0054] Persulfate species may cause mercury re-emission by initiating the reduction of ionic mercury species in the WFGD by oxidizing an organic acid (equation 1, dibasic acid (DBA) is shown as an example), which in turn yields CO_2 anion radical (equation 2), which reduces mercuric chloride, leading to mercury re-emission (equation 3).

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}\bullet \quad (1)$$

$$SO_4^{-}\bullet + C_2O_4^{2-}\ (DBA) \rightarrow SO_4^{2-} + CO_2^{-}\bullet + CO_2 \quad (2)$$

$$CO_2^{-}\bullet + Hg^{2+} \rightarrow CO_2 + Hg^{+} \quad (3)$$

[0055] The persulfate species may be formed in the WFGD via catalytic reaction of sulfite species over Mn and/or Fe solid surfaces, especially at high redox potential over 400 mV. The reaction may be initiated by the transfer of an electron from a sulfite to a transition metal, such as iron or manganese, which are both in the +3 oxidation state. The reaction yields a sulfite anion radical (equation 4).

$$M^{3+} + SO_3^{2-} \rightarrow M^{2+} + SO_3^{-}\bullet \quad (4)$$

[0056] Reaction of the sulfite anion radical with oxygen produces peroxymonosulfate radical, which in turn reacts with another sulfite anion radical to produce persulfate (equations 5 and 6).

$$O_2 + SO_3^{\bullet -} \rightarrow SO_5^{\bullet -} \quad (5)$$

$$SO_5^{\bullet -} + SO_3^{\bullet -} \rightarrow S_2O_8^{2-} \quad (6)$$

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[0057] While chloride species in the scrubber liquor act as scavengers for persulfate, the chlorine resulting from this scavenging can catalyze propagation reactions resulting in more sulfate radicals (equation 7), which may contribute to further persulfate production and mercury re-emission.

$$S_2O_8^{2-} + 2Cl^- \rightarrow 2SO_4^{2-} + Cl_2 \quad (7)$$

[0058] The oxidation of organics referred to above may also be responsible for releasing complexed mercury into the WFGD liquor, thus contributing to higher mercury re-emission.

b. Manganese Species (Mn^{4+} and Mn^{2+})

[0059] Manganese species, solid manganese species in particular, can contribute to mercury re-emission by catalyzing the formation of persulfate, which as described above, can lead to the reduction of ionic mercury to elemental mercury. Manganese species can also lead to corrosion of scrubber surfaces. Mn^{4+} species can cause corrosion by precipitating out of WFGD scrubber liquors onto surfaces of the scrubber and acting as galvanic cathodes (e.g., MnO_2 deposits on WFGD alloys can act as galvanic cathodes to promote corrosion of the WFGD metal). These precipitated species can also catalyze the formation of persulfate (equation 4).

[0060] Manganese species can be targeted to reduce mercury re-emissions and/or corrosion processes. Manganese species that can be targeted include Mn^{4+} species and Mn^{2+} species. Mn^{4+} species can be targeted by controlling the scrubber oxidation-reduction potential. Oxidation-reduction potential (ORP) has an influence on mercury re-emission and corrosion in combustion processes due to its strong influence on transition metal oxidation state within WFGD scrubber liquors. At high ORP, manganese may be in the Mn^{4+} state and can precipitate out of the scrubber liquor onto WFGD surfaces, which leads to corrosion. When ORP is lowered, the manganese may be reduced to Mn^{2+} and become soluble in the scrubber liquor.

[0061] The soluble Mn^{2+} can be optionally be targeted for removal from the scrubber liquor, eliminating the possibility of oxidation back to Mn^{4+} and its catalysis of persulfate formation. For example, both Mn^{4+} and Mn^{2+} can be targeted with binding agents to inactivate the metal surfaces for reaction. Such binding may prevent

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the reaction of the metals with sulfite, or engaging in other reactions that may contribute directly or indirectly to mercury re-emission and/or corrosion.

[0062] Targeting of persulfate species, as described above, can also be effective to reduce corrosion and/or mercury re-emission linked to Mn^{4+} activity. For example, when Mn-caused corrosion takes place, a strong oxidizer such as persulfate may be present. The oxidizer can raise the oxidation-potential of the scrubber liquor and precipitate out more manganese onto WFGD surfaces, leading to further corrosion. By reducing or preventing persulfate formation, the oxidation-reduction potential can be lowered, which results in less solid manganese precipitation and corrosion.

c. Free Radical Species

[0063] Free radical species can be targeted to reduce mercury re-emissions and/or corrosion processes. Free radical species that can be targeted include sulfite anion radicals, peroxymonosulfate radicals, and carbon dioxide anion radicals. The free radical species may be involved in the production of persulfate, as well as subsequent reactions leading to reduction of ionic mercury to elemental mercury. As shown in equations 4-6, sulfite anion radicals and peroxymonosulfate radicals may contribute to the formation of persulfate species in WFGD scrubber liquors. Equation 3 shows that carbon dioxide anion radical may contribute to mercury re-emission by reducing mercury species in WFGD scrubber liquors. Consequently, a multitude of free radicals can be targeted.

d. Mercury Species

[0064] Mercury species can be directly targeted to reduce mercury re-emissions. Mercury species that can be targeted include elemental mercury and ionic mercury species. Ionic mercury can be targeted for removal from WFGD scrubber liquors, thereby minimizing the species available for participation in mercury re-emission processes.

3. Composition & Method Design

[0065] Based on the foregoing targets for reducing mercury re-emission and/or corrosion, compositions and methods are provided for targeting one or more of these

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species. The compositions and methods can include multiple components to target multiple species that contribute to mercury re-emission and/or corrosion processes. The compositions and methods can include components that enhance the effectiveness of other components, and in particular, effectiveness at targeting a specific chemical species. The composition and method components may together exhibit a synergistic effect.

[0066] In certain embodiments, a composition or method of the invention may target persulfate in a WFGD scrubber liquor. Targeting persulfate may prevent or reduce mercury re-emission (equations 1-3). For example, a composition or method can target species that result in persulfate formation, or species resulting from persulfate activity leading to mercury re-emission. Targeting persulfate may also allow for control of scrubber liquor oxidation-reduction potential. In particular, reduction of the ORP may mitigate precipitation of manganese species and their corrosive effect.

[0067] In certain embodiments, a composition or method of the invention may target transition metal species, including precipitated transition metal species (e.g., Mn^{4+}). The composition may directly target transition metal species, or indirectly target said species by reducing oxidation-reduction potential of a WFGD scrubber liquor. The liquor, having a reduced ORP, may solubilize solid manganese, preventing its participation in corrosion of scrubber surfaces. Solubilizing the manganese may also prevent or minimize its reaction with sulfite, which would lead to persulfate formation (equation 4). The solubilized manganese can optionally be targeted by a composition or method of the invention, removing the manganese or inactivating the species in the scrubber liquor. The composition may bind to or flocculate the metal species to remove or inactivate it from the scrubber liquor. As such, the removed or inactivated metal will no longer be available to participate in corrosive processes and promotion of mercury re-emission. In certain embodiments, a composition or method of the invention can target mercury species, and in particular, can flocculate, chelate, or otherwise bind to ionic mercury species to prevent reduction of the mercury to elemental mercury.

[0068] In certain embodiments, a composition or method of the invention may target free radical species (e.g., $SO_3^{\bullet-}$, $SO_5^{\bullet-}$, $CO_2^{\bullet-}$). The composition or method may prevent

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or reduce free radical participation in processes leading to mercury re-emission (equations 1-3), and/or persulfate formation (equations 5 and 6). The composition or method may specifically target carbon dioxide anion radical to prevent its reaction with ionic mercury, which would lead to elemental mercury and re-emission.

[0069] In certain embodiments, a composition or method of the invention can target two or more of: persulfate species, transition metal species (Mn, Fe, Hg), free radical species, and oxidation-reduction potential.

[0070] Suitable approaches for reducing mercury re-emission and/or controlling corrosion thus include:

(1) reducing the availability of metal species that can react with sulfite to produce persulfate (equation 4) by binding to or otherwise inactivating solid and/or solubilized metal species from further reactions (e.g., reduction of mercury to elemental mercury; reduction of sulfite to sulfite anion radical);

(2) reducing or preventing persulfate formation in the WFGD before it leads to mercury re-emission (equations 4-6);

(3) reducing or preventing persulfate initiated mercury re-emission by targeting downstream free radicals, such as carbon dioxide anion radical, which can react with and reduce ionic mercury (equation 3); and

(4) controlling the oxidation-reduction potential of WFGD scrubber liquors in order to reduce the amount of solid Mn/Fe deposited on scrubber surfaces.

4. Compositions for Reducing Mercury Re-emission and/or Corrosion

[0071] In one aspect, disclosed are compositions for controlling mercury emissions from a scrubber process and/or reducing corrosion of scrubber equipment. The compositions may include at least two components selected from a mercury re-emission additive, a free radical scavenger, and a polymer dispersant. In certain embodiments, the compositions comprise a mercury re-emission additive and a free radical scavenger. In certain embodiments, the compositions comprise a mercury re-emission additive and a polymer dispersant. In certain embodiments, the compositions comprise a free radical scavenger and a polymer dispersant. In certain embodiments,

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the compositions comprise a mercury re-emission additive, a free radical scavenger, and a polymer dispersant.

[0072] The compositions may reduce mercury emissions and/or corrosion by one or more of the following: reducing the availability of solid metal species (e.g., Mn^{4+}) that can react with sulfite leading to persurfate formation; reducing the amount of persulfate ($S_2O_8^{2-}$) species present in a WFGD scrubber liquor; reducing the amount of free radical species (e.g., carbon dioxide anion radical) present in a WFGD scrubber liquor; and/or controlling the oxidation-reduction potential of WFGD scrubber liquors in order to reduce the amount of solid Mn/Fe deposited on scrubber surfaces.

[0073] One or more components of the disclosed compositions may bind to soluble mercury species and/or manganese species, thereby reducing mercury re-emission and/or corrosion of equipment used in the combustion process (e.g., a WFGD surface). In certain embodiments, the mercury re-emission additive and/or the polymer dispersant may bind to mercury species and/or manganese species. In certain embodiments, the composition includes a mercury re-emission additive configured to bind mercury species; and a polymer dispersant configured to bind manganese species.

[0074] The mercury re-emission additive may have a heavy metal selectivity of: Hg > Ag > Cd > Cu > Pb > Zn > Co(II) > Ni > Fe(II) > Mn. However, the manganese concentration in a scrubber liquor may be so high that it diminishes the effectiveness of a mercury re-emission additive, applied alone, to interact with and reduce emission of mercury species. A composition may include one component tailored to mercury (e.g., a mercury re-emission additive) and one component tailored to manganese (e.g., a polymer dispersant). The components may provide a synergistic effect for reducing mercury re-emission and/or corrosion.

[0075] One or more components of the composition may reduce the oxidation-reduction potential of a scrubber liquor, thereby increasing soluble manganese species (e.g., Mn^{2+}) present in the scrubber liquor compared to insoluble manganese species (e.g., Mn^{4+}). Optionally, the soluble manganese species can be targeted (e.g., via binding) by the same or another component of the composition. By solubilizing the manganese, and optionally binding it, the disclosed compositions may provide a reduction in manganese corrosion on alloy surfaces (e.g., a WFGD surface), as well as

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a reduction in the ability of solid manganese to react with sulfite to form sulfate anion radical, which leads to persulfate formation. In certain embodiments, the composition includes a mercury re-emission additive configured to reduce the oxidation-reduction potential of a scrubber liquor; and a polymer dispersant configured to bind solubilized manganese species present in the scrubber liquor.

[0076] One or more components of the composition may react with free radical species (e.g., carbon dioxide radical anion) to interrupt processes that lead to mercury re-emission and/or corrosion of metal surfaces. For example, a free radical scavenger may react with carbon dioxide anion radical before it reduces ionic mercury present in the scrubber liquor.

[0077] The dosage of the disclosed compositions may vary as necessitated to reduce or prevent mercury re-emission and/or to reduce or prevent corrosion. The dosage amounts can be selected based on, for example, a measured ionic mercury concentration and/or oxidation-reduction potential of a scrubber liquor. Process medium quality and extent of process medium treatment are a couple of factors that can be considered by one of ordinary skill in the art in selecting dosage amount. A jar test analysis is a typical example of what is utilized as a basis for determining the amount of dosage required to achieve effective metals removal in the context of a process water medium, e.g. wastewater. The dosage of the compositions may range from 1 to 10,000 ppm actives, or 100 to 1,000 ppm actives.

a. Mercury Re-emission Additives

[0078] Mercury re-emission control additives that can be used with compositions of the invention include any additive suitable to reduce and/or prevent mercury re-emission from combustion processes, and in particular, scrubber liquors. In certain embodiments, the mercury re-emission additive may bind to or inactivate mercury. In certain embodiments, the mercury re-emission additive may be used to control scrubber liquor oxidation-reduction potential (e.g., reduce ORP). In certain embodiments, the mercury re-emission additive may be used to flocculate one or more metal species (e.g., mercury, iron, and/or manganese).

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[0079] In certain embodiments, the mercury re-emission control additive may be a polymeric polydithiocarbamate compound (e.g., MerControl 8034, also referred to herein as "poly-DTC"), or another sulfur-containing additive such as sodium sulfide, sodium hydrosulfide, sodium bisulfide, or a polysulfide. In certain embodiments, the mercury re-emission additive may be a thiocarbonate or a polythiocarbonate. In certain embodiments, the mercury re-emission additive may be sodium polythiocarbonate.

[0080] In certain embodiments, the mercury re-emission control additive may be diethyldithiocarbamate or a sodium salt thereof. In certain embodiments, the mercury re-emission control additive may be dimethyldithiocarbamate or a sodium salt thereof.

[0081] In certain embodiments, the mercury re-emission control additive may be an inorganic polysulfide or blend, such as PRAVO, a product from Vosteen.

[0082] In certain embodiments, the mercury re-emission additive may be a sodium or calcium salt of 1,3,5-triazine-2,4,6(1H,3H,5H)-trithione (also referred to as trimercapto-S-triazine), such as TMT-15, a product from Degussa.

[0083] In certain embodiments, the mercury re-emission control additive may be an activated carbon, such as disclosed in US Patent 7,727,307 B2.

[0084] In certain embodiments, the mercury re-emission control additive may be a dithiol, a dithiolane, or a thiol having a single thiol group and either an oxygen or a hydroxyl group. Suitable dithiols include, but are not limited to, 2,3-dimercaptopropanol, dimercaptosuccinic acid, and 1,8-octanedithiol. Suitable dithiolanes include, but are not limited to, 1,2-dithiolane-3-valeric acid and 2-methyl 1,3-dithiolane. Suitable thiols include, but are not limited to, mercaptoacetic acid and sodium salts thereof.

[0085] In certain embodiments, the mercury re-emission control additive may be a halogen-containing compound. Suitable halogen-containing compounds include, but are not limited to, calcium bromide, sodium bromide, potassium bromide, hydrogen bromide, calcium iodide, and ammonium chloride.

[0086] In certain embodiments, a combination of mercury re-emission controlled additives may be used. In one preferred embodiment, the mercury re-emission control additive comprises a polymeric polydithiocarbamate compound.

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(i) Ethylene Dichloride Ammonia Polymer Containing Dithiocarbamate Groups

[0087] The mercury re-emission control additive may be a water-soluble ethylene dichloride ammonia polymer having a molecular weight of from 500 to 10,000, and containing from 5 to 55 mole % of dithiocarbamate salt groups to prevent re-emission of mercury across a WFGD.

[0088] The polymer may be prepared by the reaction of ethylene dichloride and ammonia to provide a polyamine or polyimine. The polyamine or polyimine may have a molecular weight range of 500-100,000. In a preferred embodiment, the molecular weight may be 1,500 to 10,000, with the most preferred molecular weight range being 1,500 to 5,000.

[0089] The dithiocarbamate groups of the polymers may be introduced by the reaction of the polyamines or polyimines with carbon disulfide to produce polymeric dithiocarbamic acid or their salts. Such reaction is preferably carried out in a solvent such as water or alcohol at a temperature of from 30 °C and 100 °C for periods of time ranging between 1 and 10 hours. Good conversion may be obtained at temperatures between 40 ° and 70 °C for 2 to 5 hours.

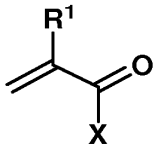
[0090] The mole % of dithiocarbamate salt groups in the finished polymer may be within the range of 5 to 55%, 20 to 40 mole %, or 25 to 30 mole %. The salts include, but are not limited to, alkaline and alkali earth such as sodium, lithium, potassium or calcium.

[0091] The finished polymer may be applied to a combustion process at a ratio of 1:1 to 2000:1 weight copolymer to weight of mercury being captured. One preferred ratio may be from 5:1 to 1000:1 more preferably from 5:1 to 500:1.

(ii) Acrylic-x and Alkylamine Polymer

[0092] The mercury re-emission control additive may be a composition comprising a polymer derived from at least two monomers: acrylic-x and an alkylamine, wherein said acrylic-x has the following formula:

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wherein X = OR, OH and salts thereof, or NHR^2 and wherein R^1 and R^2 is H or an alkyl or aryl group, wherein R is an alkyl or aryl group, wherein the molecular weight of said polymer is between 500 to 200,000, and wherein said polymer is modified to contain a functional group capable of scavenging one or more compositions containing one or more metals.

[0093] The metals can include zero valent, monovalent, and multivalent metals. The metals may or may not be ligated by organic or inorganic compounds. Also, the metals can be radioactive and nonradioactive. Examples include, but are not limited to, transition metals and heavy metals. Specific metals can include, but are not limited to: copper, nickel, zinc, lead, mercury, cadmium, silver, iron, manganese, palladium, platinum, strontium, selenium, arsenic, cobalt and gold.

[0094] The molecular weight of the polymers can vary. For example, the target species/application for the polymers can be one consideration. Another factor can be monomer selection. Molecular weight can be calculated by various means known to those of ordinary skill in the art. For example, size exclusion chromatography, as discussed in the examples below can be utilized. When molecular weight is mentioned, it is referring to the molecular weight for the unmodified polymer, otherwise referred to as the polymer backbone. The functional groups that are added to the backbone are not part of the calculation. Thus the molecular weight of the polymer with the functional groups can far exceed the molecular weight range. In one embodiment, the molecular weight of the polymer is from 1,000 to 16,000. In another embodiment, the molecular weight of said polymer is from 1,500 to 8,000.

[0095] Various functional groups can be utilized for metal scavenging. The following phraseology would be well understood by one of ordinary skill in the art: wherein said polymer is modified to contain a functional group capable of scavenging one or more compositions containing one or more metals. More specifically, the polymer is modified to contain a functional group that can bind metals. In one embodiment, the functional group contains a sulfide containing chemistry. In another

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embodiment, the functional group is a dithiocarbamate salt group. In another embodiment, the functional groups are at least one of the following: alkylene phosphate groups, alkylene carboxylic acids and salts thereof, oxime groups, amidooxime groups, dithiocarbamic acids and salts thereof, hydroxamic acids, or nitrogen oxides.

[0096] The molar amounts of the functional group relative to the total amines contained in the unmodified polymer can vary as well. For example, the reaction of 3.0 molar equivalents of carbon disulfide to a 1.0:1.0 mole ratio acrylic acid / TEPA copolymer, which contains 4 molar equivalents of amines per repeat unit after polymerization, will result in a polymer that is modified to contain 75 mole % dithiocarbamate salt group. In other words, 75 % of the total amines in the unmodified polymer have been converted to dithiocarbamate salt groups.

[0097] In one embodiment, the polymer may have between 5 to 100 mole % of the dithiocarbamate salt group. In a further embodiment, the polymer has from 25 to 90 mole % of the dithiocarbamate salt group. In yet a further embodiment, the polymer has from 55 to 80 mole % of the dithiocarbamate salt group.

[0098] Monomer selection will depend on the desired polymer. In one embodiment, the alkylamine is at least one of the following: an ethyleneamine, a polyethylenepolyamine, ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetraamine (TETA), tetraethylenepetamine (TEPA) and pentaethylenehexamine (PEHA). In another embodiment, the acrylic-x is at least one of the following: methyl acrylate, methyl methacrylate, ethyl acrylate, and ethyl methacrylate, propyl acrylate, and propyl methacrylate. In another embodiment, the acrylic-x is at least one of the following: acrylic acid and salts thereof, methacrylic acid and salts thereof, acrylamide, and methacrylamide.

[0099] The molar ratio between monomers that make up the polymer, especially acrylic-x and alkylamine can vary and depend upon the resultant polymer product that is desired. The molar ratio used is defined as the moles of acrylic-x divided by the moles of alkylamine. In one embodiment, the molar ratio between acrylic-x and alkylamine is from 0.85 to 1.5. In another embodiment, the molar ratio between acrylic-x and alkylamine is from 1.0 to 1.2. Various combinations of acrylic-x and

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alkylamines are encompassed by this invention as well as associated molecular weight of the polymers.

[00100] In one embodiment, the acrylic-x is an acrylic ester and the alkylamine is PEHA or TEPA or DETA or TETA or EDA. In a further embodiment, the molar ratio between acrylic-x and alkylamine is from 0.85 to 1.5. In yet a further embodiment, the molecular weight can encompass ranges: 500 to 200,000, 1,000 to 16,000, or 1,500 to 8,000. In yet a further embodiment, the acrylic ester can be at least one of the following: methyl acrylate, methyl methacrylate, ethyl acrylate, and ethyl methacrylate, propyl acrylate, and propyl methacrylate, which is combined with at least one of the alklyamines, which includes PEHA or TEPA or DETA or TETA or EDA. In yet a further embodiment, the resulting polymer is modified to contain the following ranges of dithiocarbamate salt groups: 5 to 100 mole %, 25 to 90 mole %, or 55 to 80 mole %.

[00101] In another embodiment, the acrylic-x is an acrylic amide and the alkylamine is TEPA or DETA or TETA or EDA. In a further embodiment, the molar ratio between acrylic-x and alkylamine is from 0.85 to 1.5. In yet a further embodiment, the molecular weight can encompass ranges: 500 to 200,000, 1,000 to 16,000, or 1,500 to 8,000. In yet a further embodiment, the acrylic amide can be at least one or a combination of acrylamide and methacrylamide, which is combined with at least one of the alklyamines, which includes PEHA or TEPA or DETA or TETA or EDA. In yet a further embodiment, the resulting polymer is modified to contain the following ranges of dithiocarbamate salt groups: 5 to 100 mole %, 25 to 90 mole %, or 55 to 80 mole %.

[00102] In another embodiment, the acrylic-x is an acrylic acid and salts thereof and the alkylamine is PEHA or TEPA or DETA or TETA or EDA. In a further embodiment, the molar ratio between acrylic-x and alkylamine is from 0.85 to 1.5. In yet a further embodiment, the molecular weight can encompass ranges: 500 to 200,000, 1,000 to 16,000, or 1,500 to 8,000. In yet a further embodiment, the acrylic acid can be at least one or a combination of acrylic acid or salts thereof and methacrylic acid or salts thereof, which is combined with at least one of the alklyamines, which includes TEPA or DETA or TETA or EDA. In yet a further embodiment, the resulting polymer is modified to contain the following ranges of dithiocarbamate salt groups: 5 to 100 mole %, 25 to 90 mole %, or 55 to 80 mole %.

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[00103] Additional monomers can be integrated into the polymer backbone made up of constituent monomers acrylic-x and alkylamine. A condensation polymer reaction scheme can be utilized to make the basic polymer backbone chain. Various other synthesis methods can be utilized to functionalize the polymer with, for example, dithiocarbamate and/or other non-metal scavenging functional groups. One of ordinary skill in the art can functionalize the polymer without undue experimentation.

[00104] In certain embodiments, the composition can be formulated with other polymers such as a water soluble ethylene dichloride ammonia polymer having a molecular weight of from 500 to 100,000 which contains from 5 to 55 mole % of dithiocarbamate salt groups. In one embodiment, the molecular weight of the polymer is from 1,500 to 10,000 and contains 15 to 50 mole % of dithiocarbamate salt groups. In a preferred embodiment, the molecular weight of the polymer is from 1,500 to 5,000 and contains 30 to 55 mole % of dithiocarbamate salt groups.

[00105] In certain embodiments, the composition can be formulated with other small molecule sulfide precipitants such as sodium sulfide, sodium hydrosulfide, TMT-15® (sodium or calcium salts of trimercapto-S-triazine), dimethyldithiocarbamate, and/or diethyldithiocarbamate.

[00106] The mercury re-emission additives may be present in the composition in an amount of 0 wt% to 99 wt%, 20 wt% to 80 wt%, or 50 wt% to 60 wt%. The mercury re-emission additives may be present in the composition in an amount of about 10 wt%, about 20 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, about 70 wt%, about 80 wt%, or about 90 wt%. The mercury re-emission additive may be present in an amount of 50 wt%, 60 wt%, or 80 wt%.

b. Free Radical Scavengers

[00107] Free radical scavengers can be used to reduce mercury re-emission and/or corrosion. The free radical scavengers can be used to target free radical species that lead to persulfate formation (e.g., reduction of sulfite) or that lead to mercury re-emission (e.g., reduction of Hg^{2+}).

[00108] Free radical scavengers that can be used in the compositions of the invention include, but are not limited to, substituted phenols (e.g., butylated hydroxytoluene, 2,6-

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di-tert-butylphenol, 2,4-dimethyl-6-tert-butylphenol), derivatives of phenylenediamine (e.g., N,N'-di-2-butyl-1,4-phenylenediamine), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), citric acid, tertiary butylhydroquinone (TBHQ), tocopherols, ascorbic acid, glutathione, lipoic acid, uric acid, and enzymes (e.g., catalase, superoxide dismutase, various peroxidases, and the like).

[00109] The free radical scavenger may be present in the composition in an amount of 0 wt% to 99 wt%, 1 wt% to 30 wt%, 1 wt% to 25 wt%, 1 wt% to 20 wt%, or 1 wt% to 10 wt%. The free radical scavenger may be present in the composition in an amount of about 1 wt%, about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, or about 30 wt%. The free radical scavenger may be present in the composition in an amount of 1 wt%, 10 wt%, 20 wt%, or 25 wt%.

c. Polymer Dispersants

[00110] Polymer dispersants can be used to reduce mercury re-emission and/or corrosion. The polymer dispersants can be used to target one or more transition metal species. The dispersants can be used to bind to or inactive mercury species, iron species, and/or manganese species (e.g., solubilized Mn^{2+}).

[00111] The compositions disclosed herein may include a polymer dispersant. Suitable polymer dispersants include, but are not limited to, polyacrylic acid, polyacrylates, polymaleic acid, maleic anhydride/ethyl acrylate/vinyl acrylate terpolymer and alkyl epoxy carboxylate (abbreviated "AEC"), phosphinocarboxylic acids, such as phosphinosuccinate oligomers (abbreviated as "PSO"), and phosphonocarboxylic acids, such as phosphonocarboxylic (sulfonated) copolymer (abbreviated "POCA", sold as Belclene 494).

[00112] The polymer dispersants may also be referred to herein as "binding agents."

[00113] The polymer dispersant may be present in the composition in an amount of 0 wt% to 99 wt%, 10 wt% to 50 wt%, or 20 wt% to 40 wt%. The dispersant may be present in the composition in an amount of about 5 wt%, about 10 wt%, about 15 wt%, about 20 wt%, about 25 wt%, about 30 wt%, about 35 wt%, about 40 wt%, about 45 wt%, or about 50 wt%. The dispersant may be present in the composition in an amount of 10 wt%, 19 wt%, 20 wt%, 25 wt%, 40 wt%, or 50 wt%.

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d. Dosage

[00114] In one embodiment, the amount of mercury re-emission control additive for effectively removing metals from contaminated waters may be within the range of 0.2 to 2 moles of dithiocarbamate per mole of metal, or 1 to 2 moles of dithiocarbamate per mole of metal contained in the water. According to one embodiment, the dosage of metal removal polymer required to chelate and precipitate 100 ml of 18 ppm soluble copper to about 1 ppm or less was 0.011 gm (11.0 mg) of polymer. The metal polymer complexes formed are self-flocculating and quickly settle. These flocculants are easily separated from the treated water.

[00115] In the context of applying the polymer to a gas system, such as a flue gas, the polymer can be dosed incrementally and capture rates for a particular metal, e.g. such as mercury, can be calculated by known techniques in the art. In certain embodiments, a mercury re-emission control additive, such as a water-soluble ethylene dichloride ammonia polymer with dithiocarbamate salt groups, may be applied to a scrubber liquor at a ratio of 1:1 to 2000:1 weight of polymer to weight of mercury being captured. One preferred dosage ratio is from 5:1 to 1000:1, more preferably from 5:1 to 500:1.

5. Applications

[00116] Methods of the present invention can be used in any process in which it is desirable to remove mercury from a flue gas and/or prevent or reduce corrosion of equipment used in combustion processes. For example, the methods of the present invention can be used in waste incineration plants (e.g., domestic waste, hazardous waste, or sewage sludge incineration plants), power stations (e.g., bituminous coal-fired, or lignite-fired power stations), other plants for high-temperature processes (e.g., cement burning), and high-temperature plants co-fired with waste or combined (multistage) high-temperature plants (e.g., power stations or cement rotary kilns having an upstream waste pyrrolysis or waste gasification.

[00117] FIG. 1 depicts an exemplary coal-fired power plant amenable to methods of the present invention. The power plant includes a boiler 10, a selective catalytic reduction device 20, an air preheater 30, a particulate control device 40 (e.g., an electrostatic precipitator), a scrubber 50 (e.g., a wet or dry flue gas desulpherization

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system), and a discharge stack 60. The coal-fired power plant may have additional components, as well as multiple devices of the same or similar type (e.g., multiple particulate control devices). The compositions of the invention can be applied upstream of the scrubber, and/or directly to the scrubber (e.g., to the scrubber liquor).

[00118] FIG. 2 depicts another exemplary EGU that includes a method of introducing a composition of the invention into a WFGD. The unit may include a controller and sensor array that can be used to measure one or more properties of the liquor (e.g., oxidation-reduction potential, heavy metal speciation, and the like). The addition of a composition of the invention can be adjusted based on the measured property to account for increased emissions, excessive corrosion, or alternatively, over-feed of the composition.

[00119] Methods of the present invention can be used in processes of any dimension. The methods can be used in processes having a flue gas volumetric flow rate of 15×10^3 m^3 S.T.P. db/h, for example for sewage sludge incineration, or of 50×10^3 m^3 S.T.P. db/h, for example in hazardous waste incineration plants, or of 150×10^3 m^3 S.T.P. db/h, for example in domestic waste incineration, and also in large power stations having, for example, $2\text{-}3\times10^6$ m^3 S.T.P. db/h.

[00120] The methods can be used with any scrubbers currently used in the industry, including spray towers, jet bubblers, and co-current packed towers. These types of particulate control devices are provided as examples and are not meant to represent or suggest any limitation.

[00121] The compositions may be introduced into a scrubber and thereby into the scrubber liquor via several routes. For example, the compositions may be added to a virgin limestone or lime slurry prior to addition to a scrubber, to the recirculation loop of a scrubber liquor, or to a "low solids" return to a scrubber from the scrubber purge stream. The addition of the compositions can be made in any suitable location in a scrubber process, wholly or fractionally (i.e. a single feed point or multiple feed points), including but not limited to the make-up water for the lime or limestone slurry or the scrubber liquor.

[00122] In certain embodiments, the compositions may be added to a wet scrubber via a "low solids" liquor return. A portion of the liquor is usually continuously

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removed from the scrubber for the purpose of separating reaction byproducts from unused lime or limestone. One means of separation that is currently used is centrifugation. In this process the scrubber liquor is separated into a "high solids" and "low solids" stream. The high solids stream is diverted to wastewater processing. The low solids fraction returns to the wet scrubber and can be considered "reclaimed" dilute liquor. The compositions can conveniently be added to the reclaimed low solids stream prior to returning to the scrubber.

[00123] In certain embodiments, the compositions may be added to the wet scrubber via a "virgin liquor." Virgin liquor is the water-based dispersion of either lime or limestone prior to exposure to flue gas and is used to add fresh lime or limestone while maintaining the scrubber liquor level and efficiency of the wet FGD. This is prepared by dispersing the lime or limestone in water. Here the composition can be added either to the dispersion water or the virgin liquor directly.

[00124] In certain embodiments, the compositions may be added to scrubber liquor injected directly into the flue gas prior to the scrubber for the purpose of controlling relative humidity of the flue gas or its temperature.

[00125] The scrubber liquors referred to herein may be water-based dispersions of calcium carbonate (limestone) or calcium oxide (lime) used in a wet Flue Gas Scrubber to capture SOx emissions. The liquor may also contain other additives such as magnesium and low-molecular weight organic acids, which function to improve the sulfur capture. One example of such an additive is a mixture of low-molecular weight organic acids known as dibasic acid (DBA). DBA consists of a blend of adipic, succinic, and glutaric acids. Each of these organic acids can also be used individually. In addition, another low-molecular weight organic acid that can be used to improve sulfur capture in a wet scrubber is formic acid. Finally, the scrubber liquor may also contain byproducts of the interaction between the lime or limestone and sulfur species, which leads to the presence of various amounts of calcium sulfite or calcium sulfate. The scrubber liquor may include the make-up liquor, return liquor, the reclaimed liquor, virgin liquor, and/or liquor injected directly into flue gasses.

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6. Examples

[00126] The foregoing may be better understood by reference to the following examples, which are presented for purposes of illustration and are not intended to limit the scope of the invention.

Example 1

Metal solubility, ORP, and Hg re-emission

[00127] It has been shown that as ORP is decreased in WFGD scrubber liquor, soluble Mn concentration increases (FIG. 3 and FIG. 4). The soluble Mn can be targeted with a binding agent and/or a mercury re-emission additive to blind the Mn surfaces to further reaction. As shown in Table 1, the oxidation-reduction potential of a scrubber liquor of a WFGD resulted in an increase in soluble Mn and Fe levels, decreasing the amount of these species present in the solids (gypsum) of the WFGD liquor.

Table 1. Soluble and insoluble Mn and Fe, chloride concentrations, ORP, Hg re-emission and additive feed.

Day		Day 1	Day 11	Day 18	Day 29	Day 32
Soluble Manganese (Mn)	mg/L	3.9	67	20	32	53
Soluble Iron (Fe)	mg/L	<0.2	<0.2	<0.2	<0.2	<0.2
Insol. Iron (Fe)	mg/kg	-	1700	1400	2300	3200
Insol. Manganese (Mn)	mg/kg	-	32	120	120	59
Chloride (Cl)	mg/L	2800	2900	2500	2500	2700
Soluble Hg	ppt	80258	275	10742	14394	136
Hg re-emission	%	61.67%	17.52%	30.52%	246.51%	5.73%
polymeric polydithiocarbamate mercury re-emission additive	GPH	0	54	0	0	54
ORP - Controller	mV	535	190	493	502	180

[00128] The addition of persulfate to a scrubber liquor of a WFGD led to an increase in the amount of soluble mercury, which has been shown to result in mercury re-emission. This may be due to persulfate oxidizing organic matter, which agglomerate mercury species to larger particles (e.g., colloidal particles) and thus making it soluble,

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as shown in Table 2. Table 3 also shows the correlation between persulfate and soluble mercury levels, as well as ORP.

Table 2. Soluble mercury levels within scrubber liquor with and without addition of persulfate.

Liquor	Mercury (liquid)/ppt
Scrubber Liquor	404
Scrubber Liquor + 0.5g $Na_2S_2O_8$	19547

Table 3. Soluble mercury levels within scrubber liquor

Date and Time	Sample Name	Mercury (liquid, ppt)	Mercury (solids, ppb)	Persulfate conc. (ppm)	ORP (mV)	Stack Hg (ug/wscm)
Day 1	1, AM	224	790	21	-	0.17
Day 1, 15:22	1, PM	84	800	35	177	0.18
Day 2, 10:00	2, AM	26332	640	63	194	2.62
Day 2, 13:45	2, PM	620	770	70	181	0.22
Day 3, 7:30	3, AM	114359	460	175	551	2.01
Day 3, 13:00	3, PM	113331	350	525	538	3.73
Day 4, 8:05	4, AM	125123	250	1050	544	-
Day 4, 13:40	4, PM	126977	260	1225	550	-

[00129] Correlating the soluble Mn concentration with mercury re-emission as well as with oxidation-reduction potential, relationships appear to be present (R2 values = ~0.72), as shown in FIG. 5 and FIG. 6. Reducing the amount of solid Mn and Fe surface species present by solubilizing them consequently leads to a reduction of catalytic active sites for the formation of the sulfite radical and thus limits the formation of persulfate.

[00130] The addition of a Mn/Fe binding agent has the ability to blind the surface from sulfites, leading to a decrease in the transition metal's ability to convert sulfite to persulfate. As shown in Table 1, although the insoluble Fe and Mn levels are high at Day 1, mercury re-emission levels during this time (+/- 2 hours) were very low. It can be inferred that the low mercury re-emission observed was due to the polymeric

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polydithiocarbamate mercury re-emission additive blinding the solid Mn and Fe surfaces, preventing persulfate formation.

[00131] The polymeric polydithiocarbamate mercury re-emission additive has however been shown to have a lower affinity for Mn and Fe over other cations (e.g., Hg^{2+}). Other polymers, such as polyacrylate have higher affinities for Mn and Fe than the polymeric polydithiocarbamate mercury re-emission additive, and thus were investigated in their ability to bind to Mn and Fe within WFGD scrubber liquors. When adding polymeric polydithiocarbamate mercury re-emission additive or polyacrylate to a scrubber liquor containing persulfate, it was possible to significantly reduce the soluble mercury concentration, likely due to flocculation. The decrease in soluble mercury has been demonstrated to be accompanied by a significant drop in ORP value. A drop in ORP value has been demonstrated to lead to an increase in soluble Mn species. Indeed, when polymeric polydithiocarbamate mercury re-emission additive is added this phenomenon is observed, as shown in Table 4. However, with polyacrylate, no real increase in soluble Mn species is observed. It appears thus that polyacrylate indeed complexes the Mn species, leading to a low soluble Mn concentration. It can be envisaged that the same occurred on the solid Mn surfaces, deactivating them for catalytic activity in converting sulfites to persulfate.

Table 4. Jar tests showing the effect of polymers on scrubber liquor

Liquor	Mercury (liquid)/ppt	Soluble Mn/ppm
Scrubber Liquor + 0.5g $Na_2S_2O_8$	19547	0.1
Scrubber Liquor + 0.5g $Na_2S_2O_8$ + 0.1g polymeric polydithiocarbamate mercury re-emission additive	196	3.2
Scrubber Liquor + 0.5g $Na_2S_2O_8$ + 0.1g polyacrylate	54	0.2

[00132] The foregoing examples demonstrate that the compositions and methods may be used to reduce mercury re-emissions and/or control corrosion. Exemplary compositions of the invention may be prepared according to Table 5.

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Table 5. Exemplary Compositions

	Mercury Re-emission Control Additive (wt%)	Free Radical Scavenger (wt%)	Polymer Dispersant (wt%)
Composition A	50	25	25
Composition B	80	10	10
Composition C	80	-	20
Composition D	50	-	50
Composition E	80	1	19
Composition F	60	20	20
Composition G	60	1	40

[00133] Any ranges given either in absolute terms or in approximate terms are intended to encompass both, and any definitions used herein are intended to be clarifying and not limiting. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all subranges (including all fractional and whole values) subsumed therein.

[00134] Furthermore, the invention encompasses any and all possible combinations of some or all of the various embodiments described herein. Any and all patents, patent applications, scientific papers, and other references cited in this application, as well as any references cited therein, are hereby incorporated by reference in their entirety.

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CLAIMS

What is claimed is:

1. A compositions comprising at least two components selected from

a mercury re-emission additive;

a free radical scavenger; and

a polymer dispersant.

2. The composition of claim 1, comprising the mercury re-emission additive and the free radical scavenger.

3. The composition of claim 1, comprising the mercury re-emission additive and the polymer dispersant.

4. The composition of claim 1, comprising the free radical scavenger and the polymer dispersant.

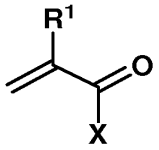
5. The composition of claim 1, comprising the mercury re-emission additive, the free radical scavenger, and the polymer dispersant.

6. The composition of claim 1, wherein the mercury re-emission additive wherein the mercury re-emission control additive is a polymeric polydithiocarbamate compound.

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7. The composition of claim 1, wherein the mercury re-emission control additive is an ethylene dichloride ammonia polymer containing from 5 to 55 mole % of dithiocarbamate salt groups.

8. The composition of claim 1, wherein the mercury re-emission control additive is a polymer derived from at least two monomers: acrylic-x and an alkylamine, wherein said acrylic-x has the following formula:



wherein X = OR, OH and salts thereof, or NHR^2 and wherein R^1 and R^2 is H or an alkyl or aryl group, wherein R is an alkyl or aryl group, wherein the molecular weight of said polymer is between 500 to 200,000, and wherein said polymer is modified to contain a functional group capable of scavenging one or more compositions containing one or more metals.

9. The composition of claim 8, wherein the functional group capable of scavenging one or more compositions containing one or more metals is a sulfur containing functional group.

10. The composition of claim 1, wherein the mercury re-emission control additive is selected from the group consisting of: a polymeric polydithiocarbamate compound, sodium sulfide, sodium hydrosulfide, sodium bisulfide, a polysulfide, diethyldithiocarbamate or a sodium salt thereof, dimethyldithiocarbamate or a sodium salt thereof, a sodium polythiocarbonate, an inorganic poly-sulfide or blend, a sodium or calcium salt of 1,3,5-triazine-2,4,6(1H,3H,5H)-trithione, an activated carbon, 2,3-dimercaptopropanol, dimercaptosuccinic acid, 1,8-octanedithiol, 1,2-dithiolane-3-valeric acid, 2-methyl 1,3-dithiolane, mercaptoacetic acid or a sodium salt thereof, and a halogen-containing compound, or any combination thereof.

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11. The composition of claim 1, wherein the free radical scavenger is selected from the group consisting of: substituted phenols, derivatives of phenylenediamine, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), citric acid, tertiary butylhydroquinone (TBHQ), tocopherols, ascorbic acid, glutathione, lipoic acid, uric acid, and free radical scavenging enzymes, or any combination thereof.

12. The composition of claim 1, wherein the polymer dispersant is selected from the group consisting of: polyacrylic acid, polyacrylates, polymaleic acid, maleic anhydride/ethyl acrylate/vinyl acrylate terpolymer and alkyl epoxy carboxylate, phosphinocarboxylic acids, and phosphonocarboxylic acids, or any combination thereof.

13. The composition of claim 1, wherein the polymer dispersant is a polyacrylate or a phosphinosuccinate oligomer.

14. A method of controlling mercury re-emission from a combustion process and/or reducing corrosion of equipment used in a combustion process, the method comprising applying to the combustion process at least two components selected from:

a mercury re-emission additive;

a free radical scavenger; and

a polymer dispersant.

15. The method of claim 14, wherein the components are applied to a scrubber liquor of a wet flue gas desulphurization (WFGD) unit.

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16. The method of claim 14, wherein the percent mercury re-emission from the scrubber liquor is reduced to 10% or less.

17. The method of claim 14, wherein the percent mercury re-emission from the scrubber liquor is reduced to 1% or less.

18. The method of claim 14, wherein the mercury re-emission control additive is a polymeric polydithiocarbamate compound.

19. A method of reducing mercury re-emission from a combustion process and/or reducing corrosion of equipment used in a combustion process, the method comprising:

dispersing manganese species;

inhibiting the formation of persulfate species; or

complexing mercury and/or manganese.

20. The method of claim 20, comprising at least two of:

dispersing manganese species;

inhibiting the formation of persulfate species; and

complexing mercury and/or manganese.

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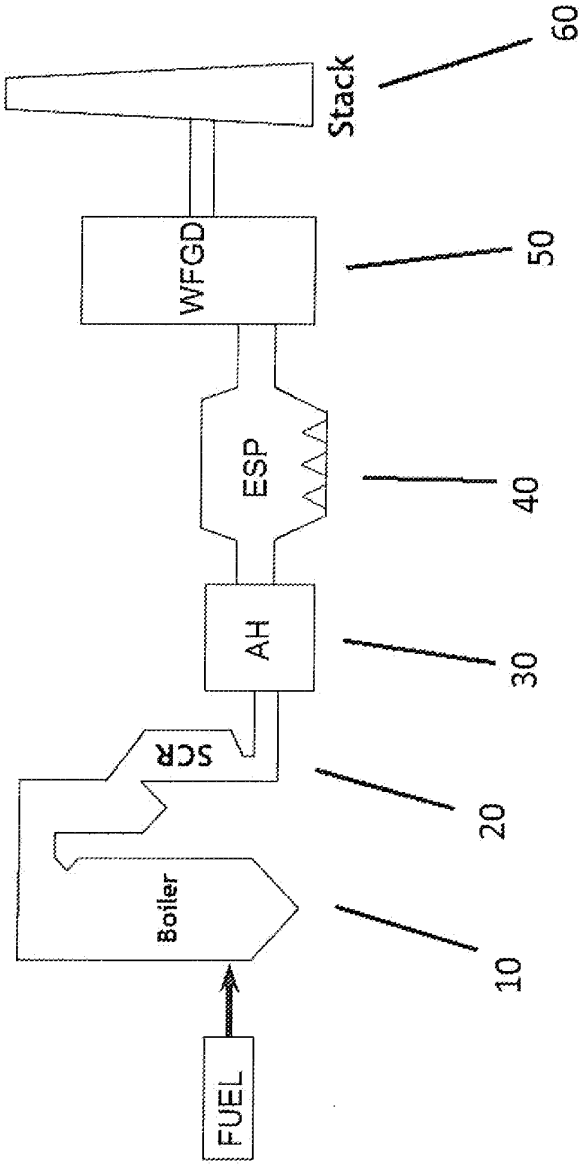


FIG. 1

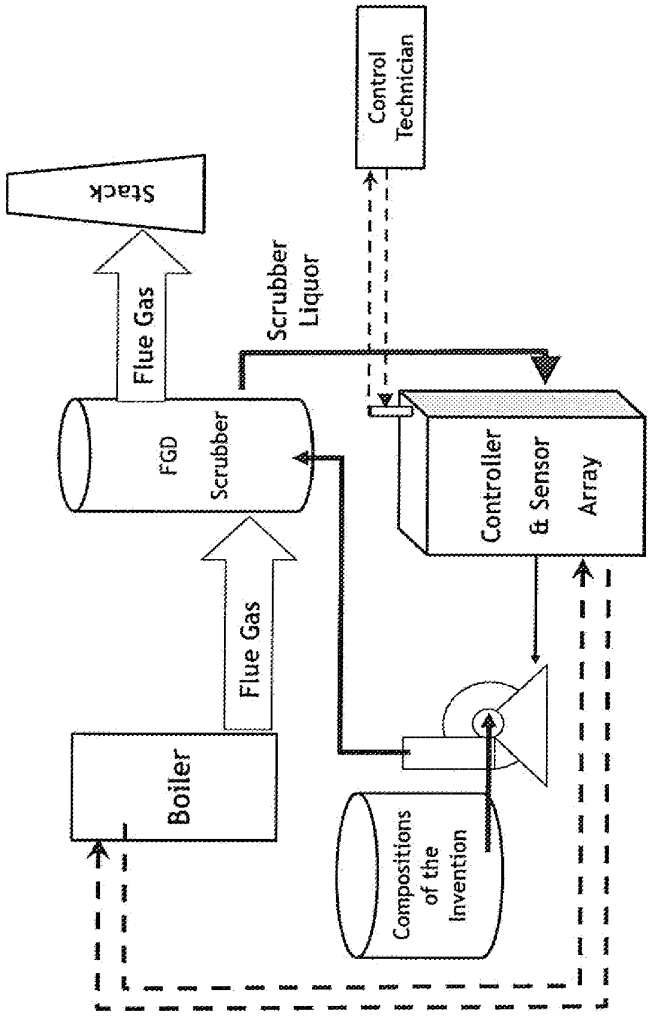

Control Technician
Stack
Flue Gas
Scrubber Liquor
FGD Scrubber
Controller & Sensor Array
Flue Gas
Boiler
Compositions of the Invention

FIG. 2

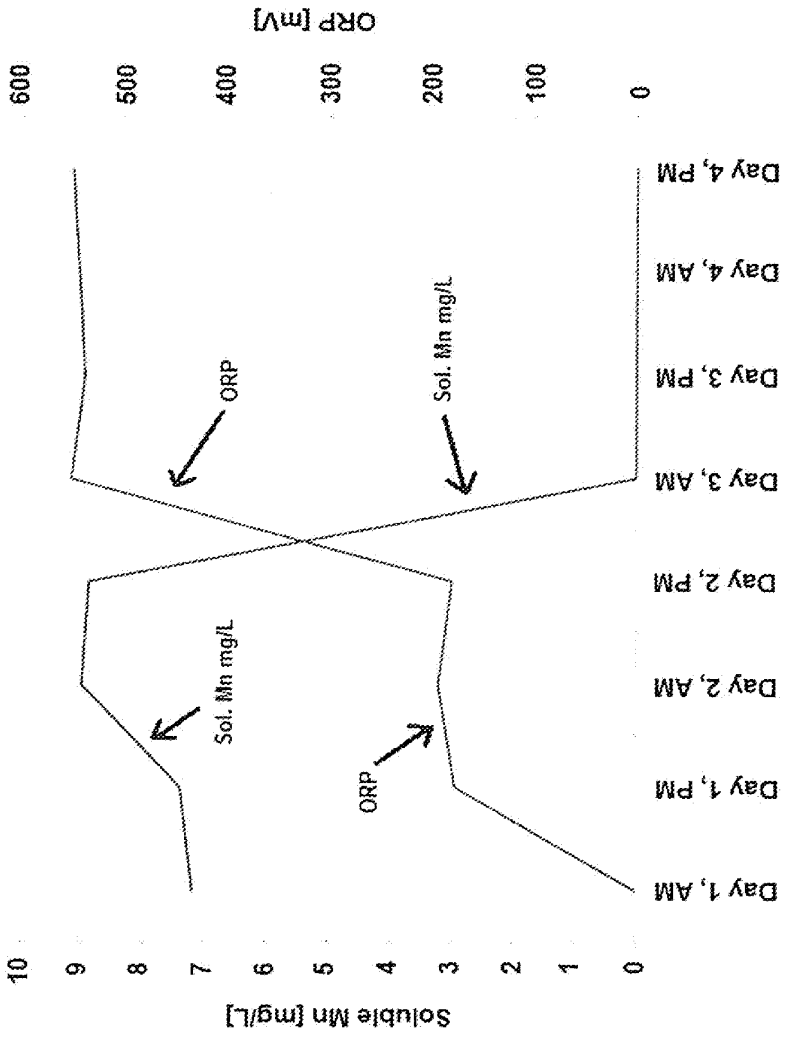

ORP [mV]
600
500
400
300
200
100
0
Day 4, PM
Day 4, AM
Day 3, PM
Day 3, AM
Day 2, PM
Day 2, AM
Day 1, PM
Day 1, AM
ORP
Sol. Mn mg/L
Sol. Mn mg/L
ORP
Soluble Mn [mg/L]
10
9
8
7
6
5
4
3
2
1
0

FIG. 3

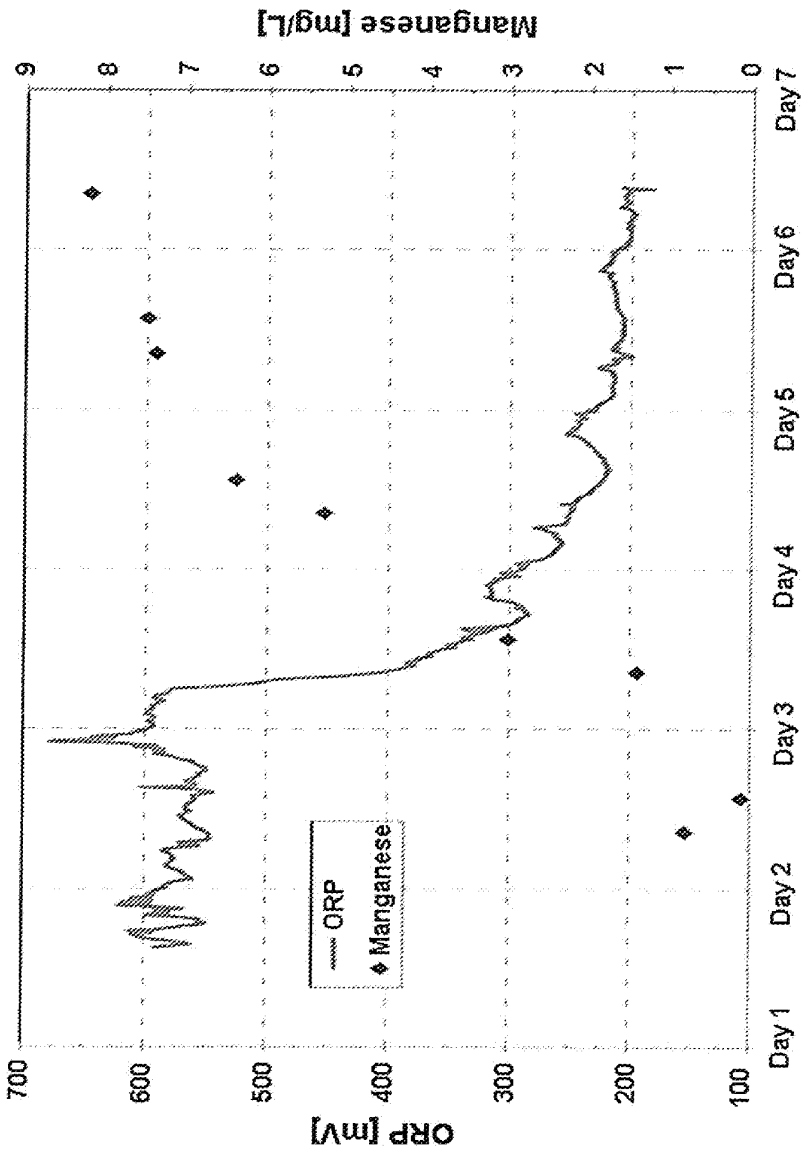

Manganese [mg/L]
ORP [mV]
ORP
Manganese
Day 1
Day 2
Day 3
Day 4
Day 5
Day 6
Day 7
700
600
500
400
300
200
100
9
8
7
6
5
4
3
2
1
0

FIG. 4

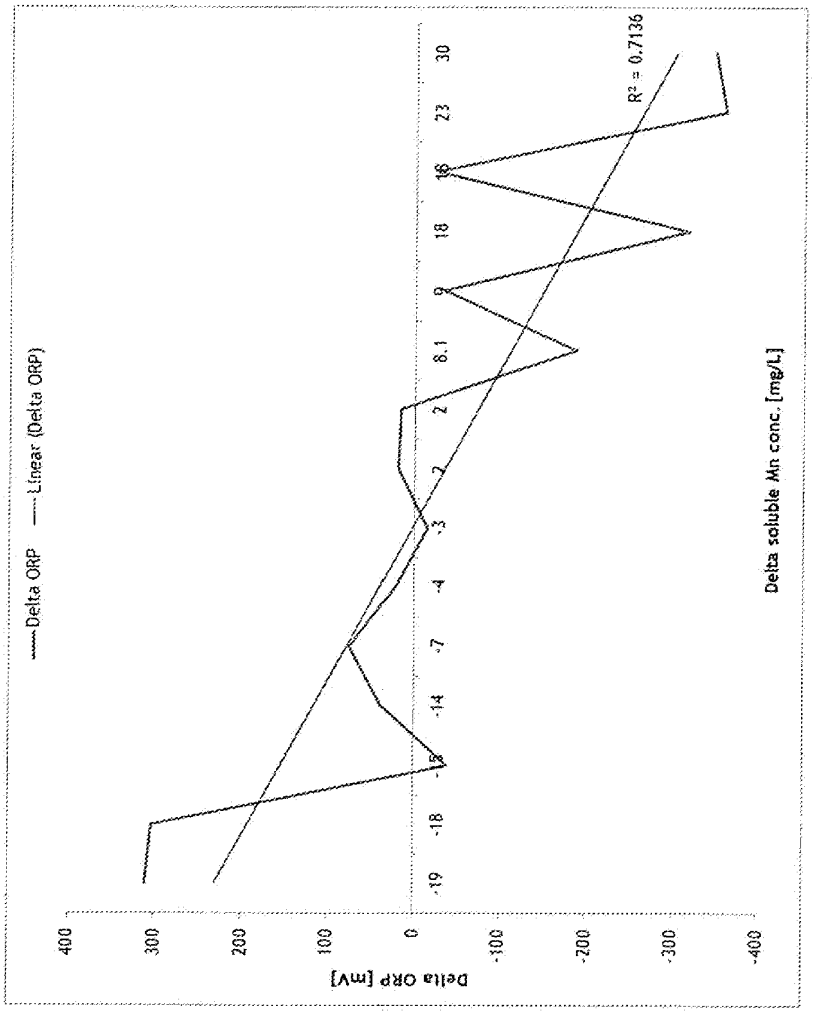

Delta ORP
Linear (Delta ORP)
Delta ORP [mV]
400
300
200
100
0
-100
-200
-300
-400
-19
-18
-14
-7
-4
-3
2
8.1
9
18
23
30
R² = 0.7136
Delta soluble Mn conc. [mg/L]

FIG. 5

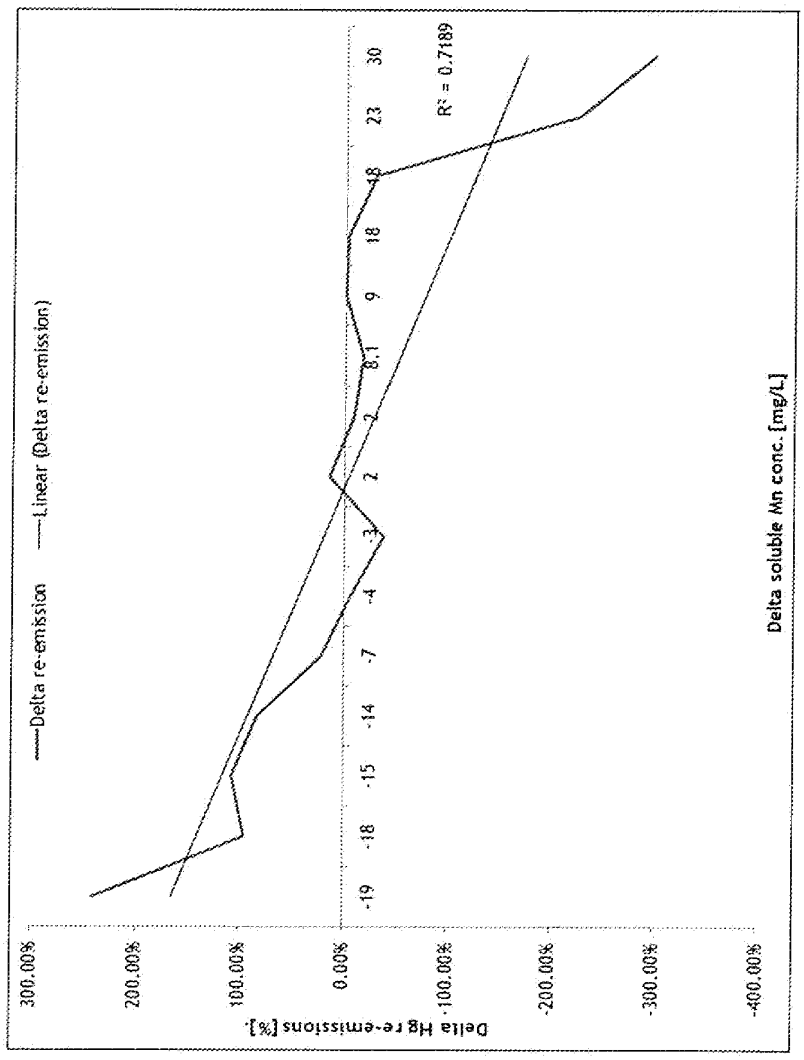

Delta re-emission
Linear (Delta re-emission)
R² = 0.7189
Delta Hg re-emissions [%]
300.00%
200.00%
100.00%
0.00%
-100.00%
-200.00%
-300.00%
-400.00%
-19
-18
-15
-14
-7
-4
-3
2
-2
8.1
9
18
48
23
30
Delta soluble Mn conc. [mg/L]

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/071978

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/64(2006.01)i, B01D 53/79(2006.01)i, B01D 53/83(2006.01)i, B01D 53/48(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D 53/64; B01D 53/50; B01D 50/00; B01D 53/46; B01D 53/79; B01D 53/83; B01D 53/48

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: mercury re-emission, free radical scavenger, polymeric dispersant, manganese, persulfate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009-0202407 A1 (HURLEY, P. J.) 13 August 2009 See abstract, claims 1, 10, paragraphs [0043]-[0044].	1,3,14-17
Y		10
A		2,4-9,11-13,18-20
Y	US 2011-0262326 A1 (STEEN, W. A. et al.) 27 October 2011 See claims 4, 6-8, 13-14.	10
A		1-9,11-20
X	US 2010-0284878 A1 (UKAI, N. et al.) 11 November 2010 See abstract, claims 3-4, paragraph [0018].	19
A		1-18,20
A	US 2011-0014104 A1 (GHORISHI, S. B. et al.) 20 January 2011 See abstract, claim 1, paragraphs [0061]-[0063].	1-20
A	US 2012-0177554 A1 (KEISER, B. A. et al.) 12 July 2012 See abstract, paragraphs [0099]-[0101].	1-20

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 March 2014 (14.03.2014)	**17 March 2014 (17.03.2014)**

Name and mailing address of the ISA/KR
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/071978

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US 8617493 B2	31/12/2013
		WO 2013-119544 A1	15/08/2013

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

(54) **Title**: REFRIGERATED VAPOR RECOVERY SYSTEM

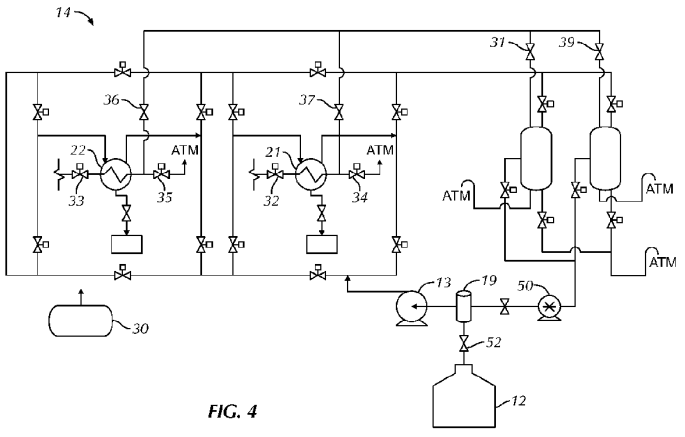


FIG. 4

(57) **Abstract**: Volatile vapors are removed from a storage vessel by establishing a flow of a stream of volatile vapors from the storage vessel and directing the vapor stream through a heat exchange module for condensing a portion of the vapors in the stream flowing through a cooled heat exchange condensers in the heat exchange module. The uncondensed vapors in the vapor stream are then directed to a carbon adsorption module including a pair of carbon adsorption units. The vapor recovery system also provides a means of desorbing a carbon adsorption unit that approaches its capacity for adsorbing volatile organic molecules and recycling the desorbed vapor stream through a cooled heat exchange condenser to convert the volatile organic material into a liquid state that may be sold as a product or utilized as a raw material rather than being combusted or otherwise disposed of in the atmosphere.

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REFRIGERATED VAPOR RECOVERY SYSTEM

STATEMENT OF RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/797,306 filed December 4, 2012 and entitled "Refrigerated Vapor Recovery System."

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0002] This invention relates to the field of purging tanks and vessels and more particularly, to methods and apparatus for using heat exchangers and carbon adsorption tanks to efficiently remove and recover volatile materials entrained within vapors residing in tanks and vessels.

DESCRIPTION OF THE RELATED ART

[0003] Volatile liquids, such as benzene, petroleum and the like, are often stored in tanks at bulk terminals, refineries and end-user facilities, and transported in tanks aboard barges or ships, tank trucks and rail cars. All such containers shall be referred to herein as liquid storage vessels. While resident in these liquid storage vessels, volatilization of the liquid occurs leaving residual vapors which must be removed before workmen can be permitted to enter the vessel and before the vessel can be filled with a different liquid.

[0004] In some cases, such residual vapors are purged by flooding liquid storage vessels with a sufficient volume of water, steam or an inert gas to entrain the vapors and carry them out of the vessel. The resulting mixture of diluted vapors, in many cases, is simply combusted and emitted to the atmosphere and/or the surrounding water supply where they pollute the environment.

[0005] Recently companies have had to minimize the release of volatile materials into the atmosphere during the preparation of storage vessels for maintenance in order to meet environmental standards. One environmentally friendly way to reduce the release of volatile materials into the atmosphere has been to cool and the vapors and to recycle the condensed liquids.

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[0006] A need exists for methods for recovering the volatile materials that are removed from a storage vessel so that the material may be utilized as a product or raw material rather than being disposed of.

SUMMARY OF THE INVENTION

[0007] One embodiment of the present invention is a carbon absorption module having: (a) a first carbon absorption unit having a first inlet in selectable communication with an outlet of a cooled heat exchanger and a first outlet; (b) a second carbon absorption unit having a second inlet in selectable communication with the outlet of the cooled heat exchanger and a second outlet; (c) a monitoring device for measuring the concentration of a volatile organic component in an effluent from the first or the second carbon adsorption unit; (d) a first effluent flow path passing from the first outlet through the monitoring device; (e) a second effluent flow path passing from the second outlet through the monitoring device; (f) an atmospheric discharge outlet in selectable communication with the first and second effluent flow paths; (g) a pump in selectable communication with the first and second effluent flow paths; and (h) a desorption flow path in communication with the pump and the cooled heat exchanger.

[0008] Another embodiment of the present invention is A carbon absorption module having: (a) a first carbon absorption unit having (i) a first inlet in selectable communication with an outlet of a cooled heat exchanger, (ii) a first flow path for a coolant, and (iii) a first outlet; (b) a second carbon absorption unit having (i) a second inlet in selectable communication with the outlet of the cooled heat exchanger, (ii) a second flow path for the coolant, and (iii) a second outlet, (c) a monitoring device for measuring the concentration of a volatile organic component in an effluent from the first or the second carbon adsorption unit; (d) a first effluent flow path passing from the first outlet through the monitoring device; (e) a second effluent flow path passing from the second outlet through the monitoring device; (f) an atmospheric discharge outlet in selectable communication with the first and second effluent flow paths; (f) a pump in selectable communication with the first and second effluent flow paths; and (e) a desorption flow path in communication with the pump and the cooled heat exchanger.

[0009] Yet another embodiment of the present invention is a method for removing and recovering a volatile organic component from a vapor stream including the steps of: (a) directing a flow of the vapor stream to a first carbon adsorption unit from a cooled heat

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exchanger; (b) measuring the vapor stream exiting from the first carbon adsorption unit for the volatile organic component; (c) releasing the exiting vapor stream from the first carbon adsorption unit into the atmosphere if a measured concentration of the volatile organic component is below a desired concentration; (d) diverting the flow of the vapor stream to a second carbon adsorption unit whenever the measured concentration of the volatile organic component in the vapor stream exiting from the first carbon adsorption unit is equal to or greater than the desired concentration; (e) lowering the pressure in the first carbon adsorption unit to desorb the volatile organic component; and (f) directing the desorbed volatile organic component through the cooled heat exchanger to condense a portion of the volatile organic compound.

[0010] Still another embodiment of the present invention is a method for recovering a volatile organic component from a vapor stream comprising: (a) directing the vapor stream from a storage vessel to a heat exchange module having at least one heat exchange condenser; (b) starting a refrigerant flow through at least one heat exchange condenser to cool the condenser; (c) directing the flow of the vapor stream through the heat exchange module, wherein a portion of the volatile organic component in the vapor stream flowing through the cooled heat exchange condenser is condensed; (d) draining the condensed volatile organic component from the cooled heat exchange condenser; (e) directing the uncondensed vapor stream from the heat exchange module to a first carbon adsorption unit from the cooled heat exchanger to adsorb the volatile organic component; (f) measuring the vapor stream exiting from the first carbon adsorption unit for the volatile organic component; (g) releasing the exiting vapor stream from the first carbon adsorption unit into the atmosphere if a measured concentration of the volatile organic component is below a desired concentration; (h) diverting the flow of the vapor stream to a second carbon adsorption unit whenever the measured concentration of the volatile organic component in the vapor stream exiting from the first carbon adsorption unit is equal to or greater than the desired concentration; (i) lowering the pressure in the first carbon adsorption unit to desorb the volatile organic component; and (j) directing the desorbed volatile organic component through the cooled heat exchanger to condense a portion of the volatile organic compound.

[0011] The foregoing has outlined rather broadly several aspects of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention. It should be appreciated by those

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skilled in the art that the conception and the specific embodiment disclosed might be readily utilized as a basis for modifying or redesigning the structures for carrying out the same purposes as the invention. It should be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0013] FIG. 1 is a general schematic of a system for removing volatile vapors from a storage vessel.

[0014] FIG. 2A is a more detailed schematic of the system shown in FIG. 1 showing the volatile vapor flow from the storage tank through the first heat exchange condenser and then through a refrigerated second heat exchange condenser.

[0015] FIG. 2B is a more detailed schematic of the system shown in FIG. 1 showing the volatile vapor flow from the storage tank through the second heat exchange condenser and then through a refrigerated first heat exchange condenser.

[0016] FIG. 3 is a schematic flow diagram of the system shown in FIG. 1 showing the volatile vapor flow from the storage tank through the heat exchange module and then through a carbon adsorption module with two carbon adsorption units.

[0017] FIG. 4 is a schematic for the system where the coolant used in the heat exchange module is used to selectively cool the carbon adsorption units.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] Embodiments of the present invention relate to methods for removing volatile organic vapors from a storage vessel and recovering the volatile organic components (VOCs) from those vapors.

[0019] Storage vessels are used for storing many volatile products such as gasoline, gasoline blending components, diesel, kerosene, solvents, petrochemicals, and organic compounds. Before entry into the vessels by personnel assigned to perform maintenance on the empty storage vessel, before the vessel is refilled with a different product, or while the vessel is being filled with a different product the vessel must be purged of the harmful

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volatile organic components, commonly referred to as VOCs, which were generated while the storage vessel was in use.

[0020] Figure 1 illustrates a general schematic of the refrigerated vapor removal and recovery system 10. In general, a blower 13 suctions a gas source 11 (such as air, nitrogen, or carbon dioxide) through a storage vessel 12 to push the volatile vapor stream from within the storage vessel out of the vessel 12 to circulate the vapor stream through a heat exchange module 14. The heat exchange module 14 will typically contain a series of heat exchange condensers wherein at least one of the heat exchange condensers is refrigerated.

[0021] The vapor stream is cooled as it passes through the refrigerated heat exchange condenser. The volatile organic components in the vapor stream are condensed and drained from the heat exchange condenser into a condensate tank 15 and can be sold a useful product.

[0022] Generally the majority of the VOCs are condensed and removed as the vapor stream passes through the heat exchange module 14. However, the vapor stream is then pumped through a carbon adsorption module 16 where whatever VOCs remain in the vapor stream after it leaves the heat exchange module 14 are adsorbed by the carbon adsorption module 16.

[0023] If, after the vapor stream passes through the vapor recovery system 10, the vapor stream is suitably free of harmful volatile organic components or VOCs the cleaned vapor stream may be released into the atmosphere. However, if an undesirable concentration (i.e., any concentration surpassing an environmentally safe standard) of one or more volatile organic components remains in the vapor stream, the vapor stream is recycled back through the removal/recovery system 10. The circulation/recirculation process through the series of heat exchange condensers and carbon adsorption tanks is continued until the vapor stream is suitably free of harmful volatile vapors.

[0024] Figure 2 shows a more detailed schematic of the refrigerated vapor recovery system 10. While one or more blowers is a preferred apparatus for establishing the flow of the stream of volatile vapors for circulation through the series of condensers within the heat exchange module 14, other apparatus are also suitable, either alone or in combination with a blower such as, for example, rotary compressors, fans, reciprocating compressors, centrifugal compressors, or other vapor pumps known to those having ordinary skill in the art and combinations thereof. The blowers may be driven by electric motors, pneumatic motors, turbines or other drivers known to those having ordinary skill in the art. Preferably, flame

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arrestors (not shown) may be included on both the suction and discharge of the blower 13 to protect the storage vessel 12 from flashback.

[0025] The stream of volatile vapors from the storage vessel 12 is circulated through the vapor removal system 10 through suitable conduits that connect the storage vessel 12, the vapor pump 13, the heat exchange module 14 and the carbon adsorption module 16. Preferably, metal piping is used such as, for example, carbon steel piping. Alternatively, plastic piping may be useful as well as flexible hose or hose made of woven metal. Material selection for the conduits may be properly selected by one having ordinary skill in the art for each given application.

[0026] HEAT EXCHANGE MODULE

[0027] A preferred embodiment of the heat exchange module 14 is shown in Figures 2A and 2B. The illustrated embodiment has a first heat exchange condenser 21 and a second heat exchange condenser 22. Each of the two heat exchange condensers are plumbed such that a refrigerant or coolant can selectably pass through one or both of the heat exchangers at any given time. The preferred coolant for the system is liquid nitrogen; however other refrigerants such as ammonia or cold water may also be used. Alternatively, or in combination with the above, a refrigerant or coolant may be used to cool a circulating coolant stream.

[0028] The volatile vapor stream pumped from the storage vessel is typically passed through both of the heat exchange condensers and the refrigerant or coolant is used to cool the vapor stream in the second condenser that the vapor stream passes through. The refrigerant selected for use is pumped through the second condenser at a temperature equal to or less than the condensing temperature of the known volatile vapors of concern in the vapor stream.

[0029] Although there are a variety of flow paths by which the vapor stream can pass through the first and second heat exchange condensers 21 and 22, Figure 2A and figure 2B each show an example of one flow path. The operation of the pumps, valves, coolant circulation, temperature monitors, pressure monitors, etc. may all be operated manually or by preprogrammed processing units.

[0030] Figure 2A shows the vapor stream pumped from the storage vessel 12 through an optional inlet knock-out tank 19. The suction pump 13 continues to pump the vapor stream into the piping connecting the storage vessel exit to the first heat exchange condenser

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21 through open valve 24A. Typically, the refrigerant or coolant is not circulating through the first condenser 21 but is circulating through the second heat exchange condenser 22.

[0031] Thus, the vapor stream passes through the first condenser 21 and continues toward the second heat exchange condenser 22 through open valves 24B, 24C and 24D. Since the refrigerant is circulating through the second heat exchange condenser 22, the temperature in the second condenser 22 is lower than the temperature of the first heat exchange condenser 21 and is generally lower than the condensing temperature for the VOCs in the vapor stream. Thus, as the vapor stream passes through the second heat exchange condenser 22 and is cooled by the refrigerant, condensate from the volatile organic components in the cooled vapor stream will accumulate at the bottom of the second condenser 22.

[0032] The condensate may be drained manually opening the valve 29B into a condensate collection vessel 15, or alternatively the condensate may be drained automatically using a controller that monitors a liquid level in the condenser to send a signal to open the valve 29B and allow the condensate to drain from the second condenser 22 into the condensate collection vessel 15.

[0033] The flow path illustrated in Figure 2A shows the vapor stream leaving the second heat exchange condenser 22 and passing through open valves 24E and 24F toward the carbon adsorption module 16.

[0034] As the volatile vapors condense in the second heat exchange condenser 22, some of the condensate does not accumulate in the bottom of the condenser but instead freezes within the condenser and plugs a portion of the condenser 22. As the condenser 22 begins to plug the condenser 22, an additional pressure drop is added to the system, thereby reducing the circulation rate of the vapor stream. As more condensate freezes, the frozen condensate plugs a greater volume of the condenser until all circulation is stopped and the system is shut down.

[0035] To prevent shutting down the system due to frozen condensate, the flow path of the vapor stream through the first and second heat exchange condensers 21 and 22 is altered. Typically, the direction of the flow of the vapor stream is reversed either at preset time intervals (e.g., 10-30 minutes) or whenever the pressure across one or both of the condensers drops to a particular setpoint.

[0036] For example, the vapor flow stream shown in Figure 2A is stopped and the vapor flow stream shown in Figure 2B may be employed. Figure 2B illustrates a vapor

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stream flow path that pumps the vapor stream into the piping connecting the storage vessel exit to the second heat exchange condenser 22 through open valves 26A, 24C, and 24D. The refrigerant or coolant is shut off to the second condenser 22 and the refrigerant begins circulating through the first condenser 21.

[0037] In the flow path shown in Figure 2B, the vapor stream initially passes into the second condenser 22 from the storage tank 12. The vapor stream is generally warmer than ambient temperature, having been warmed by the blower 13, and is warmer than the second heat exchange condenser 22 that contains some frozen condensate. Thus, the warm vapor stream coming from the storage vessel 12 is warm enough to begin melting the frozen condensate in the second condenser 22. Likewise, the temperature in the second condenser 22 is lower than the temperature of the incoming vapor stream and may condense some of the VOCs entrained in the vapor stream. Any condensate that melts or any vapor condensate will accumulate at the bottom of the second condenser 22 and can be removed by opening valve 29B and allowing the condensate to drain into the condensate collection vessel 15.

[0038] The flow path illustrated in Figure 2B shows the vapor stream leaving the second heat exchange condenser 22 and passing through open valves 24E and 26B into the first heat exchange condenser 21. Since the refrigerant is circulating through the first heat exchange condenser 21, the temperature in the first condenser 21 is generally lower than the condensing temperature for the VOCs in the vapor stream. Thus, as the vapor stream passes through the first heat exchange condenser 21 and is cooled by the refrigerant, condensate from the volatile vapors in the cooled vapor stream will accumulate at the bottom of the first condenser 21.

[0039] The condensate may be drained manually opening the valve 29A into a condensate collection vessel 15, or alternatively the condensate may be drained automatically using a controller that monitors a liquid level in the condenser to send a signal to open the valve 29A and allow the condensate to drain from the first condenser 21 into the condensate collection vessel 15.

[0040] The flow path illustrated in Figure 2B shows the vapor stream leaving the first heat exchange condenser 21 and passing through open valves 26C into the carbon adsorption module 16.

[0041] As the volatile vapors condense in the first heat exchange condenser 21, some of the condensate will freeze within the condenser 21 and plug a portion of the condenser 21. As the condenser 21 begins to plug, an additional pressure drop is added to the system,

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reducing the circulation rate of the vapor stream containing the VOCs. As more condensate freezes, the frozen condensate plugs a greater volume of the condenser and if the vapor stream is not redirected the frozen condensate might become sufficient to stop all circulation of the vapor stream and the system.

[0042] In order to prevent problems associated with the build up of frozen condensate in one of the condensers, the direction of the flow of the vapor stream is reversed either at preset time intervals (e.g., 10-30 minutes) or whenever the pressure across one or both of the condensers drops to a particular setpoint.

[0043] For example, an operator of the system may determine when to switch or reverse the order of the heat exchange condensers in which the vapor stream flows, by monitoring the pressure drop across each of the heat exchange condensers, or across both of the condensers. The monitoring equipment may include pressure transmitters, differential pressure transmitters, pressure gauges or combinations thereof. When the pressure drop increases to a predetermined setpoint that indicates one of the heat exchange condensers is becoming plugged due to frozen condensate, the circulation of the volatile vapor stream is reversed, or switched from the partially plugged condenser to the other condenser.

[0044] The switching from one heat exchange condenser to the other may be made manually or may be accomplished with a controller that is on a timing switch or that monitors the pressure drop and sends a signal to a set of control valves to switch the flow when the pressure drop is at or near the setpoint limit.

[0045] Any of the controllers mentioned herein may be digital controllers, analogue controllers or combinations thereof and may be individual controllers suitable for controlling one process condition or one controller, such as a computer or microprocessor controller capable of controlling and monitoring multiple process conditions, or combinations thereof.

[0046] CARBON ADSORPTION MODULE

[0047] The vapor stream is routed from the heat exchange module 14 to the carbon adsorption module 16. Figures 3 and 4 illustrate a couple of preferred embodiments of the carbon adsorption module 16. The carbon adsorption module shown in Figure 4 has a first carbon adsorption unit 41 and a second carbon adsorption unit 42. Each of the carbon adsorption units contains a carbon adsorption material that reversibly adsorbs volatile organic vapor molecules to its surface.

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[0048] The adsorption of volatile vapors is exothermic and causes the heat to increase in the carbon adsorption units. As the temperature in the carbon adsorption unit increases, the chance of a resulting bed fire in the carbon adsorption unit increases. In addition, as the heat in a carbon absorption unit increases the adsorption of the VOCs becomes less efficient. Thus, the first and second carbon adsorption units 41, 42 are optionally plumbed, as shown in Figure 4, to selectably allow the refrigerant or coolant to circulate through the absorption units whenever the temperature in one of the carbon adsorption units increases above a desired limit. The preferred temperature for the operation of the carbon absorption unit will depend on the refrigerant or coolant used (preferably nitrogen), the VOCs being absorbed, and the binding coefficient of the carbon absorption unit for the VOCs.

[0049] The first and second carbon adsorption units are plumbed so that the entire first and/or second carbon adsorption unit is flooded with a non-flammable refrigerant or coolant in the case that a bed fire does start. This allows for the quick asphyxiatiation of the bed fire. Alternatively the first and second carbon adsorption units are plumbed with piping through the units to allow refrigerant or coolant to be circulated through the piping within the first and/or second carbon adsorption units at a controlled rate.

[0050] As the vapor stream leaves the heat exchange module 14 it passes into one of the carbon adsorption units in the carbon adsorption module 16. If the valve 43 is opened and the valve 44 is closed the vapor will pass into the first carbon adsorption unit 41; whereas if the valve 44 is open and the valve 43 is closed the vapor will pass into the second carbon adsorption unit 42. There are numerous permutations as to how and when each carbon unit may be used to remove volatile organic components from the vapor stream. One example of the use of the first and second carbon adsorption units is discussed below.

[0051] In the example shown in Figure 3, a majority of the volatile vapors will typically have been condensed and recovered in the heat exchange module 14. Thus, there will be fewer volatile vapor molecules to be removed before the vapor stream can be released into the atmosphere.

[0052] As shown in Figure 3, if the valve 44 is closed and the valve 43 is opened the vapor stream passes into the first carbon adsorption unit 41. At first, all of the volatile organic components will be adsorbed by the first carbon adsorption unit 41 so that the exit flow from the first carbon adsorption unit 41 can pass through open valve 47 out into the atmosphere.

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[0053] The vapor effluent from the first carbon adsorption unit 41 is constantly monitored for the presence of the volatile organic components that are not wanted to be released into the atmosphere. When the presence of one or more of the volatile organic components of concern is first detected, valve 43 and 47 are closed and valve 44 and 48 are opened to divert the vapor stream into the second carbon adsorption unit 42.

[0054] The vapor stream will be sent to the second carbon unit 42 until its capacity to absorb the volatile organic compounds is reached and the vapor stream is then diverted back to a rejuvenated first carbon adsorption unit 41.

[0055] The carbon adsorption units are rejuvenated by desorbing the volatile organic components from the carbon adsorption unit's surfaces. Desorption is accomplished by applying a vacuum to, with or without some increase in temperature, the carbon adsorption unit. Since the vaporization of a liquid is endothermic and decreases the temperature in the carbon adsorption unit being desorbed, generally the circulation of the refrigerant or coolant to a carbon adsorption unit is cut off during desorption of the VOCs and the temperature in the carbon absorption unit is maintained high enough that the absorbed VOCs can be pulled off the carbon absorption unit with a vacuum.

[0056] One embodiment of the desorption of the first carbon adsorption unit 41 includes closing off the inflow of a coolant, such as by closing valve 31 or valve 39. Once the circulation of the coolant to the carbon adsorption unit 41 or 42 has been done, a vacuum is applied to the carbon adsorption unit to be desorbed.

[0057] For example, the desorption of carbon absorption unit 41 involves closing valve 43 and 47 and opening valve 45. A vacuum is applied to the first carbon adsorption unit 41 by engaging the pump 50. The vacuum pump is used to lower the pressure in the carbon adsorption unit 41 to below the vapor pressure of the adsorbed volatile organic components, which causes the volatile organic components to evaporate off the adsorption unit 41 at the temperature that is ambient in the adsorption unit, instead of a higher temperature.

[0058] A similar process is used for the desorption of the second carbon adsorption unit 42 whenever the vapor stream effluent from the second carbon adsorption unit 42 is detected to contain unadsorbed volatile organic components. Typically, valves 44 and 48 are closed and valve 46 is opened. A vacuum is applied to the second carbon adsorption unit 42 by engaging the pump 50. The vacuum pump is used to lower the pressure in the carbon adsorption unit 42 to below the vapor pressure of the adsorbed volatile organic components,

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causing the volatile organic components to evaporate off the adsorption unit 42 at the temperature that is ambient in the adsorption unit, instead of a higher temperature. Alternatively, hot air or another liquid that is kept at ambient temperature or warmer is circulated through the refrigerant or coolant flow path through the first and/or second carbon adsorption units to increase the evaporation of the volatile organic components off of the carbon adsorption units.

[0059] Typically, the desorbed vapors are at a higher concentration than when they were initially adsorbed in the carbon adsorption unit 41 or 42. The desorbed vapors or VOCs are then routed to the inlet knock-out tank 19 and back through the heat transfer module 14. The valve 52 from the storage tank is typically closed while the desorbed vapors are being routed to the knock-out tank 19. The desorbed VOCs are recovered as condensate from the heat transfer module 14.

[0060] CIRCULATION OF REFRIGERANT

[0061] The preferred refrigerant or coolant used in the heat exchange module is nitrogen. Typically liquid nitrogen is supplied from a liquid gas canister 30 shown in Figure 4, such as a cryogenic tank. The refrigerant or coolant is selectably circulated through the first heat exchange unit 21 or the second heat exchange unit 22 as described above. The flow of the refrigerant may be manually controlled with valves, or with actuators that are controlled by a controller or microprocessor.

[0062] The pressure of the liquid nitrogen inside the heat exchangers is controlled. Typically, the pressure of the liquid nitrogen at the inlet of the cooled heat exchanger is maintained at a pressure between 40-50 psi (preferably about 43 psi) and the pressure of the liquid nitrogen on the outlet ranges between 30-45 psi (preferably about 36 psi).

[0063] When the refrigerant is circulated to the second heat exchange condenser 22, the inlet valve 33 is opened and the refrigerant is pumped into the condenser 22. The refrigerant inlet valve 33 is typically closed when the condenser 22 is offline. The circulated refrigerant is typically vented from the heat exchange condenser 22 either to the atmosphere when valve 35 is open and/or to the carbon adsorption units of the carbon adsorption module 16 when the valve 36 is open to assist in maintaining a temperature within an actively adsorbing unit to prevent bed fires.

[0064] Similarly, when the refrigerant or coolant is circulated to the first heat exchange condenser 21, the inlet valve 32 is opened and the refrigerant is pumped into the

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condenser 21. The refrigerant inlet valve 32 is typically closed when the condenser 21 is offline. The circulated refrigerant is typically vented from the heat exchange condenser 21 either to the atmosphere when the valve 34 is open and/or to the carbon adsorption units of the carbon adsorption module 16 when the valve 37 is open to assist in maintaining a temperature within an actively adsorbing unit to prevent bed fires.

[0065] Whenever the refrigerant or coolant is sent to the carbon absorption module 16 from the second heat exchanger condenser 22, valve 35 is closed to stop the refrigerant from venting to the atmosphere and valves 36 and 38 are opened. Similarly, when the refrigerant or coolant is sent to the carbon absorption module 16 from the first heat exchange condenser 21, valve 34 is closed and valves 37 is opened. Valve 31 controls the circulation of the refrigerant or coolant through the first carbon absorption unit 41 and valve 39 controls the circulation of the coolant through the second carbon absorption unit 42.

[0066] **ADVANTAGES OF THE INVENTION**

[0067] One advantage of the refrigerated vapor recovery system is that any failure of a single component in the system does not result in the release of harmful vapors or VOCs to the atmosphere. For example, even if both condensers failed to condense the volatile organic components from the vapor stream due to operator inattention resulting in allowing the condenser temperature to become too high, from mechanical failure of a valve or the blower, running out of refrigerant, or any other cause, the vapors proceed to the carbon adsorption module 16 and stay within the system and are not vented to the atmosphere as may occur in a system that utilizes combustion of the volatile organic components in the vapor stream.

[0068] Another advantage of the vapor recovery system is that the volatile organic components removed from the storage vessel are not combusted or otherwise disposed of in the atmosphere but rather are converted into a liquid state that may be sold as a product or utilized as a raw material for a process.

[0069] Yet another advantage is that the vapor recovery system allows for multiple cycles of use and reuse with a minimum of energy input. For example, the heat exchange module 14 allows for the diversion of the vapor stream from one heat exchange condenser to another heat exchange condenser if a problem develops in one of the heat exchange condensers. Likewise, the system is easily diverted from one carbon adsorption unit to another carbon adsorption unit whenever one carbon adsorption unit needs to be rejuvenated.

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[0070] The terms "comprising," "including," and "having," as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term "consisting essentially of," as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic and novel characteristics of the claimed invention. The terms "a," "an," and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. For example, the phrase "a solution comprising a phosphorus-containing compound" should be read to describe a solution having one or more phosphorus-containing compound. The terms "at least one" and "one or more" are used interchangeably. The term "one" or "single" shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as "two," are used when a specific number of things is intended. The terms "preferably," "preferred," "prefer," "optionally," "may," and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention.

[0071] It should be understood from the foregoing description that various modifications and changes may be made in the preferred embodiments of the present invention without departing from its true spirit. The foregoing description is provided for the purpose of illustration only and should not be construed in a limiting sense. Only the language of the following claims should limit the scope of this invention.

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WHAT IS CLAIMED IS:

1. A carbon absorption module having:

(a) a first carbon absorption unit having a first inlet in selectable communication with an outlet of a cooled heat exchanger and a first outlet;

(b) a second carbon absorption unit having a second inlet in selectable communication with the outlet of the cooled heat exchanger and a second outlet;

(c) a monitoring device for measuring the concentration of a volatile organic component in an effluent from the first or the second carbon adsorption unit;

(d) a first effluent flow path passing from the first outlet through the monitoring device;

(e) a second effluent flow path passing from the second outlet through the monitoring device;

(f) an atmospheric discharge outlet in selectable communication with the first and second effluent flow paths;

(g) a pump in selectable communication with the first and second effluent flow paths; and

(h) a desorption flow path in communication with the pump and the cooled heat exchanger.

2. The carbon absorption module of claim 1, further comprising a temperature control means for controlling the temperature in the first and second carbon absorption units.

3. The carbon absorption module of claim 1, further comprising a first coolant flow path passing through the first carbon absorption unit and a second coolant flow path passing through the second carbon absorption unit.

4. The carbon absorption module of claim 3, wherein the first and second coolant flow paths are in communication with a third coolant flow path through the cooled heat exchanger.

5. The carbon absorption module of claim 1, wherein when the first inlet is closed, the first effluent flow path is opened to the pump, and the pump is activated causing the pressure in the first carbon absorption unit to decrease.

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6. The carbon absorption module of claim 1, wherein when the second inlet is closed, the second effluent flow path is opened to the pump, and the pump is activated causing the pressure in the second carbon absorption unit to decrease.

7. A carbon absorption module having:

(a) a first carbon absorption unit having

(i) a first inlet in selectable communication with an outlet of a cooled heat exchanger,

(ii) a first flow path for a coolant, and

(iii) a first outlet;

(b) a second carbon absorption unit having

(i) a second inlet in selectable communication with the outlet of the cooled heat exchanger,

(ii) a second flow path for the coolant, and

(iii) a second outlet,

(c) a monitoring device for measuring the concentration of a volatile organic component in an effluent from the first or the second carbon adsorption unit;

(d) a first effluent flow path passing from the first outlet through the monitoring device;

(e) a second effluent flow path passing from the second outlet through the monitoring device;

(f) an atmospheric discharge outlet in selectable communication with the first and second effluent flow paths;

(f) a pump in selectable communication with the first and second effluent flow paths; and

(e) a desorption flow path in communication with the pump and the cooled heat exchanger.

8. The carbon absorption module of claim 7, wherein the first and second flow paths for the coolant are in selective communication with a flow path for the coolant through the cooled heat exchanger.

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9. The carbon absorption module of claim 7, further comprising a temperature control means for controlling the temperature in the first and second carbon absorption units.

10. The carbon absorption module of claim 7, wherein the desorption flow path passes through a knock-out tank.

11. The carbon absorption module of claim 7, wherein the cooled heat exchanger is connected to a condensate tank.

12. A method for removing and recovering a volatile organic component from a vapor stream including the steps of:

(a) directing a flow of the vapor stream to a first carbon adsorption unit from a cooled heat exchanger;

(b) measuring the vapor stream exiting from the first carbon adsorption unit for the volatile organic component;

(c) releasing the exiting vapor stream from the first carbon adsorption unit into the atmosphere if a measured concentration of the volatile organic component is below a desired concentration;

(d) diverting the flow of the vapor stream to a second carbon adsorption unit whenever the measured concentration of the volatile organic component in the vapor stream exiting from the first carbon adsorption unit is equal to or greater than the desired concentration;

(e) lowering the pressure in the first carbon adsorption unit to desorb the volatile organic component; and

(f) directing the desorbed volatile organic component through the cooled heat exchanger to condense a portion of the volatile organic compound.

13. The method of claim 12, wherein the first carbon adsorption unit is cooled during the adsorption of the volatile organic component.

14. The method of claim 13, wherein a coolant used to cool the first carbon absorption unit is the coolant used to cool the heat exchanger.

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15. The method of claim 14, wherein the coolant is nitrogen.

16. The method of claim 12, wherein the desorbed volatile organic component passes through a knock-out tank and an uncooled heat exchanger before passing the desorbed volatile organic component through the cooled heat exchanger.

17. The method of claim 12, wherein the condensed portion of the volatile organic component is removed from the cooled heat exchanger to a condensate tank.

18. The method of claim 12, further including the step of selectably controlling the temperature in the first or second carbon adsorption unit.

19. The method of claim 12, further including the step of passing coolant through the first or second carbon adsorption unit to asphyxiate a bed fire.

20. A method for recovering a volatile organic component from a vapor stream comprising:

(a) directing the vapor stream from a storage vessel to a heat exchange module having at least one heat exchange condenser;

(b) starting a refrigerant flow through at least one heat exchange condenser to cool the condenser;

(c) directing the flow of the vapor stream through the heat exchange module, wherein a portion of the volatile organic component in the vapor stream flowing through the cooled heat exchange condenser is condensed;

(d) draining the condensed volatile organic component from the cooled heat exchange condenser;

(e) directing the uncondensed vapor stream from the heat exchange module to a first carbon adsorption unit from the cooled heat exchanger to adsorb the volatile organic component;

(f) measuring the vapor stream exiting from the first carbon adsorption unit for the volatile organic component;

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(g) releasing the exiting vapor stream from the first carbon adsorption unit into the atmosphere if a measured concentration of the volatile organic component is below a desired concentration;

(h) diverting the flow of the vapor stream to a second carbon adsorption unit whenever the measured concentration of the volatile organic component in the vapor stream exiting from the first carbon adsorption unit is equal to or greater than the desired concentration;

(i) lowering the pressure in the first carbon adsorption unit to desorb the volatile organic component; and

(j) directing the desorbed volatile organic component through the cooled heat exchanger to condense a portion of the volatile organic compound.

21. The method of claim 20, wherein the heat exchange module contains two heat exchange condensers and a second heat exchange condensers is cooled with refrigerant.

22. The method of claim 20, further comprising the step of selectably cooling the first or second carbon absorption units.

23. The method of claim 20, further comprising the step of controlling the temperature in the first or second carbon absorption units during the absorption of the volatile organic component.

24. The method of claim 22, wherein the refrigerant is directed to the first or second carbon absorption units from the cooled heat exchange condenser.

25. The method of claim 20, wherein the desorbed volatile organic component passes through a knock-out tank and an uncooled heat exchanger before the desorbed volatile organic component enters the cooled heat exchanger.

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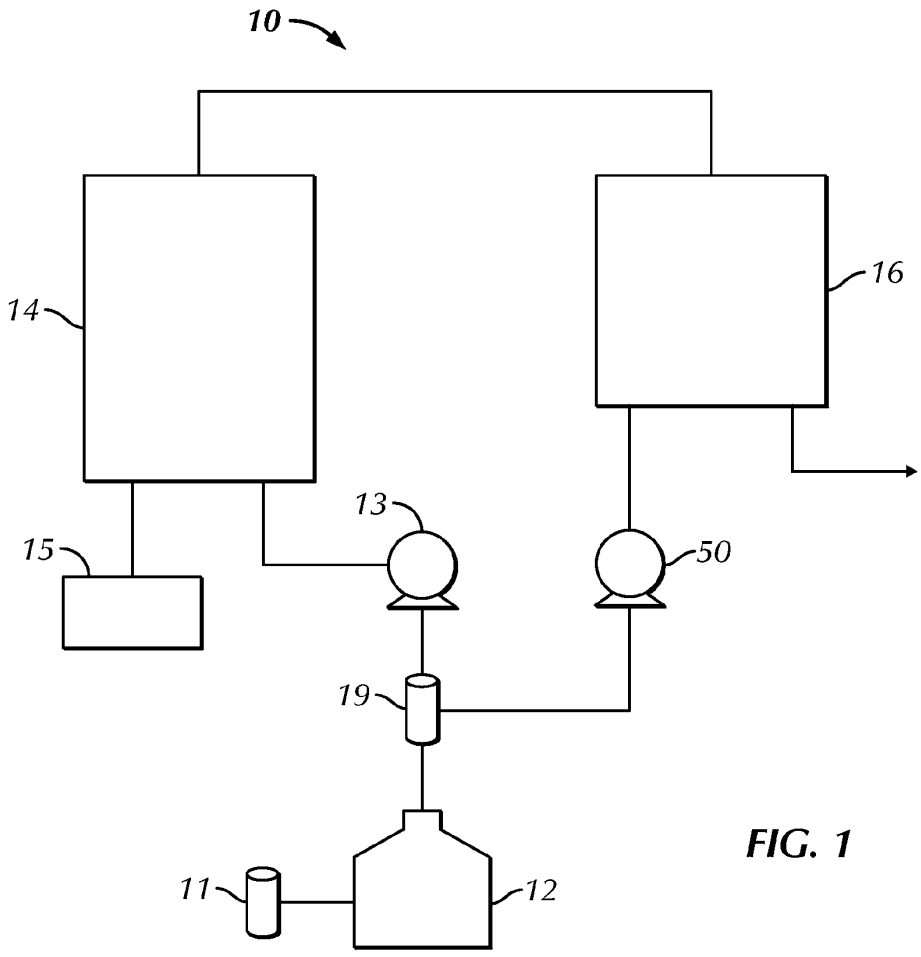


FIG. 1

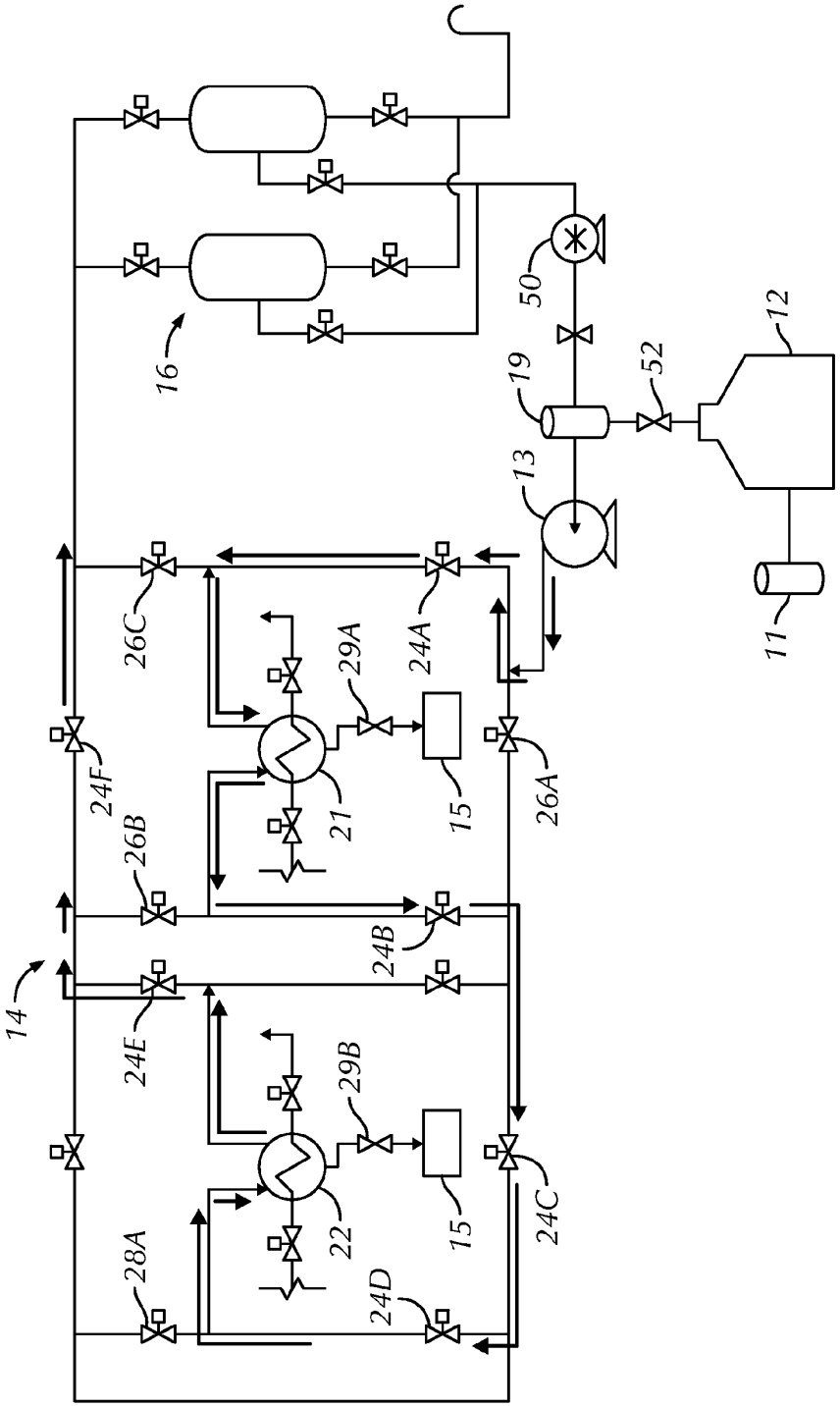

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FIG. 2A

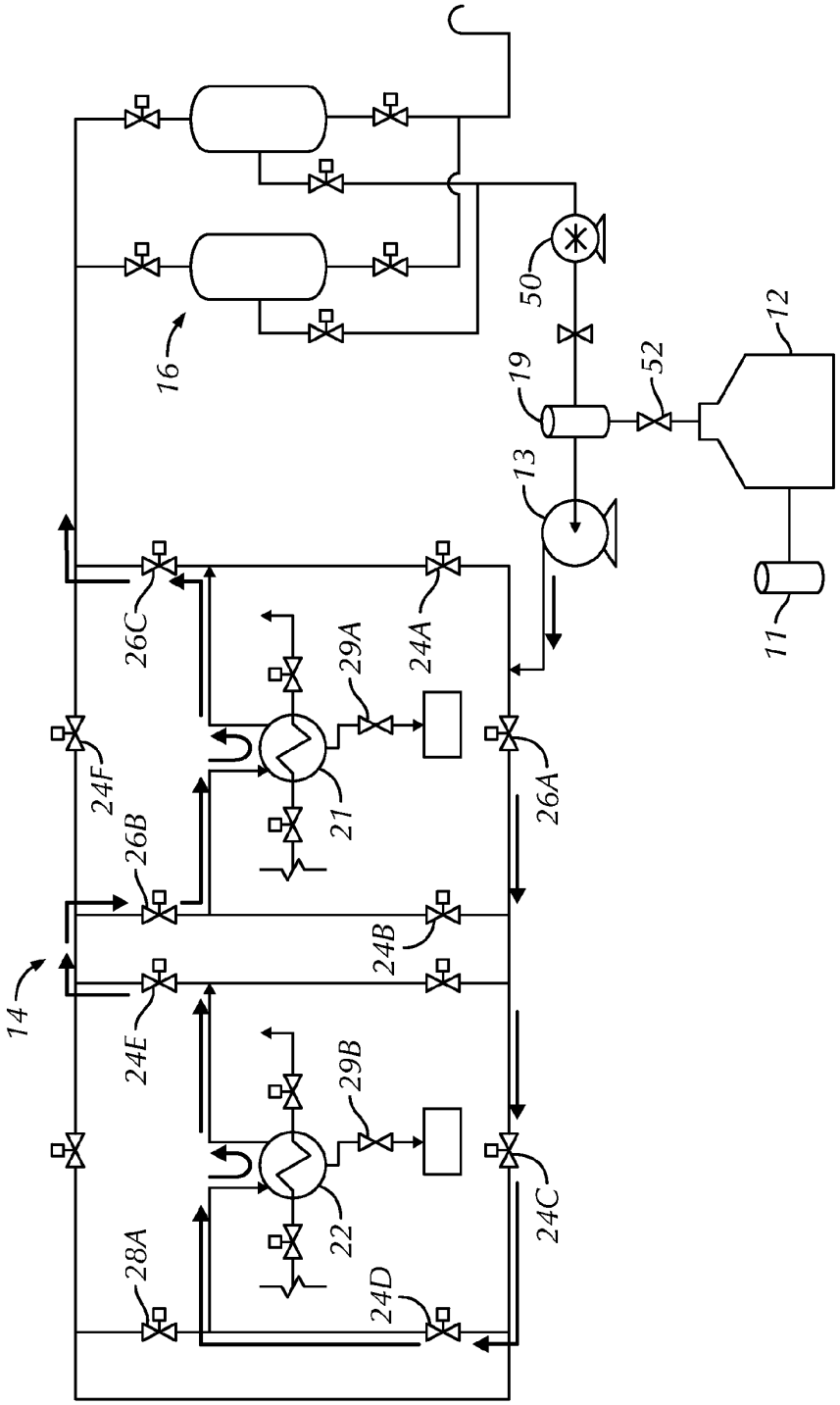

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FIG. 2B

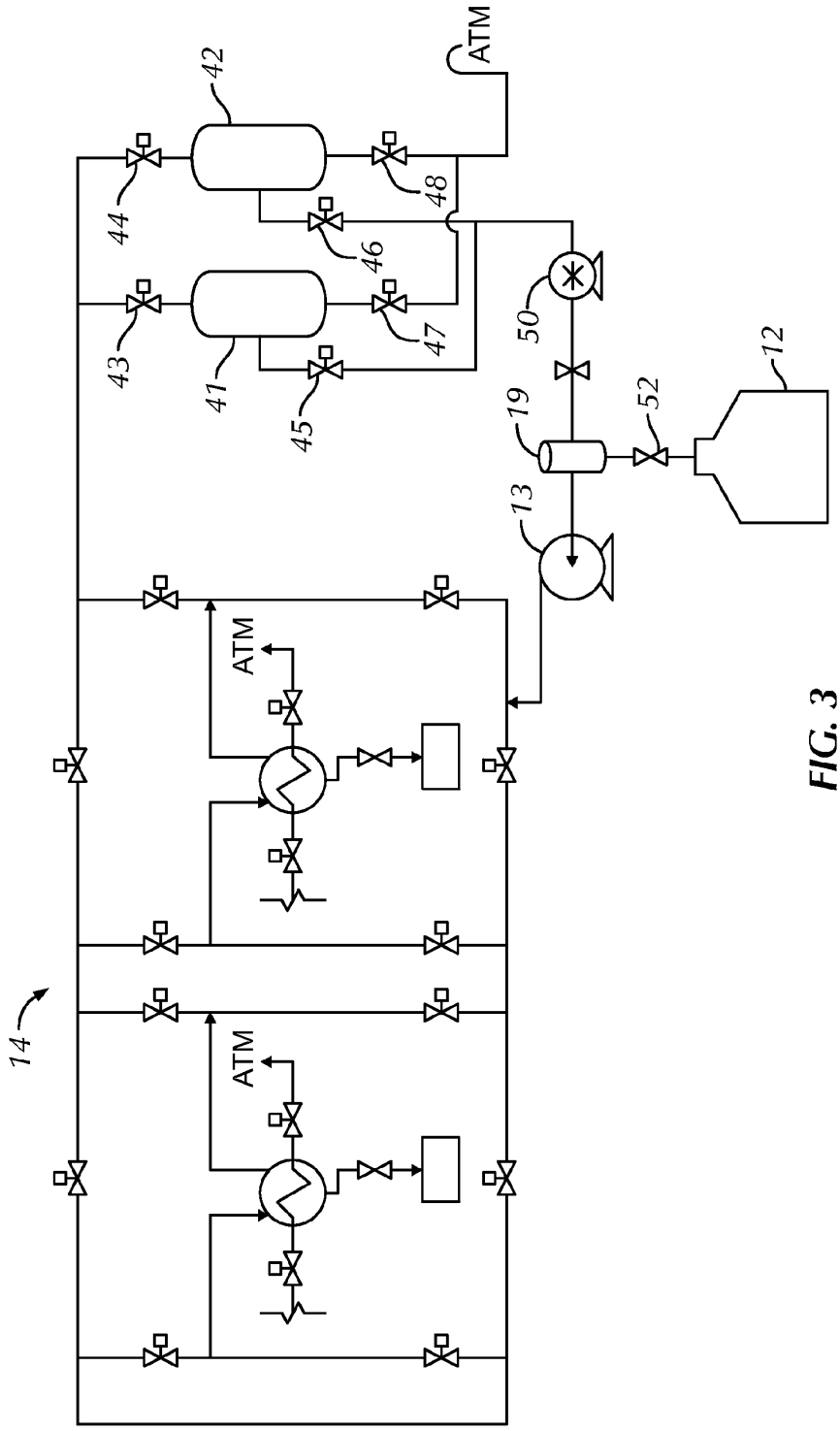


FIG. 3

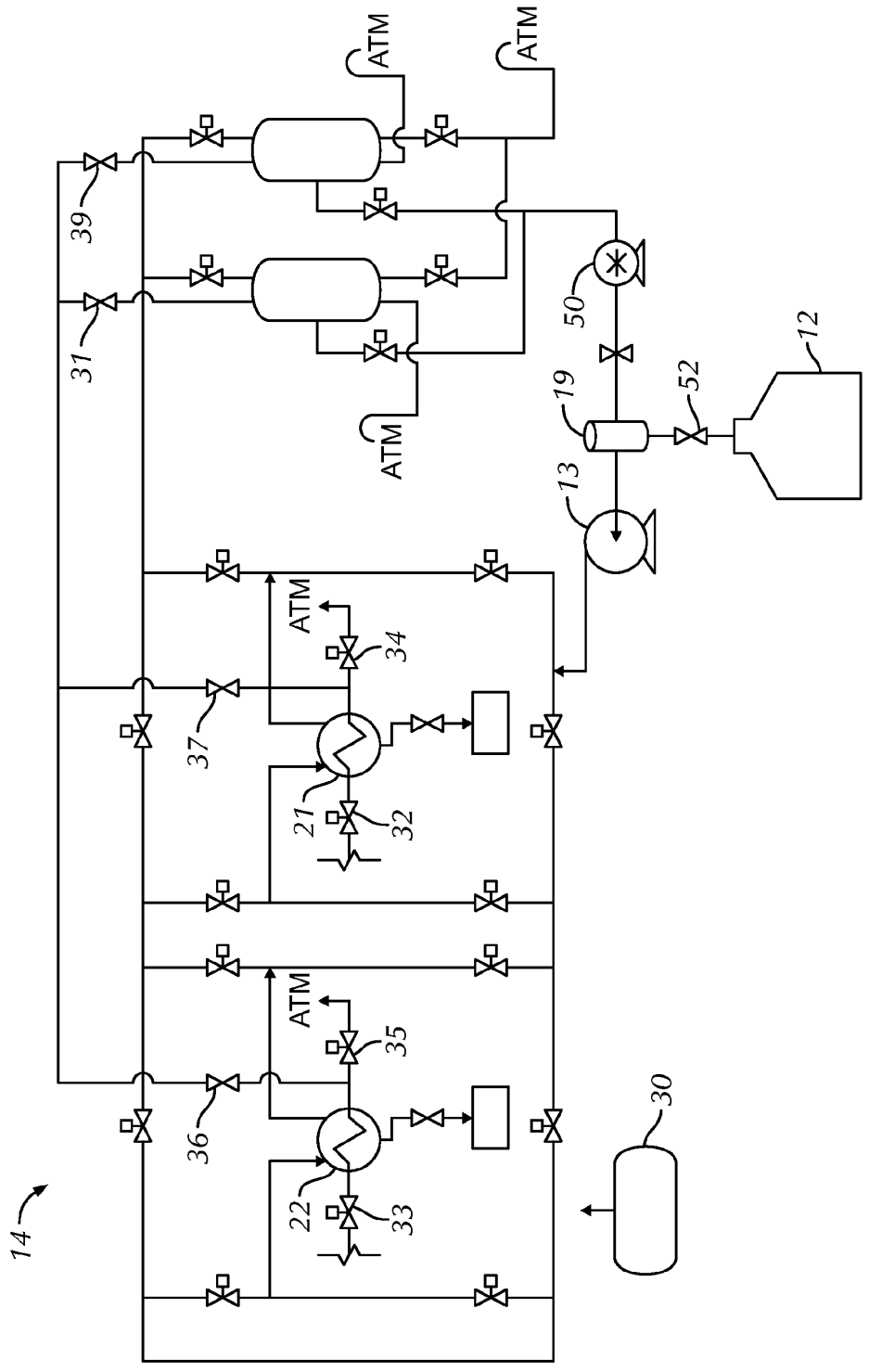


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 13/33078

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 59/26 (2013.01)
USPC - 96/108
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - B01D 59/26 (2013.01)
USPC - 96/108

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
423/414;62/623,617,912 (Search terms - See below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase and Google. Search terms: carbon, adsorption, absorption, volatile, oganic, voc, hydrocarbon, monitor, measure, test, analyze, examine, temperature, refrigerate, cool, cooler, chill, heat, exchange, pump, select, switch, shift and choose.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,755,854 A (Nanaji) 26 May 1998 (26.05.1998) Entire document, especially Fig 1, it 54 and 55 and col 2, ln 23-43; col 4, ln 38-62 col 5, ln 22-25; and col 6, ln 1-61; col 7, ln 1-5 and ln 40-55; col 9, ln 30-40.	1-25
Y	US 6,015,451 A (Anderson et al.) 18 January 2000 (18.01.2000) Entire document, especially Fig 1, it 42, 66 and 88; col 5, ln 10-11 and col 6, ln 2-7.	1-25
Y	US 5,450,728 A (Vora et al.) 19 September 1995 (19.09.1995) Entire documene, especially (col 5, ln 10-17	15 and 20-25

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 May 2013 (12.05.2013)	05 JUN 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) Title: METHODS FOR MITIGATING THE LEACHING OF HEAVY METALS FROM ACTIVATED CARBON

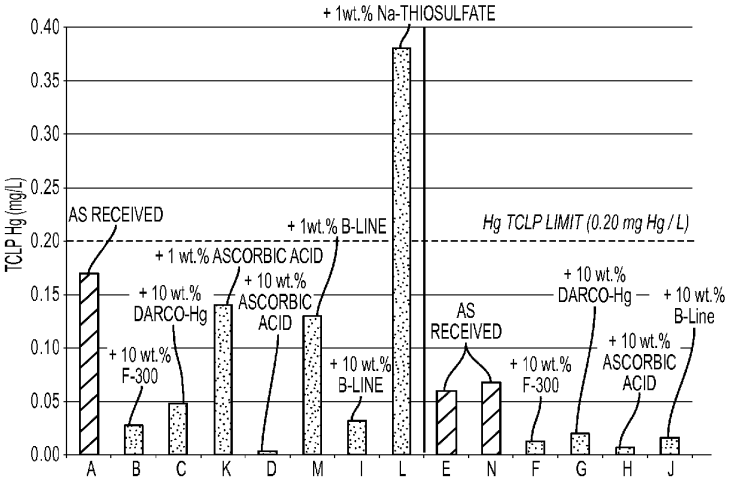


FIG. 3

(57) Abstract: Compositions, methods, and systems for reducing leaching of heavy metals from sorbents having adsorbed heavy metals are described herein. Such compositions and methods may include reducing agents.

WO 2014/205200 A1

A. Title:

METHODS FOR MITIGATING THE LEACHING

OF HEAVY METALS FROM ACTIVATED CARBON

B. Cross-Reference to Related Applications:

[0001] This application claims priority to U.S. Provisional No. 61/836,945 entitled "Methods For Mitigating The Leaching Of Heavy Metals From Activated Carbon" filed June 19, 2013 and U.S. Provisional No. 61/839,962 entitled "Methods For Mitigating The Leaching Of Heavy Metals From Activated Carbon" filed June 27, 2013, the entire contents of which are hereby incorporated by reference.

C. Government Interests: Not applicable

D. Parties to a Joint Research Agreement: Not applicable

E. Incorporation by Reference of Material submitted on a Compact Disc: Not applicable

F. Background: Not applicable

G. Summary of the Invention:

[0002] Various embodiments of the invention are directed to methods for reducing heavy metal leaching from sorbents having associated heavy metals. Such methods may include the step of contacting a sorbent having associated heavy metals with a reducing agent. The sorbents having associated heavy metals may be any sorbent including, for example, carbonaceous char, activated carbon, reactivated carbon, carbon black, graphite, natural zeolite, synthetic zeolite, silica, silica gel, alumina clay, diatomaceous earths, and combinations thereof, and the heavy metals may be associated with the sorbent in any way. For example, the heavy metals may be adsorbed to a surface of the sorbent, absorbed by the sorbent, or otherwise attached or electronically bound with the sorbent.

[0003] The reducing agent may be any reducing agent such as, for example, ascorbic acid, gallic acid, caffeic acid, ferulic acid, chlorogenic acid, formic acid, oxalic acid, maleic acid, tocopherols, tocotrienols, desferrioxamine, pyruvic acid, including salts of pyruvic acid, cysteine, glutathione, and the like and combinations thereof. In various embodiments, the reducing agent may be about 1 wt.% to about 15 wt.% based on the total weight of the sorbent. In some embodiments, the reducing agent may be ascorbic acid, and in other embodiments, the reducing agent may be monosodium ascorbate, calcium diascorbate, monopotassium ascorbate, magnesium diascorbate, and the like and combinations thereof.

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[0004] In some embodiments, the sorbent may further include a halogen precursor such as, but not limited to, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof. In certain embodiments, the halogen precursor may be impregnated onto the sorbent.

[0005] Other embodiments are directed to flue gas adsorbents including a sorbent and a reducing agent such as, for example, ascorbic acid, gallic acid, caffeic acid, ferulic acid, chlorogenic acid, formic acid, oxalic acid, maleic acid, tocopherols, tocotrienols, desferrioxamine, pyruvic acid, including salts of pyruvic acid, cysteine, glutathione, and combinations thereof. The sorbent of such embodiments may be carbonaceous char, activated carbon, reactivated carbon, carbon black, graphite, natural zeolite, synthetic zeolite, silica, silica gel, alumina clay, diatomaceous earths, and combinations thereof.

[0006] In some embodiments, the reducing agent may be about 1 wt.% to about 15 wt.% based on the total weight of the sorbent. In certain embodiments, the reducing agent may be ascorbic acid, and in other embodiments, the reducing agent may be monosodium ascorbate, calcium diascorbate, monopotassium ascorbate, magnesium diascorbate, and the like and combinations thereof.

[0007] In some embodiments, the adsorbent may be a dry admixture of sorbent and reducing agent, and in other embodiments, the reducing agent may be impregnated onto the sorbent. In certain embodiments, the adsorbent may further include a halogen precursor such as, but not limited to, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and the like and combinations thereof. In particular embodiments, the halogen precursor may be calcium bromide ($CaBr_2$), ammonium bromide (NH_4Br), and combinations thereof. The halogen precursor may be a dry halogen precursor, or in some embodiments, the halogen precursor may be impregnated onto the sorbent.

H. Description of Drawings:

[0008] For a fuller understanding of the nature and advantages of the present invention, reference should be made to the following detailed description taken in connection with the accompanying drawings, in which:

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[0009] **FIG. 1** shows a flow chart showing elements of an exemplary coal fired power plant.

[0010] **FIG. 2** shows a chart comparing the percent removal of mercury versus the injection rate for activated carbon.

[0011] **FIG. 3** shows a bar graph illustrating the reduced leaching of heavy metals using the methods described herein.

I. Detailed Description:

[0012] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0013] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a combustion chamber" is a reference to "one or more combustion chambers" and equivalents thereof known to those skilled in the art, and so forth.

[0014] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0015] As used herein, the term "sorbent material" is meant to encompass all know materials from any source capable of adsorbing mercury. For example, sorbent materials include, but are not limited to, activated carbon, natural and synthetic zeolite, silica, silica gel, alumina, and diatomaceous earths.

[0016] The term "heavy metal" will mean toxic metals or metalloids, and in particular, metals and metalloids of environmental and health concern. Examples of heavy

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metals include, but are not limited to, arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.

[0017] Mercury is a known environmental hazard and leads to health problems for both humans and non-human animal species. Approximately 50 tons per year are released into the atmosphere in the United States, and a significant fraction of the release comes from emissions from coal burning facilities such as electric utilities. To safeguard the health of the public and to protect the environment, the utility industry is continuing to develop, test, and implement systems to reduce the level of mercury emissions from its plants. In the combustion of carbonaceous materials, it is desirable to have a process wherein mercury and other undesirable compounds are captured and retained after the combustion phase so that they are not released into the atmosphere.

[0018] One of the most promising solutions for mercury removal from flue gas is Activated Carbon Injection (ACI). Activated carbon is a highly porous, non-toxic, readily available material that has a high affinity for mercury vapor. This technology is already established for use with municipal incinerators. Although the ACI technology is effective for mercury removal, the short contact time between the activated carbon and the flue gas stream results in an inefficient use of the full adsorption capacity of the activated carbon.

[0019] Various embodiments of the invention are directed to methods for removing heavy metals such as, for example, mercury, from a fluid stream produced as a result of combustion of a heavy metal containing fuel source by applying a molecular halogen or halogen precursor to the fuel source or introducing a molecular halogen or halogen precursor into a combustion chamber during combustion of the fuel source or introducing a molecular halogen or halogen precursor into an exhaust stream resulting from the combustion of the fuel source near the combustion chamber and injecting sorbent material into the exhaust stream, *i.e.* flue gas, resulting from consumption of the fuel source. In such embodiments, the combination of applying the molecular halogen or halogen precursor to the fuel source or injecting the molecular halogen or halogen precursor into the combustion chamber and injection of sorbent material into the exhaust stream may result in substantial reduction in heavy metal emissions from the exhaust stream while significantly reducing the amount of both the molecular halogen or halogen precursor and the sorbent material used in such methods. In particular embodiments, mercury removal is improved over conventional methods. In some embodiments, greater than about 80% or greater than about 90% of the heavy metal can be removed from the exhaust stream based on the heavy metal content of the fuel source. Thus, the combination achieves similar or improved removal rates while

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reducing consumption of the molecular halogen or halogen precursor and sorbent material thereby reducing costs.

[0020] The methods and systems described above may implemented into any conventional system that involves combustion of a fuel source that includes heavy metals. Numerous systems and facilities that burn heavy metal-containing fuels are known and used in the art. For example, some embodiments provide compositions, methods, and systems for reducing emissions of heavy metals from incinerators, including solid waste incinerators. Other embodiments provide compositions, methods, and systems for reducing emissions of heavy metals such as mercury that arise from the combustion of heavy metal containing fossil fuels at, for example, power plants.

[0021] FIG. 1 provides a flow chart depicting relevant portions of an exemplary coal fired power plant. As indicated in FIG. 1, some such facilities may include a feeding mechanism such as a conveyor **1** for delivering fuel such as coal into a furnace or combustion chamber **2** where the fuel source is burned. The fuel fed into the furnace is burned in the presence of oxygen with typical flame temperatures in the combustion chamber of the furnace from about 2700° F to about 3000° F as indicated to the right of the flow chart. In operation, the fuel may be fed into the furnace at a rate suitable to achieve the output desired from the furnace the heat from which can be used to boil water for steam or provide direct heat that can be used to turn turbines that are eventually used to produce electricity (not pictured). From the furnace or combustion chamber **2**, ash, combustion gases, and air move downstream, away from the fireball, into a convective pathway, or exhaust stream, (large arrow to the left of the diagram) that can include various zones of decreasing temperature as indicated to the right. From the combustion chamber, the heated ash, combustion gases, and air can move through a superheater **3** and, in cases, a reheater **4** where, for example, water is heated to provide steam which will eventually power a turbine that is used to generate electricity. The ash, combustion gases, and air can also pass through, for example, an economizer **5** where water fed into the superheater **3** and/or reheater **4** is preheated, and an air preheater **6** where air that is fed into the combustion chamber **2** is preheated. The combustion gases and ash may eventually pass through a baghouse or electrostatic precipitator **7** where particulate matter is collected. By this time, the temperature of the ash, combustion gases, and air is reduced to about 300° F before being emitted from the stack **8** and released into the atmosphere.

[0022] In some embodiments, the halogen source may be introduced during combustion by injecting molecular halogen or a halogen precursor **B** into the combustion

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chamber **2** or by applying the halogen source directly to the fuel source prior to combustion **A**. In other embodiments, the halogen may be found in the fuel source. For example, waste that includes plastics or rubbers may include halogen containing components that may release halogen ions or molecular halogens during incineration. In various embodiments, sorbent material may be injected into the exhaust stream anywhere along the convection pathway before emission of the ash, combustion gases, and air into the atmosphere, and in particular embodiments, sorbent material may be injected upstream of the baghouse or electrostatic precipitator **7**. In certain embodiments, sorbent material may be injected upstream **C** of the air preheater (APH) **6**, and in some embodiments, sorbent material may be injected into the exhaust stream downstream **D** of the APH **6**. In still other embodiments, sorbent material may be injected both upstream **C** of the APH **6** and downstream **D** of the APH **6**.

[0023] The molecular halogen or halogen precursor of various embodiments may be obtained from any source. For example, in some embodiments, molecular sources such as chlorine gas, bromine gas, or iodine gas can be injected into the exhaust stream near the combustion chamber alone or in combination with halogen precursor. In other embodiments, one or more halogen precursors may be applied to the fuel source, introduced into the combustion chamber, injected into the exhaust stream near the combustion chamber, or a combination thereof.

[0024] Numerous halogen precursors (halogen precursors) are known in the art and may be used in embodiments of the invention. In some embodiments, the halogen precursor may be a gaseous precursor such as, for example, hydrogen chloride, hydrogen bromide, or molecular chloride or bromide. The halogen precursor may be an organic or inorganic halogen-containing compound. For example, in some embodiments, the halogen precursor may be one or more inorganic halogen salts, which for bromine may include bromides, bromates, and hypobromites, for iodine may include iodides, iodates, and hypoiodites, and for chlorine may be chlorides, chlorates, and hypochloriates. In certain embodiments, the inorganic halogen salt may be an alkali metal or an alkaline earth element containing halogen salt where the inorganic halogen salt is associated with an alkali metal such as lithium, sodium, and potassium or alkaline earth metal such as beryllium, magnesium, and calcium counterion. Non-limiting examples of inorganic halogen salts including alkali metal and alkali earth metal counterions include calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride,

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potassium tri-bromide, potassium tri-iodide, and the like. In other embodiments, the halogen may from an organic source, which contains a suitably high level of the halogen. Organic halogen precursors include, for example, methylene chloride, methylene bromide, methylene iodide, ethyl chloride, ethyl bromide, ethyl iodide, chloroform, bromoform, iodoform, carbonate tetrachloride, carbonate tetrabromide, carbonate tetraiodide, and the like.

[0025] In some embodiments, the halogen precursor may include one or more additional elements such as, for example, a calcium source, a magnesium source, a nitrate source, a nitrite source, or a combination thereof. Exemplary calcium and magnesium sources are well known in the art and may be useful to aid in the removal of sulfur in the flue gas that is released from the fuel source during combustion. In such embodiments, the calcium or magnesium source may include inorganic calcium such as, for example, calcium oxides, calcium hydroxides, calcium carbonate, calcium bicarbonate, calcium sulfate, calcium bisulfate, calcium nitrate, calcium nitrite, calcium acetate, calcium citrate, calcium phosphate, calcium hydrogen phosphate, and calcium minerals such as apatite and the like, or organic calcium compounds such as, for example, calcium salts of carboxylic acids or calcium alkoxylates or inorganic magnesium such as, for example, magnesium oxides, magnesium hydroxides, magnesium carbonate, magnesium bicarbonate, magnesium sulfate, magnesium bisulfate, magnesium nitrate, magnesium nitrite, magnesium acetate, magnesium citrate, magnesium phosphate, magnesium hydrogen phosphate, and magnesium minerals and the like, or organic magnesium compounds such as, for example, magnesium salts of carboxylic acids or magnesium alkoxylates. In certain embodiments, the calcium or magnesium source may be associated with the halide precursor such as, for example, calcium bromide, magnesium bromide, calcium chloride, magnesium chloride, calcium iodide, magnesium iodide, and the like. Nitrate and nitrite sources are also well known in the art and any source of nitrate of nitrite can be formulated with halogen precursor.

[0026] The halogen precursor may be a solid such as a powder, a liquid, or a gas. For example, in some embodiments, the halogen precursor may be an aqueous solution that can be sprayed onto the fuel source such as coal before combustion or can be injected into the combustion chamber or exhaust stream near the combustion chamber. A liquid halogen precursor composition may be prepared at any suitable concentration. For example, in some embodiments, an aqueous solution of a halogen precursor such as, for example, calcium bromide or calcium chloride, may have a concentration of up to about 75%, and in other embodiments, the halogen precursor concentration in the aqueous solution may be up to about 60% by weight, 55% by weight, 50% by weight, 45% by weight, or 40% by weight or

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any concentration between these values.. In still other embodiments, an aqueous solution of a halogen precursor may include about 10% to about 75% by weight, about 20% to about 60% by weight, about 30% to about 55% by weight, or about 40% to about 55% by weight of the halogen precursor. Similarly, in other embodiments, dry, powdered halogen precursor may be applied to the coal at a concentration necessary to achieve a similar concentration of halogen in the flue gas stream.

[0027] In various embodiments, the molecular halogen or halogen precursor, which may be in solid, such as a powder, liquid, or a gaseous form, may be continuously supplied to the combustion chamber or provided incrementally during combustion. The rate of addition of the molecular halogen and halogen precursor may vary among embodiments and may depend, for example, on the rate of combustion of the fuel source, the origin of the fuel source, the amount of mercury in the fuel source, the adsorption of mercury, and the like. For example, in some embodiments, an about 40% to about 55% by weight aqueous solution of a halogen precursor such as, for example, calcium bromide or calcium chloride, may be introduced into a combustion chamber or injected into an exhaust stream near the combustion chamber at a rate of about 500 gallons/hr or less, and in other embodiments, an about 40% to about 55% by weight aqueous solution of the halogen precursor introduced into a combustion chamber or injected into an exhaust stream near the combustion chamber at a rate of about 400 gallons/hr or less, 300 gallons/hr or less, 200 gallons/hr or less, or 100 gallons/hr or less. In certain embodiments, an about 40% to about 55% by weight aqueous solution of the halogen precursor introduced into a combustion chamber or injected into an exhaust stream near the combustion chamber at a rate of less than 50 gallons/hr or less than 25 gallons/hr or less than 20 gallons/hr.

[0028] The feed rate of the molecular halogen or halogen precursor may vary among embodiments and may vary depending on, for example, the feed rate of the fuel source and/or the rate of consumption of the fuel source. For example, a combustion chamber burning about 330 tons/hr of a fuel source such as coal in six mills each burning about 55 tons/hr where about 10 gal/hr of a 50% by weight aqueous solution of calcium bromide ($CaBr_2$) is introduced into the combustion chamber during burning can result in about 125 ppm bromine added to the coal based on dry weight. Thus, in various embodiments, the concentration and/or feed rate the molecular halogen or halogen precursor may be modified based on the rate of consumption of the fuel source such that up to about 400 ppm (dry basis), up to about 500 ppm (dry basis) or up to about 700 ppm (dry basis) bromine may be added the fuel source. In some embodiments, about 50 ppm to about 500 ppm (dry basis), about 75 ppm to

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about 400 ppm (dry basis), about 100 ppm to about 300 ppm (dry basis), or about 125 ppm to about 200 ppm (dry basis) of bromine may be added to the fuel source.

[0029] In some embodiments, the methods and systems described herein may be utilized in a multi-stage furnace having for example, a primary and secondary combustion chambers, a rotary kiln, afterburning chambers, and any combinations thereof. In such embodiments, molecular halogen or halogen precursor in a solid or liquid form may be introduced into any one or any combination of the chambers of the furnace. For example, in some embodiments, the molecular halogen or halogen precursor may be introduced into one combustion chamber, and in other embodiments, the molecular halogen or halogen precursor may be introduced into a combination of combustion chambers. In still other embodiments, molecular halogen or halogen precursor may be introduced into one or more combustion chambers and into an exhaust stream after combustion.

[0030] In certain embodiments, the halogen precursor may be introduced into one or more combustion chambers and/or exhaust stream as an aqueous solution that is sprayed or injected into the chamber or exhaust stream. For example, in some embodiments, an aqueous solution of a halogen precursor may be sprayed or injected into a combustion gas stream downstream of a waste-heat boiler. In still other embodiments, an aqueous solution of the halogen precursor may be introduced into a recirculated substream such as, for example, a recirculated flue gas, recirculated ash, or recirculated fly ash. While embodiments are not limited by the zone where the molecular halogen or halogen precursor is introduced into the exhaust gas stream, the temperature in the injection zone should be sufficiently high to allow dissociation and/or oxidation of the elemental halogen from the halogen precursor. For example, the temperature at the injection zone may be greater than about 1000° F, and in some embodiments, greater than about 1500° F.

[0031] Without wishing to be bound by theory, halogens from the molecular halogen or halogen precursor can oxidize with heavy metals released from the fuel source when it is burned in the combustion chamber. In general, oxidized heavy metals, such as mercuric halide species are adsorbable by alkaline solids in the exhaust stream such as fly ash, alkali fused acidic ash (*e.g.,* bituminous ash), dry flue gas desulfurization solids such as calcium oxide, calcium hydroxide or calcium carbonate, and removed from the flue gas by commonly used heavy metal control systems such as, for example, electrostatic precipitators, wet flue gas desulphurization systems, fabric filters, and baghouses. In certain embodiments, oxidized heavy metals may be adsorbed by activated carbon. Without wishing to be bound by theory, the rate at which a solution of a halogen precursor may be significantly reduced by

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combining the application of a halogen-containing composition with injection of sorbent material into the fluid stream of the combustion gases even when the mercury content of the fuel source is relatively high.

[0032] Activated carbon may be used in any embodiment. In such embodiments, the activated carbon may be obtained from any source and can be made from a variety of starting materials. For example, suitable materials for production of activated carbon include, but are not limited to, coals of various ranks such as anthracite, semianthracite, bituminous, subbituminous, brown coals, or lignites; nutshells, such as coconut shell; wood; vegetables such as rice hull or straw; residues or by-products from petroleum processing; and natural or synthetic polymeric materials. The carbonaceous material may be processed into carbon adsorbents by any conventional thermal or chemical method known in the art. The adsorbents will inherently impart different surface areas and pore volumes. Generally, for example, lignites can result in carbon having surface areas about 500-600 m^2/g and, typical fiber-based carbons areas are about 1200-1400 m^2/g. Certain wood-based carbons may have areas in the range of about 200 m^2/g, but tend to have a very large pore volume.

[0033] Surface area and pore volume of coal based carbon may also be made to allow for some control of surface area and pore volumes and pore size distributions. In some embodiments, the activated carbon adsorbent may have large surface area as measured by the Brunauer-Emmett-Teller ("BET") method, and may have a substantial micropore volume. As used herein, "micropore volume" is the total volume of pores having diameter less than about 2 nm. In some embodiments, suitable carbon adsorbents may have a BET surface areas greater than about 10 m^2/g or about 50 m^2/g, greater than about 200 m^2/g, or greater than about 400 m^2/g. In other embodiments, the carbon adsorbent may have a micropore volume of greater than about 5 $cm^3/100$ g, and in still other embodiments, the adsorbent may have a micropore volume greater than about 20 $cm^3/100$ g.

[0034] Sorbent materials, such as activated carbon, of various sizes have been used to capture heavy metals in systems currently utilized, and any size sorbent material can be used in various embodiments. For example, in some embodiments, the sorbent material may have a mean particle diameter (MPD) of about 0.1 μm to about 100 μm, and in other embodiments, the MPD may be about 1 μm to about 30 μm. In still other embodiments, the MPD of the sorbent material may be less than about 15 μm, and in some particular embodiments, the MPD may be about 2 μm to about 10 μm, about 4 μm to about 8 μm, or about 5 μm or about 6 μm.

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[0035] In some embodiments, the sorbent material may be treated with, for example, a halogen containing salt. For example, in various embodiments, the sorbent material may be impregnated with a bromine by, for example, immersing the sorbent material in a solution of a hydrogen bromide or a stream of elemental bromine gas for sufficient time to allow the bromine to impregnate the sorbent material. Various methods for impregnating the sorbent material and types of impregnated sorbent material are known and used in the art, and any such sorbent material may be used in embodiments.

[0036] The sorbent material may be injected into the exhaust stream anywhere along the convection pathway downstream of the combustion chamber and before the exhaust is emitted from the stack. The sorbent material of various embodiments may generally be injected downstream of a heavy metal control systems such as, for example, electrostatic precipitators, wet flue gas desulphurization systems, fabric filters, and baghouses or other ash or fly ash collection means where particulate matter can be collected and upstream of the combustion chamber. In certain embodiments, the sorbent material may be injected at any zone in the convection pathway having a temperature of less than about 700° F, less than about 500° F, less than about 400° F or less than about 350° F. For example, in some embodiments, sorbent material may be injected into an exhaust stream either upstream or downstream of an air pre-heater (APH), and in other embodiments, the sorbent material may be injected upstream of an air pre-heater (APH).

[0037] In some embodiments, the rate of injection of the sorbent material may depend upon the flow rate of the exhaust stream. For example, in a plant having an exhaust (flue) gas flow rate of about 2,000,000 actual cubic feet per minute (acfm) in which about 100 lbs/hr of sorbent material is injected into the exhaust stream in the ductwork of the plant, the rate of addition of sorbent material is about 0.8 pounds per million actual cubic feet (lbs/MMacf). Therefore, in various embodiments, the injection rate of the sorbent material may vary depending up on the flow rate of the exhaust gas in the ductwork. In such embodiments, the rate of addition of sorbent material based on the flow rate of the exhaust gas may be up to about 4 lbs/MMacf or up to about 5 lbs/MMacf. In other embodiments, the rate of addition of the sorbent material based on the flow rate of the exhaust gas may be from about 0.25 lbs/MMacf to about 5 lbs/MMacf, about 0.5 lbs/MMacf to about 4.0 lbs/MMacf, or about 0.75 lbs/MMacf to about 3.0 lbs/MMacf, and in particular embodiments, the rate of addition may be about 0.75 lbs/MMacf to about 1.5 lbs/MMacf.

[0038] Particular embodiments, for exemplary purposes, include methods and systems including the introduction of a halogen precursor, such as, calcium bromide, calcium

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chloride, sodium bromide, or sodium chloride, into a combustion chamber where a heavy metal containing fuel source is being burned, and injection of sorbent material having an MPD of less than about 15 μm into an exhaust stream upstream of a heavy metal and/or particulate control systems such as, for example, electrostatic precipitators, wet flue gas desulphurization systems, fabric filters, and baghouses or other ash or fly ash collection means where particulate matter can be collected. In some such embodiments, less than about 10 gallons/hour of the an aqueous halogen precursor may be introduced into the combustion chamber, and less than about 100 lbs/hour of sorbent material may be injected into the exhaust stream. As a result of such treatment, mercury emission from the plant employing such methods and systems may be reduced by greater than about 80% and in some embodiments, greater than 90%.

[0039] Further embodiments, include methods for reducing mercury emissions from flue gas in which the ratio of halogen to sorbent material provided is from about 0.7 to about 4.6 moles of halogen per pound of activated carbon, and in some embodiments, from about 0.8 to about 3.1 or about 1.2 to about 2.0 moles of halogen per pound of activated carbon. In such embodiments, the sorbent material may have an MPD of less than about 15 μm and, in certain embodiments, the sorbent material may have an MPD of less than about 10 μm. In still other embodiments, the sorbent material may have an MPD of about 6 μm or less. The halogen and sorbent material may be provided anywhere during the process. For example, in some embodiments, the halogen may be applied to the fuel source before combustion, and in other embodiments, the halogen may be introduced into the combustion chamber while the fuel is burned. In still other embodiments, the halogen may be introduced into the flue gas stream either before or after the sorbent material. In further embodiments, the halogen may be provided with the activated carbon. For example, in some embodiments, the halogen may be injected into the flue gas stream separately with the activated carbon, and in other embodiments, the halogen may be applied to the sorbent material before it is introduced into the flue gas stream.

[0040] In embodiments in which the halogen is applied to the sorbent material before being injected into the flue gas stream, the ratio of halogen to sorbent material may be the same as the ratio of halogen to sorbent material when sorbent material is introduced separately. For example, in some exemplary embodiments, a halogen salt such as any of the halogen salts described above may be applied to an adsorbent material having an MPD of less than 15 μm, less than 12 μm, less than 10 μm in a ratio of from about 0.14 to about 1.0

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pounds of halogen salt per pound of sorbent material to provide a composition that is from about 12 wt. % to about 50 wt. % halogen salt or about 15 wt. % to about 40 wt. % halogen salt. In another exemplary embodiment, a halogen salt such as calcium bromide ($CaBr_2$) or ammonium bromide (NH_4Br) may be applied to sorbent material having an MPD of about 6 μm at a ratio of about 0.43 pounds of halogen salt per pound of sorbent material or about 30 wt. % halogen salt, and the sorbent material/halogen salt combination may be introduced into the flue gas stream. These ratios can also be expressed as moles of halogen per pound of adsorbent material. For example, in some embodiments, the ratio of moles of halogen per pound of sorbent material may be from about 0.7 moles/lb to about 5.7 moles/lb, 0.8 moles/lb to about 3.1 moles/pound or any ratio there between, and in particular embodiments, the ratio of halogen per pound of sorbent material can be 2.0 moles/lb. In such embodiments, the halogen salt may be applied by conventional impregnation process or the halogen salt may be applied by mixing dry sorbent material with dry halogen salt. In other embodiments, the sorbent material can be impregnated using a gaseous halogen. In certain embodiments, such as those described above, the sorbent material may be activated carbon.

[0041] Coal fired power plants utilizing conventional methods for reducing mercury emissions where a halogen precursor is introduced into a combustion chamber and no sorbent material is injected into the exhaust generally inject halogen precursor at a rate of greater than 20 gallons/hour to reduce the mercury emission sufficiently. Coal fired power plants that utilize sorbent material injection without introducing a halogen precursor during combustion can inject greater than about 250 lbs/hour of sorbent material into the exhaust stream to effectively reduce mercury emissions. In contrast, some embodiments of the invention provide mercury reduction of greater than about 80% or greater than 90% while using less than about 10 gallons/hour of a halogen precursor and less than 100 lbs/hour of an activated carbon, and in particular embodiments, less than 100 lbs/hour of sorbent material having a MPD of less than about 15 μm. This is a dramatic and surprising reduction in the amount of consumables necessary to effectively reduce mercury emissions to below regulatory levels. Such embodiments, therefore, provide substantial economic advantages over currently used methods for reducing mercury emission, while simultaneously reducing the amount of ash produced by plants that employ sorbent material injection and the amount of halogen precursor consumed.

[0042] In some embodiments, mercury levels can be monitored with conventional analytical equipment using industry standard detection and determination methods, and in

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such embodiments, monitoring can be conducted periodically, either manually or automatically. For example, mercury emissions can be monitored once an hour to ensure compliance with government regulations and to adjust the rate of halogen precursor introduction into the combustion chamber, the rate of sorbent material injection, or both. Mercury can be monitored in the convective stream at suitable locations. For example, in some embodiments, mercury released into the atmosphere can be monitored and measured on the clean side of a particulate control system.

[0043] In some embodiments, the sorbent material may include a reducing agent to mitigate the leaching of heavy metals captured by the sorbent materials. The reducing agent may be included in the composition injected into the flue gas stream or combined with the sorbent material after collection. The "reducing agent" can be any compound or chemical species known in the art that is capable of reducing, i.e., donating an electron, to another compound or chemical species. In some embodiments, the reducing agent is an organic antioxidant, and such compounds may include, and are not limited to, ascorbic acid, gallic acid, caffeic acid, ferulic acid, chlorogenic acid, formic acid, oxalic acid, maleic acids and the like, tocopherols, tocotrienols, desferrioxamine, pyruvic acid, including salts of pyruvic acid, cysteine, glutathione, and the like and combinations thereof. In certain embodiments, the reducing agent may be ascorbic acid including both dextrorotatory and the levorotatory enantiomers of ascorbic acid as well as the mineral ascorbates, such as, but not limited to, monosodium ascorbate, calcium diascorbate, monopotassium ascorbate, magnesium diascorbate, and related compounds.

[0044] Without wishing to be bound by theory, reducing agent may mitigate leaching of heavy metals that have been adsorbed by the sorbent material. The reducing agent may reduce the adsorbed mercury halides from a +2 oxidation state, which is soluble, to an insoluble +1 oxidation state. The standard reduction potential (E^0) of ascorbic acid at a pH of about 7 and a temperature of about 25°C is about 0.06 volts. Ascorbic acid may effect this reaction within about 30 minutes in a pH range of about 2 to about 8, and within about 10 minutes in a pH range of about 3 to about 6.

[0045] The amount of reducing agent used may vary among embodiments and may be from about 1 wt.% to about 15 wt.%. In some embodiments, the amount of reducing agent added may be about 1 wt.% to 5 wt.%. In other embodiments, the amount of reducing agent added may be about 5 wt.% to about 10 wt.%. In yet other embodiments, the amount of reducing agent added may be about 10 wt.% to about 15% wt.%.

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[0046] In some embodiments, the reducing agent may be injected into a vessel containing the sorbent material. In some embodiments, injection occurs downstream of the adsorption of the heavy metals. In other embodiments, injection occurs upstream of the adsorption of the heavy metals. In yet other embodiments, injection occurs simultaneously with the adsorption of the heavy metals. In still further embodiments, the ascorbic acid or related compound may be mixed with the activated carbon after the sorbent has been removed from the convective stream.

EXAMPLES

[0047] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

EXAMPLE 1

[0048] A coal-fired power plant fitted with a system to add calcium bromide onto the coal prior to the combustion chamber and lances for injecting activated carbon into the ductwork of the power plant at various locations was utilized for testing. Coal burned at this facility was periodically tested for mercury content to ensure accuracy of mercury removal testing. Various powdered activated carbons (PACs) tested at this facility are provided in Table 1.

TABLE 1: Powdered Activated Carbon (PAC)

Identifier	Particle Size (MPD)	Brominated
Std	16 μm	No
Std Br	16 μm	Yes
PAC 6	6 μm	No
PAC 30	30 μm	No

[0049] Each of the PACs described in Table 1 was injected into the exhaust stream of the plant downstream of the APH at rate of about 100 lbs/hr or about 200 lbs/hr either with or without calcium bromide ($CaBr_2$) injection into the combustion chamber. The results are provided in Table 2 and are illustrated in FIG. 2.

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TABLE 2: Injection Rate Raw Data

Symbol FIG. 2	Particle	CaBr	PAC Injection Rate (lbs/hr)	Removal (%)
■	Std.	0	100	48.2
	Std.	0	200	60.0
▲	None	1X	0	20.0
	Std.	1X	100	67.5
	Std.	1X	200	77.6
□	None	2X	0	33.4
	Std.	2X	200	83.3
Δ	None	3X	0	39.2
●	None	4X	0	37.1
	Std.	4X	200	88.0
○	Std.	8X	200	87.4
*	Std. Br	0	100	70.4
	Std. Br	0	200	82.7
	Std. Br	0	200	79.4
×	PAC 30	0	100	36.5
	PAC 30	0	200	48.4
◊	PAC 6	0	100	55.3
	PAC 6	0	200	67.6
♦	PAC 6	4X	100	87.4
	PAC 6	4X	200	92.7

[0050] As indicated in FIG. 1, $CaBr_2$ alone, PAC injection rate 0, resulted in less than about 50% mercury removal based on the mercury content of the coal consumed. The addition of PAC at 100 lbs/hr (PAC 30, PAC 16, PAC 6) resulted in similar reduction in mercury emission, about 50%, which varied slightly depending on the MPD of the PAC. The combination of $CaBr_2$ injection into the combustion chamber and PAC injection in the exhaust stream (Std + 1x $CaBr_2$) showed improved reduction in mercury emission, as did the injection of brominated PAC (Std Br) into the exhaust stream. Notably, the combination of

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$CaBr_2$ injection into the combustion chamber and injection of a PAC having a smaller MPD into the exhaust stream (PAC 6 + 4x $CaBr_2$) resulted in nearly 90% reduction in mercury emissions, which represents almost 20% greater reduction in mercury emissions over brominated PAC (Std Br) and larger MPD PAC and $CaBr_2$ (Std. + 1x $CaBr_2$). Similarly, when the injection rate for PAC was increased to 200 lbs/hr, small MPD PAC outperformed brominated PAC (Std. Br) and larger MPD PAC and various injection rates of $CaBr_2$ (Std. 1x $CaBr_2$; Std. 2x $CaBr_2$; Std. 3x $CaBr_2$; Std. 4x $CaBr_2$; and Std. 8x $CaBr_2$).

EXAMPLE 2

[0051] Further testing was carried out to determine the injection rate for a given aqueous solution of $CaBr_2$ and PAC when the PAC is injected into the exhaust stream upstream of the APH (Post APH Injection) and downstream of the APH (Pre APH Injection) required to obtain 90% removal of mercury from plant emissions. The results are provided in Tables 3 and 4, respectively.

TABLE 3: Consumption at 90% mercury removal

POST APH INJECTION

Identifier	$CaBr_2$ (gal/hr)	PAC (lbs/hr)	#/MMacf
Std.	20	300	2.5
PAC 6	20	150	1.2
Std. Br		420	3.4

TABLE 4: Consumption at 90% mercury removal

PRE APH INJECTION

Identifier	$CaBr_2$ (gal/hr)	PAC (lbs/hr)	#/MMacf
Std.	18	125	1.0
PAC 6	6	60	0.5
Std. Br		320	2.6

[0052] Tables 3 and 4 show that a rate of $CaBr_2$ injection of 20 gal/hr and a PAC injection rate of 150 lbs/hr is sufficient to remove 90% of the mercury from the coal tested when small MPD PAC (PAC 6) is injected downstream of the APH whereas twice as much large MPD PAC (Std.) is required to achieve a similar result. When the PAC is injected upstream of the APH, 6 gal/hr of $CaBr_2$ and 60 lbs per hour of small MPD PAC (PAC 6) is

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necessary to remove 90% of the flue gas mercury at the same plant whereas 18 gal/hr of $CaBr_2$ and 125 lbs/hr of standard MPD PAC (Std.) are required to achieve the same result. These data demonstrate that a decrease in carbon particle size, especially below about 12 μm or about 10 μm, creates its own synergistic effect in that, surprisingly, both less carbon and less halogen are needed for the same level of mercury removal, especially at levels around or above 90% mercury removal. The combined savings in both halogen and sorbent result in greatly improved economics as well as fewer balance-of-plant impacts such as reduced carbon in the fly ash, allowing more of the ash to retain commercial value as a concrete additive.

EXAMPLE 3

[0053] Various materials were added to two samples of spent activated carbon that had adsorbed about 12 mg Hg/g carbon and were tested to see if the added materials altered the amount of mercury that was leached during a Toxicity Characteristic Leaching Profile Test ("TCLP Test."). As received for testing, the samples of spent sorbent typically range from a TCLP value of about 0.4 mg Hg/L to about 0.06 mg Hg/L. A spent sorbent is considered to pass the TCLP test if the leached mercury and/or mercury compounds is below a threshold of 0.2 mg Hg/L.

[0054] FIG. 3 is a bar graph showing TCLP scores for various spent sorbents (columns a, e, and n). The addition of the addition of 10 wt. % virgin activated carbon, F-300 from Calgon Carbon (b, f), Darco-Hg (c, g), and bituminous PAC (i, j) was effective at lowering the mercury TCLP values (mg/L). FIG. 3 also shows the effects of combining a reducing agent with the spent sorbent. In particular, ascorbic acid (d, h) reduced leaching more effectively than any of the virgin sorbents. These data also show that the use of ascorbic acid at an amount of about 1 wt. % (k) and about 10 wt. % (d, h) were effective in keeping the sorbent below the TCLP threshold of 0.2 mg Hg/L. In contrast, the use of sodium thiosulfate (l), a known reducing agent, was found to exacerbate the leaching of the mercury, bringing the levels of mercury leached to almost double the TCLP threshold of 0.2 mg Hg/L.

EXAMPLE 4

[0055] Chromium (VI) leaching was tested on a sample having a TCLP score as received of 0.033 mg/L. The addition of 10 wt. % ascorbic acid mitigated Chromium (VI) leaching to undetectable levels.

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J. CLAIMS

1. A method for reducing heavy metal leaching comprising contacting a sorbent having associated heavy metals with a reducing agent.

2. The method of claim 1, wherein the sorbent is selected from the group consisting of carbonaceous char, activated carbon, reactivated carbon, carbon black, graphite, natural zeolite, synthetic zeolite, silica, silica gel, alumina clay, diatomaceous earths, and combinations thereof.

3. The method of claim 1, wherein reducing agent comprises about 1 wt.% to about 15 wt.% based on the total weight of the sorbent.

4. The method of claim 1, wherein the reducing agent is ascorbic acid.

5. The method of claim 1, wherein the reducing agent is selected from the group consisting of monosodium ascorbate, calcium diascorbate, monopotassium ascorbate, magnesium diascorbate, and combinations thereof.

6. The method of claim 1, wherein the sorbent further comprises a halogen precursor.

7. The method of claim 6, wherein the halogen precursor is selected from the group consisting of the calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

8. The method of claim 6, wherein the halogen precursor is impregnated onto the sorbent.

9. A flue gas adsorbent comprising:

a sorbent; and

a reducing agent selected from the group consisting of ascorbic acid, gallic acid, caffeic acid, ferulic acid, chlorogenic acid, formic acid, oxalic acid, maleic acid, tocopherols, tocotrienols, desferrioxamine, pyruvic acid, including salts of pyruvic acid, cysteine, glutathione, and combinations thereof.

10. The flue gas adsorbent of claim 9, wherein the sorbent is selected from the group consisting of carbonaceous char, activated carbon, reactivated carbon, carbon black,

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graphite, natural zeolite, synthetic zeolite, silica, silica gel, alumina clay, diatomaceous earths, and combinations thereof.

11. The flue gas adsorbent of claim 9, comprising about 1 wt.% to about 15 wt.% reducing agent.

12. The flue gas adsorbent of claim 9, wherein the reducing agent is ascorbic acid.

13. The flue gas adsorbent of claim 9, wherein the reducing agent is selected from the group consisting of monosodium ascorbate, calcium diascorbate, monopotassium ascorbate, magnesium diascorbate, and combinations thereof.

14. The flue gas adsorbent of claim 9, wherein the adsorbent is a dry admixture of sorbent and reducing agent.

15. The flue gas adsorbent of claim 9, wherein the reducing agent is impregnated onto the sorbent.

16. The flue gas adsorbent of claim 9, further comprising a halogen precursor.

17. The flue gas adsorbent of claim 16, wherein the halogen precursor is selected from the group consisting of the calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, ammonium chloride, ammonium bromide, ammonium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

18. The flue gas adsorbent of claim 16, wherein the halogen precursor is selected from the group consisting of calcium bromide ($CaBr_2$), ammonium bromide (NH_4Br), and combinations thereof.

19. The flue gas adsorbent of claim 16, wherein the halogen precursor is dry halogen precursor.

20. The flue gas adsorbent of claim 16, wherein the halogen precursor is impregnated onto the sorbent.

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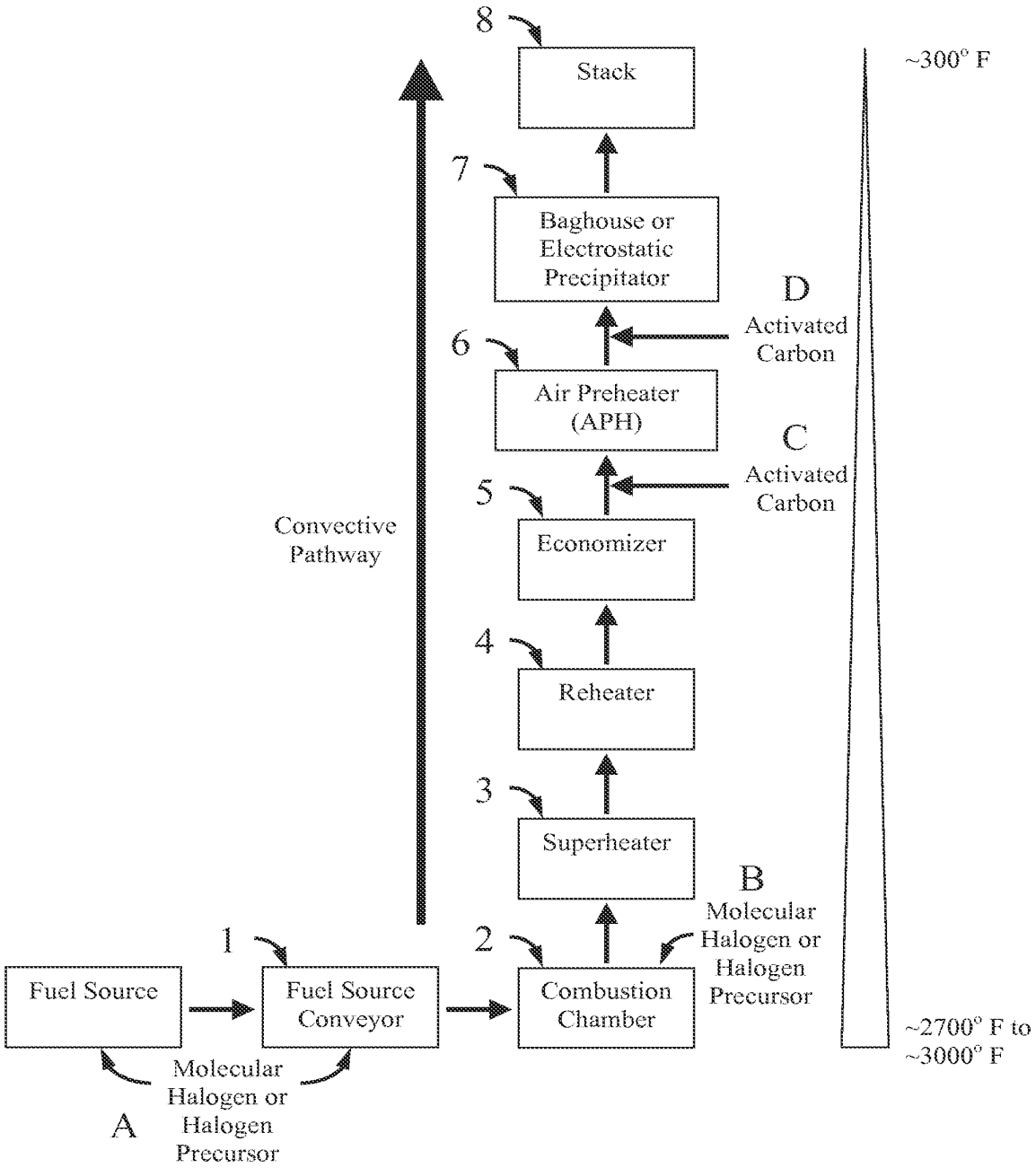

8
Stack
~300° F
7
Baghouse or Electrostatic Precipitator
D
Activated Carbon
6
Air Preheater (APH)
C
Activated Carbon
5
Economizer
Convective Pathway
4
Reheater
3
Superheater
B
Molecular Halogen or Halogen Precursor
1
2
Fuel Source
Fuel Source Conveyor
Combustion Chamber
~2700° F to ~3000° F
Molecular Halogen or Halogen Precursor
A

FIG. 1

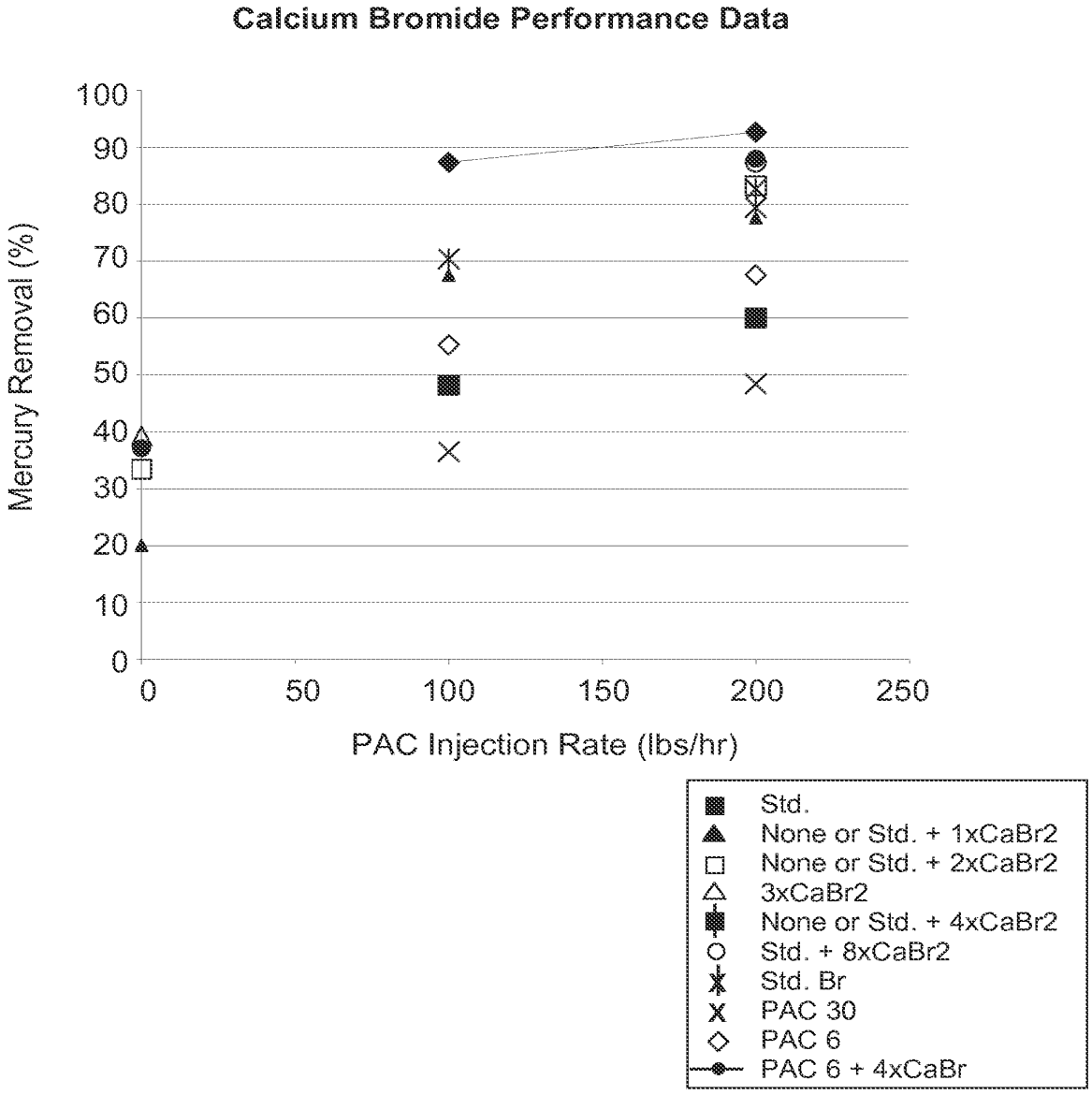

Calcium Bromide Performance Data
Mercury Removal (%)
100
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
PAC Injection Rate (lbs/hr)
Std.
None or Std. + 1xCaBr2
None or Std. + 2xCaBr2
3xCaBr2
None or Std. + 4xCaBr2
Std. + 8xCaBr2
Std. Br
PAC 30
PAC 6
PAC 6 + 4xCaBr

FIG. 2

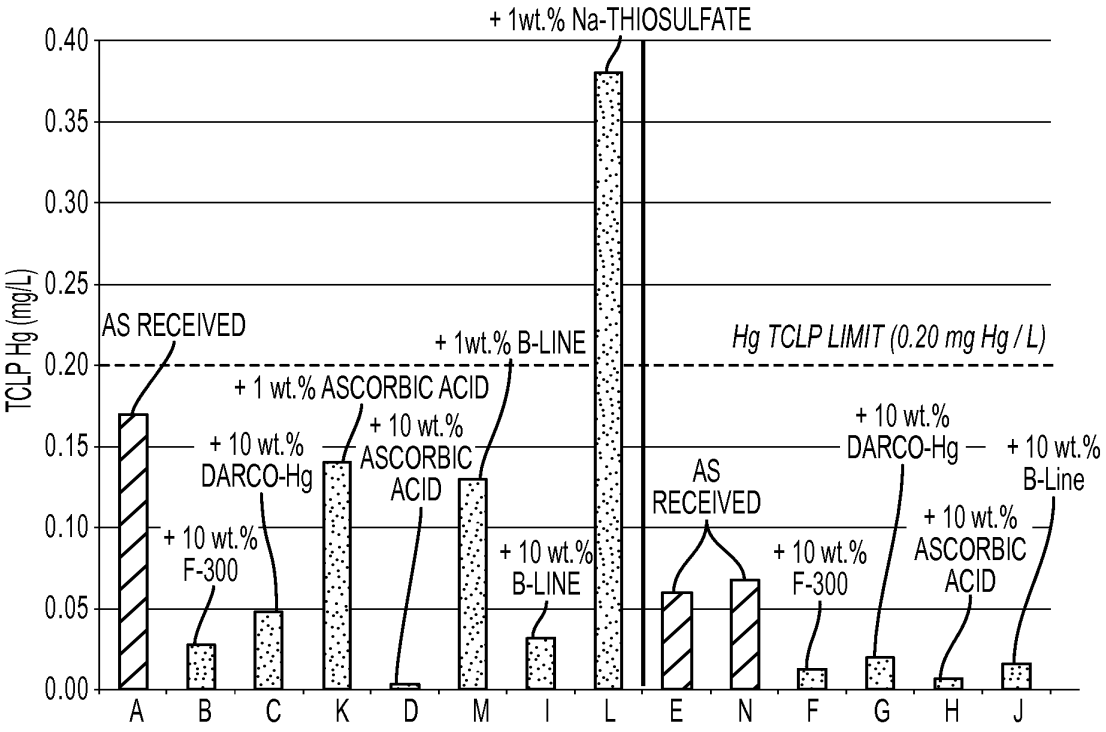

+ 1wt.% Na-THIOSULFATE
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
TCLP Hg (mg/L)
AS RECEIVED
+ 10 wt.% F-300
+ 10 wt.% DARCO-Hg
+ 1 wt.% ASCORBIC ACID
+ 10 wt.% ASCORBIC ACID
+ 1wt.% B-LINE
+ 10 wt.% B-LINE
Hg TCLP LIMIT (0.20 mg Hg / L)
AS RECEIVED
+ 10 wt.% F-300
+ 10 wt.% DARCO-Hg
+ 10 wt.% ASCORBIC ACID
+ 10 wt.% B-Line
A
B
C
K
D
M
I
L
E
N
F
G
H
J

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/043158

A. CLASSIFICATION OF SUBJECT MATTER

C22B 13/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B 13/00; B01D 53/06; B01D 53/64; B05D 3/02; B05D 1/36; A62D 3/00; C10G 25/00; B09B 1/00; C04B 18/08; B01D 53/26

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: heavy metal, sorbent, absorbent, reducing agent, flue gas, and leaching

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0433677 A1 (CALGON CARBON CORPORATION) 26 June 1991 See abstract; and claims 1,4,9.	1-5,9-15
Y		6-8,16-20
Y	US 8057576 B1 (POLLACK, NICHOLAS R.) 15 November 2011 See abstract; column 2, line 56 - column 3, line 47; and claims 1,10.	6-8,16-20
A	US 6186939 B1 (FORRESTER, KEITH E.) 13 February 2001 See abstract; column 4, line 60 - column 5, line 59; and claims 1-4.	1-20
A	US 2008-0121142 A1 (COMRIE et al.) 29 May 2008 See abstract; paragraphs [0055]-[0057]; and claim 1.	1-20
A	US 2003-0188663 A1 (BARTHEL et al.) 09 October 2003 See abstract; paragraphs [0026],[0027],[0029],[0030]; and claims 1,2,13,18,56.	1-20

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
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Information on patent family members

International application No.
PCT/US2014/043158

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Espacenet

Bibliographic data: WO2018144588 (A1) — 2018-08-09

SORBENT DEVICES

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Applicant(s): CALGON CARBON CORP [US] + (CALGON CARBON CORPORATION)

Classification: - international: ***B01D53/02; B01D53/04; B01D53/14***
- cooperative: **B01D53/02 (EP)**; **B01D53/0415 (EP, US)**; **B01J20/20 (EP, US)**; **B01J20/28011 (EP, US)**; **B01J20/28035 (EP, US)**; **B01J20/2804 (EP, US)**; **B67D7/0476 (EP)**; B01D2253/102 (EP, US); B01D2253/34 (EP); B01D2257/702 (EP, US); B01D2259/4516 (EP, US); B01D2259/4566 (EP)

Application number: WO2018US16213 20180131 Global Dossier

Priority number(s): US201762452704P 20170131

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Abstract of WO2018144588 (A1)

Sorbent material sheets provide for enhanced performance in vapor adsorbing applications over conventional canisters and other emissions control equipment. The sorbent material sheets can be formed as part of a small, lightweight canister, or can be integrated into a fuel tank. The sorbent material sheets can also be used as part of an onboard refueling vapor recovery system to control volatile organic compound emissions from fuel tanks of gasoline vehicles, such as automobiles.

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(54) Title: SORBENT DEVICES

(57) Abstract: Sorbent material sheets provide for enhanced performance in vapor adsorbing applications over conventional canisters and other emissions control equipment. The sorbent material sheets can be formed as part of a small, lightweight canister, or can be integrated into a fuel tank. The sorbent material sheets can also be used as part of an onboard refueling vapor recovery system to control volatile organic compound emissions from fuel tanks of gasoline vehicles, such as automobiles.

A. Title:

SORBENT DEVICES

B. Cross-Reference to Related Applications: This application claims priority to US Provisional Application No. 62/452,704 filed on January 31, 2017, the entirety of which is incorporated by reference.

C. Government Interests: Not applicable

D. Parties to a Joint Research Agreement: Not applicable

E. Incorporation by Reference of Material submitted on a Compact Disc: Not applicable

F. Background:

[0001] Evaporative emissions from gasoline and other liquid hydrocarbon fuels are a significant source of air pollution because the various hydrocarbons contained in the fuels can form photochemical smog on exposure to sunlight. The compounds of this smog and the hydrocarbons themselves cause degrading health effects in humans and animals as well as environmental damage. Evaporative emissions are especially problematic during vehicle refueling because the "empty" fuel tank is actually filled with fuel vapors, and the act of filling the tank with liquid fuel displaces the vapors from the tank. Evaporative emissions also occur when the fuel within the tank is heated, such as from hot ambient conditions or from nearby hot exhaust system components. Without controls, fuel vapors would be released as pollution into the atmosphere.

[0002] In the automotive sector, gasoline vapors are typically recovered during refueling by an Onboard Refueling Vapor Recovery system (ORVR). These devices include multiple components which are designed to capture the displaced vapors from gasoline refueling and allow the engine to burn them at a later time. Vapors remain sealed within the fuel tank by specially designed tanks and fuel filler neck, and excess vapor is captured and adsorbed within a chemical canister. During engine operation, the Engine Control Unit (ECU) permits adsorbed vapors to be released from the canister and into the engine fuel system, burning the gasoline vapors as normal and permitting the canister to be used again.

[0003] While ORVR systems have been successful in reducing vapor emissions, they still have drawbacks. The chemical canisters are filled with loose adsorbent particulates such as activated carbon or charcoal, which can be messy to handle and package. These canisters are bulky and heavy because the adsorbent particulates cannot physically support themselves, and because stringent emissions regulations now prohibit the release of even small amounts

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of vapor emissions, which requires higher adsorbent capacity. Manufacturing, maintenance and disposal of the canisters is also cumbersome because of the loose adsorbent particulates, and the complexity of ORVR devices increases the cost of each vehicle while cutting into valuable passenger and cargo space. With automakers demanding lighter weights from all components to meet increasing fuel efficiency targets, as well as cost reductions and greater passenger and cargo space, there is a need for new ORVR devices and that are smaller, lighter, simpler, and more cost effective, while still complying with stricter emissions targets.

G. Summary of the Invention:

[0004] In one embodiment, the invention discloses sorbent material sheets that have improved performance over the equivalent amount of adsorbent compound provided as a powder.

[0005] In another embodiment, the invention discloses sorbent material sheets enclosed within a housing.

[0006] In another embodiment, the invention discloses sorbent material sheets that omit the housing and which are instead contained directly within a fuel tank.

[0007] In another embodiment, the invention discloses an emissions control system, such as an ORVR which includes sorbent material sheets. The sorbent material sheets within the ORVR may be enclosed within a housing or the housing may be omitted.

[0008] The invention is also directed to the embodiments listed below:

1. A sorbent material sheet product, comprising

   at least two sorbent material sheets, each of which has a defined upper surface and lower surface which have a combined total surface area, and

   wherein each sorbent material sheet comprises a sorbent material and a binder, and

   wherein each sorbent material sheet is stacked and arranged such that adjacent upper and lower surfaces of the separate sheets are substantially parallel and are aligned to allow fluid flow at least between the adjacent upper and lower surfaces.

2. The sorbent material sheet product of embodiment 1, wherein the sorbent material sheet product has a BWC stacking multiplier ratio of about 1.1 to about 1.3, wherein the BWC stacking multiplier ratio is defined by the formula:

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BWC stacking multiplier ratio = [(measured BWC of entire sorbent material sheet product) / (measured BWC of individual sorbent material sheet outside of product)] / number of sorbent material sheets in the sorbent material sheet product.

3. The sorbent material sheet product of embodiment 1, wherein the individual sorbent material sheets, measured individually, have BWC values that are 5-15% higher than the BWC of the same weight of sorbent material in pelletized or powdered forms.

4. The sorbent material sheet product of embodiment 1, wherein at least one of the sorbent material sheets are configured as being flat, wound in a spiral cylinder, wound in an elliptical form, wound in an elongate rectangular bar, folded, laminated in an "S" shape, formed as concentric cylinders, formed as concentric ellipses, formed as a concentric rectangular bar, or as combinations of these forms.

5. The sorbent material sheet product of embodiment 1, wherein at least one of the sorbent material sheets has raised and/or depressed portions.

6. The sorbent material sheet product of embodiment 5, wherein the raised and/or depressed portions are present on adjacent sheets and are nested.

7. The sorbent material sheet product of embodiment 5, wherein the raised and/or depressed portions are present on adjacent sheets and are not nested.

8. The sorbent material sheet product of embodiment 1, wherein the sorbent material sheet product has a void volume of about 10% or less.

9. The sorbent material sheet product of embodiment 1, wherein each individual sorbent material sheet has a density of about 0.08 g/cc to about 1.5 g/cc.

10. The sorbent material sheet product of embodiment 1, wherein the sorbent material sheet product has a BWC greater than about 10 g/100cc.

11. The sorbent material product of embodiment 1, wherein the sorbent material sheet product has a BWC of about 7.0 g/100cc to about 30 g/100cc.

12. The sorbent material sheet product of embodiment 1, wherein the sorbent material sheets comprise sorbent material particles having at least two populations having different average particle diameters, and wherein the average particle diameters of the two populations have ratios of about 1:2 to about 1:10.

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13. The sorbent material sheet product of embodiment 1, wherein the amount of binder and the amount of sorbent material sheet products are present in a gradient such that the amount of binder is highest at an outer portion of the sorbent material sheet product, and that the amount of binder is lowest at an inner portion of the sorbent material sheet product.

14. The sorbent material sheet product of embodiment 1, wherein at least one sorbent material sheet include holes, cuts, or apertures.

15. The sorbent material sheet product of embodiment 1, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

16. A rolled sorbent material sheet product, comprising:

    a sorbent material sheet defining an upper surface and a lower surface and having a total surface area, and which comprises a sorbent material and a binder,

    wherein the sorbent material sheet is spiral wound to form adjacent sheet layers which allow fluid flow around and between adjacent sheet layers.

17. The rolled sorbent material sheet product of embodiment 16, wherein the sorbent material sheet in its rolled form has a BWC that is at least 10% higher than the BWC of the same sorbent material sheet in an unrolled form.

18. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheet product has a BWC that is at least 10% higher than the BWC of a pelletized or powdered form of the substantially the same amount of sorbent material in the sorbent sheet.

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19. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheet product has a generally cylindrical shape having a length that is greater than its diameter.

20. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheet product is wound to an average roll density of 500-700 kg/m^3.

21. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheet product has a butane working capacity greater than about 10 g/100cc.

22. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheet product has a butane working capacity of about 7.0 g/100cc to about 30 g/100cc.

23. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheet comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters.

24. The rolled sorbent material sheet product of embodiment 16, wherein the rolled sorbent material sheets comprise sorbent material particles having at least two populations having different average particle diameters, and wherein the average particle diameters of the two populations have ratios of about 1:2 to about 1:10.

25. The rolled sorbent material sheet product of embodiment 16, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

26. A vapor adsorbing canister, comprising:

The sorbent material sheet product of embodiment 1, and

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a housing at least partially encapsulating the sorbent material sheet product of embodiment 1

27. The vapor adsorbing canister of embodiment 26, wherein the housing is flexible.

28. The vapor adsorbing canister of embodiment 26, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

29. The vapor adsorbing canister of embodiment 26, wherein the shape of the housing substantially conforms to the shape of the enclosed sorbent material sheet product of embodiment 1.

30. The vapor adsorbing canister of embodiment 26, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

31. A vapor adsorbing canister, comprising,

    a. the rolled sorbent material sheet product of embodiment 16, and

    b. a housing at least partially encapsulating the rolled sorbent material sheet product of embodiment 16.

32. The vapor absorbing canister of embodiment 31, wherein the housing is flexible.

33. The vapor adsorbing canister of embodiment 31, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers,

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para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

34. The vapor absorbing canister of embodiment 31, wherein the shape of the housing substantially conforms to the shape of the enclosed rolled sorbent material sheet product of embodiment 16.

35. The vapor adsorbing canister of embodiment 31, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

36. A tank with integral vapor adsorption, comprising:

a tank structure, and

at least one sorbent material sheet which has a defined upper surface and lower surface which have a combined total surface area, and

wherein each sorbent material sheet comprises a sorbent material and a binder, and

at least one fastening device which fastens the sorbent material sheet to a surface of the tank that is not regularly immersed in the volatile liquids contained within the tank.

37. The tank with integral vapor adsorption of embodiment 36, wherein the fastening device is an adhesive layer which is formed between one surface of the sorbent material sheet and a wall of the tank.

38. The tank with integral vapor adsorption of embodiment 36, wherein the adhesive comprises at least one of pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, reactive multi-part adhesives, acrylic and (meth)acrylic adhesives, acrylate and (meth)acrylate adhesives, epoxy adhesives in one- or two-part formulations, urethane adhesives, and copolymers and combinations thereof.

39. The tank with integral vapor adsorption of embodiment 36, wherein the tank further includes at least one fuel pump(s), fuel sending line(s), fuel return line(s), atmospheric

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vent line, port(s), valve(s), sensor(s), air inlet(s), open cell foam, baffle(s), bladder(s) and combinations of those.

40. The tank with integral vapor adsorption of embodiment 36, wherein the tank is a fuel tank with a "ship in a bottle" configuration.

41. An onboard refueling vapor recovery apparatus comprising the sorbent material sheet product of embodiment 1.

42. An onboard refueling vapor recovery apparatus comprising the rolled sorbent material sheet product of embodiment 16.

43. An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of embodiment 26

44. An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of embodiment 31.

45. An onboard refueling vapor recovery apparatus comprising the tank with integral vapor adsorption of embodiment 36.

H. Description of Drawings: Not Applicable.

I. Detailed Description:

[0009] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0010] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a combustion chamber" is a reference to "one or

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more combustion chambers" and equivalents thereof known to those skilled in the art, and so forth.

[0011] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0012] As used herein, the term "sorbent material" is meant to encompass all known materials from any source that are capable of adsorbing liquids and/or gases. For example, sorbent materials include, but are not limited to, activated carbon, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths.

[0013] As used herein, the term "may" means that the subsequently listed element may or may not be included in an embodiment. For example, an embodiment that may include a polymer substrate means that the embodiment can include that polymer substrate, but that it is also contemplated that the embodiment can exclude the polymer substrate.

[0014] As used herein, descriptions and claims of multiple sorbent material sheets mean that there are multiple, separated sheets, with sides and/or surfaces in proximity to each other. Alternatively, descriptions and claims of multiple sorbent material sheets mean that there is only a single sheet, but that it has been wound or folded over on itself to yield a stacked, wound, or otherwise constructed mass of sheets with sides and/or surfaces in proximity to each other. The term also envisions that multiple sheets are stacked together and then wound or otherwise folded over, forming alternating layers in a single mass.

[0015] Embodiments of the invention are directed to devices containing one or more sheets of sorbent material, sorbent material sheets, and methods for making sorbent material sheets and devices containing these sheets. In various embodiments, the sorbent material sheets may be composed of a sorbent material and a binder and have a thickness of less than about 1 mm. The devices of various embodiments may include a housing and one or more of sorbent material sheets. In some embodiments, the devices may have a void fraction of about 10% or more of the total volume of the housing.

[0016] The Sorbent Material Sheets

[0017] The sorbent material sheets of the invention may include any of the sorbent materials described above including, but are not limited to, activated carbon, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths, and in certain embodiments, the sorbent material sheets may be composed of activated carbon. The sorbents may be used alone or in combination.

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[0018] The activated carbon may be of various grades and types selected based on performance requirements, cost, and other considerations. The activated carbon may be granular from reagglomerating a powder, granular from crushing or sizing nutshells, wood, coal or pellets created by extrusion, or activated carbon in powdered form. The activated carbon may be formed by processes of carbonization and activated. The raw material, such as wood, nutshell, coal, pitch, etc. is oxidized and devolatized, with steam and/or carbon dioxide gasified to form the pore structure in the activated carbon which is useful for adsorption. The initial oxidation and devolatilization process may include a chemical treatment with a dehydrating chemical, such as phosphoric acid, sulfuric acid, sodium hydroxide, potassium hydroxide, and combinations of those.

[0019] A variety of activation processes are known in the art. The most useful processes for providing activated carbon for the sorbent material sheets of the claimed invention involve a step of providing wood and/or wood byproduct, acid treating the wood and/or wood byproducts by exposure to phosphoric acid, and carbonizing the wood and/or wood byproducts using steam and/or carbon dioxide gasification. This process results in activated carbon particles having the highest butane working capacity ("BWC"), which is a measure of activated carbon performance. More details of the BWC testing and results are described in the Examples.

[0020] The activated carbon may be formed from materials including bagasse, bamboo, coconut husks, peat, wood such as hardwood and softwood sources in the form of sawdust and scrap, lignite, coal and coal tar, petroleum pitch, asphalt and bitumen, corn stalks and husks, wheat straw, spent grains, rice hulls and husks, nutshells, and combinations thereof.

[0021] The sorbent material sheets may further include one or more binders. Embodiments are not limited to particular binders, which can include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and

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combinations thereof. The binders can be thermoplastic or thermosetting as conditions require, and can include mixtures of thermoplastic and thermosetting compounds.

[0022] The amount of binder may be about 2% to about 30% by weight of the total composition, and in certain embodiments, the amount of binder may be about 2% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassing these example amounts. In some embodiments, the sorbent material sheets may include a solvent, which may generally be present in small, residual, amounts of, for example, less than 10%, less than 5%, or less than 2% and greater than about 0.1 % or 0.2 % by weight. In particular, in some embodiments the sorbent material sheets may have no (0%) solvent.

[0023] In some embodiments, the sorbent material sheets may have a thickness of less than about 1 mm, about 0.01 mm to about 1.0 mm, about 0.02 mm to about 0.90 mm, about 0.05 to about 0.95 mm, about 0.05 to about 0.90 mm or any individual thickness or range encompassed by these example ranges. The sorbent material sheets of various embodiments may have a density of about 0.05 g/cc to about 2.0 g/cc as measured by the particle density test, and in other embodiments, the sorbent material sheets may have a density of 0.08 g/cc to about 1.5 g/cc, about 0.1 g/cc to about 1.3 g/cc as measured by the particle density test, or any density or range encompassed by these example ranges. In some embodiments, the sorbent material sheet may have a resistivity of less than 20 ohm-cm, and in certain embodiments, the sorbent material sheets may have a resistivity of about 10 ohm-cm to about 20 ohm-cm, about 8 ohm-cm to about 18 ohm-cm or any individual resistivity or range encompassed by these example ranges. The BWC for each sorbent material sheet may be greater than about 10 g/100cc, and in some embodiments, the BWC may be from about 7.0 g/100cc to about 30 g/100cc, about 8.0 g/100 cc to about 25 g/100cc, about 10 g/100 cc to about 20 g/100 cc, about 10 g/100 cc to about 15 g/100 cc, about 11 g/100cc to about 15 g/100 cc, about 12 g/100cc to about 15 g/100cc or any individual BWC or range encompassed by these example ranges. In other examples, the BWC may be about 9 g/100 cc to about 15 g/100 cc, about 12 g/100 cc to about 20 g/100 cc, about 13 g/100 cc to about 20 g/100cc, about 14 g/100cc to about 20 g/100cc, or about 15 g/100cc to about 20 g/100cc. It is also contemplated that any of the endpoints of the above ranges may be combined to form new and distinct ranges.

[0024] The sorbent material sheets of the present invention have higher performance as measured by the BWC than conventional sorbent materials which are provided in powders or other particulate forms.

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[0025] The sorbent material sheets of embodiments can be made by any process. In some embodiments, sorbent material sheets can be made by pulverizing granular or pelletized sorbent material to a powder, mixing the powder with a binder to form a mixture, heating and blending the mixture, and rolling the mixture to form the sorbent material sheet. The step of pulverizing may produce sorbent particles having an average particle diameter of about 0.001 mm to about 0.2 mm, about 0.005 mm to about 0.1 mm, about 0.01 mm to about 0.075 mm, or any individual particle diameter or range encompassed by these example ranges, and in certain embodiments, the pulverized sorbent particles may have an average particle diameter of about 0.001 mm to about 0.01 mm. The step of mixing the powder with a binder may include mixing the sorbent particle powder with about 2% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassed by these example ranges. Heating can be carried out at any temperature sufficient to remove residual solvent such as, for example, about 50°C to about 200°C.

[0026] The sorbent material sheet of the invention may include various distributions of different sized particles to increase the packing efficiency of the powder within the sorbent material sheets. The selection of different sized particles can also improve rheological properties of the powder and surrounding binders, which allows improved mixing and uniform particle distribution before formation of the sorbent material sheets. In some embodiments, the particles of the sorbent material sheet may have a single particle size distribution, and in other embodiments, the particles may have two different particle size distributions. In further embodiments, the particle may have at least three different particle size distributions.

[0027] The mean particle sizes of the at least two different particle populations, each having a particular size distribution, may be selected so that they have a ratios of between about 1:1 and about 1:15: In other embodiments, the mean particle sizes of the two different particle populations may have a ratio of about 1:2 to about 1:10. The mean particle sizes may also have a ratio of about 1:2 to about 1:5, or combinations of any of the above listed ratios.

[0028] The sorbent material sheets have significantly higher sorbent capacity than prior art fuel vapor recovery canisters for a given volume and weight. This capability can be utilized in various ways. In some embodiments, the sorbent material sheets can provide enhanced pollution controls in jurisdictions where such high levels of control are required. In other embodiments, the overall size, cost, and weight of the ORVR can be reduced for a specific level of performance. In further embodiments, an ORVR adsorption device can be designed which has increased performance over conventional adsorption canisters, thereby

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allowing the designer to omit costly and complex returnless fuel pump systems which would otherwise be required to reduce evaporative emissions. Higher performance adsorption devices may also render active condensing vapor systems unnecessary, which avoids the size, weight, and cost of compressor pumps and condensate storage tanks. It should be understood, however, that the ORVR adsorption device using the sorbent material sheets of the invention can also be combined with these devices for exceptionally high performance and a minimal size, weight, and cost penalty over conventional systems.

[0029] The sorbent material sheets may be configured together in a variety of ways depending on the physical space that they must conform to, the required device performance, and the features which are included in proximity to the sheets. In some embodiments, the sheets may be corrugated, include folds, and/or include holes or apertures to increase the surface area of the sorbent material sheets that is exposed to the passing fluid, therefore increasing performance for a given total sheet surface area. The various corrugations, folds, holes, and apertures can also be sized and placed to make way for internal and external features, such as fluid channels, tubing, sensors, and valves. The folds of the sorbent material sheets may take a variety of forms, such as a spiral wrapped configuration in either a cylindrical or elliptical form. The folds may also be in the form of an "S" shape, or a convex or concave "C" shape depending on the required device dimensions and/or any other required internal or external features. The sorbent material sheets may also be stacked in a flat or curved configuration, and the stacked sheets may be square, rectangular, circular, oval, or other irregular shape as needed to fit the space intended. This, in combination with the housing features discussed below, enables devices formed from the sorbent material sheets to fit in smaller, more irregularly shaped spaces than prior art canister devices, which maximizes vehicle interior space.

[0030] In addition to the above described configurations, the sorbent material sheets may also have surface features. In some embodiments, the sorbent material sheets may include raised portions, and in other embodiments, the sorbent material sheets may include depressed portions. These surface features may be combined within the same sheet. The inclusion of raised and/or depressed portions in the sheets may be utilized to form various configurations between the sheets as they are stacked, wrapped, and so forth. For instance, the sheets can be aligned so that the raised and/or depressed portions nest with each other, which brings the adjacent sheets closer together. The sheets can also be aligned so that the raised and/or depressed portions do not nest with each other, which forms a gap between the

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adjacent sheets. The alignment can be used to form various open and closed channels for vapor adsorption between the sheets.

[0031] Sorbent Material Sheet Product

[0032] The sorbent material sheets described above are combined into a sorbent material sheet product. The combination of the sorbent material sheets takes advantage of one or more of the above described features, such as increased surface area/volume ratio, reduced void space, improved sorbent performance, etc. In general, the individual sorbent material sheets are arranged next to each other to form a sorbent material sheet product that comprises sheets that are stacked, rolled, wound, folded, and/or laminated such that the surfaces of the sorbent material sheets are in close proximity to, or adjacent to each other. Whatever the arrangement, the goal is to maximize the surface area of the sheets exposed to the vapor, fluid, and/or gas stream and thus the performance of the sorbent material sheets.

[0033] *Stacked Sorbent Material Sheet Product*: The stacked sorbent material sheet product of the invention comprises two or more sorbent sheets each defining an upper surface and a lower surface, and having a known combined total surface area, wherein each sorbent sheet comprises a sorbent material and a binder; where adjacent sorbent sheets are stacked and arranged such that adjacent upper and lower surfaces are substantially congruent with each other, and aligned to allow fluid flow at least between adjacent upper and lower surfaces.

[0034] This arrangement results in an improved BWC. For example, each individual sorbent material sheet may have a BWC of about 12, and the stacked sorbent sheet media has a BWC that is at least about 1-10%, at least about 5-15%, at least about 2-20%, at least about 5-10%, or at least about 7% higher than the sum of the BWC of the individual sheets. The sorbent sheet media of claim 1 wherein the stacked sorbent sheet product has a BWC at least about 5% higher than the BWC of an unstacked sheet having the same known surface area.

[0035] Performance improvements of the stacked sorbent material sheet product of the invention can also be measured as the performance of the product having a given amount of activated carbon versus the performance of that same amount and grade of activated carbon if provided within a canister in a pelletized or powdered form. In some embodiments, the stacked sorbent sheet product has a BWC that is about 3% higher, about 5% higher, about 7% higher, about 9% higher, about 10% higher, about 12% higher, about 14% higher, and about 16% higher than the same amount and grade of activated carbon within a canister in

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pelletized or powdered form. Ranges based on these amounts are also contemplated, such as performance that is between about 5-14% higher, between about 5-10% higher, between about 10-16% higher, and so forth.

[0036] It should be noted that these improvements are only measured as between the weights of the pelletized or powdered activated carbon and the stacked sorbent material sheet product, without accounting for other improvements of the stacked sorbent material sheet product. One key difference, described above, is the omission of a rigid canister body that would otherwise be required. The omission of the rigid canister body, which is needed in prior art systems involving pelletized or powdered activated carbon because the loose activated carbon cannot support itself, drives further weight savings and therefore even further performance for a given weight.

[0037] The stacked sorbent sheet product has a BWC at least 10% higher than the BWC of a pelletized/powdered form of the same amount by weight of the sorbent material in the sorbent sheet. The stacked sorbent sheet product has a butane working capacity greater than about 10 g/100cc. The stacked sorbent sheet product has a butane working capacity of about 7.0 g/100cc to about 30 g/100cc, or greater than about 12 g/100cc, or greater than about 13 g/100cc, or greater than about 14 g/100 cc, or greater than about 15 g/100cc, or greater than 20 g/100cc. Ranges are also contemplated, such as about 10-20 g/cc, about 10-12 g/cc, about 10-14 g/cc, about 12-14 g/cc, about 12-15 g/cc, and about 15-20 g/cc.

[0038] In some embodiments, the stacked sheets are held in a spaced apart relationship which controls one or more of void volume, flow rate, pressure drop, and other characteristics. Such spacing is achieved in some embodiments where at least one of the two or more sorbent material sheets is corrugated. The spacing can also be achieved with various folds in the sheets, and can also be achieved by the corresponding raised and/or depressed portions of the sheets which are aligned to form gaps between the sheet. If the sheets are arranged deliberately so that the raised and/or depressed portions of the sheets do not nest between sheets, this results in additional spacing between the sheets and permits fluid flow in those portions. If the sheets are arranged deliberately so that at least some raised and/or depressed portions nest between sheets, this results in a tighter fitting stack of sheets and decreases the spacing between the sheets, with a corresponding decrease or even stop in fluid flow. Combinations of these features can be used to form stacked sorbent sheet products with directed regions or channels for fluid flow and barriers or edge seals to prevent fluid leakage. These features for fluid flow can also include holes, cuts, or apertures through one or more of the sheets in the stacked sorbent sheet product.

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[0039] Each sorbent sheet defines opposed lateral edges which are substantially parallel to fluid flow. The congruent lateral edges of adjacent sorbent sheets may be separate from each other, bound together or some combination thereof. In this manner, the edges of the stacked sorbent material sheet product may be sealed, partially sealed, or unsealed. The sealed or unsealed nature can be chosen to achieve desired results such as modifying fluid flow rate and/or patterns or other properties.

[0040] In some embodiments, the stacked sorbent material product yields a void volume of about 10% or less. In some embodiments, the void volume is about 8% or less, in some embodiments, the void volume is about 6% or less, in some embodiments, the void volume is about 4% or less.

[0041] In some embodiments, each sorbent sheet has a density of about 0.08 g/cc to about 1.5 g/cc.

[0042] In some instances, the sorbent material sheet product comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters. See the above description of the bimodal particle size distribution which was discussed with respect to the individual sorbent material sheets. The same distribution ratios as between populations of sorbent particles are contemplated with respect to product formed of multiple sorbent material sheets. In some instances, the density of the sorbent material particles achieved by the at least two populations is greater than the density achieved by either population alone. The inclusion of a bimodal particle size distribution can also be used to improve the mechanical properties of the sorbent material sheet product because it makes the polymeric sheets much more resistant to shear forces.

[0043] In some instances, a sorbent material sheet product comprises at least two sorbent material sheets, each of which has a defined upper surface and lower surface which have a combined total surface area, and wherein each sorbent material sheet comprises a sorbent material and a binder, and wherein each sorbent material sheet is stacked and arranged such that adjacent upper and lower surfaces of the separate sheets are substantially parallel and are aligned to allow fluid flow at least between the adjacent upper and lower surfaces.

[0044] The sorbent material sheet product may have a BWC stacking multiplier ratio of about 2.0, wherein the BWC stacking multiplier ratio is defined by the formula:

[0045] BWC stacking multiplier ratio = [(measured BWC of entire sorbent material sheet product) / (measured BWC of individual sorbent material sheet outside of product)] / number of sorbent material sheets in the sorbent material sheet product.

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[0046] The BWC stacking multiplier ratio may be at least about 1.0, at least about 1.1, at least about 1.2, at least about 1.3, at least about 1.4, at least about 1.5, at least about 1.6, at least about 1.7, at least about 1.8, at least about 1.9, at least about 2.0, at least about 2.1, at least about 2.2, at least about 2.3, at least about 2.4, at least about 2.5, at least about 2.6, at least about 2.7, at least about 2.8, at least about 2.9, and at least about 3.0. Additionally, endpoints can be combined, for instance about 1.0-1.5, about 1.1-1.2, about 1.1-1.3, about 1.5-2.0, about 2.0-2.5, and about 2.5-3.0.

[0047] The sorbent material sheet product of claim 1, wherein the sorbent material sheet product has a BWC value about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, and about 50% higher than the BWC of the same weight of sorbent material in pelletized or powdered forms. These can also be combined to formed ranges, for example, between about 5-25% higher. The invention also contemplates that these amounts are the endpoints on ranges, such as at least about 40% higher.

[0048] The sorbent material sheets in the sorbent material sheet product, may be configured as being flat, wound in a spiral cylinder, wound in an elliptical form, wound in an elongate rectangular bar, folded, laminated in an "S" shape, formed as concentric cylinders, formed as concentric ellipses, formed as a concentric rectangular bar, or as combinations of these forms.

[0049] In some embodiments, the sorbent material sheet product will comprise a single sorbent material sheet that is wound or rolled to achieve the desired characteristics including, but not limited to density, void space, pressure drop, etc.

[0050] *Wound/Rolled Sorbent Material Sheet Product:* The sorbent material sheet product can also be wound or rolled as an alternative or in combination with stacked embodiments. A wound or rolled sorbent material sheet product comprises a sorbent sheet defining an upper surface and a lower surface, and combined has a known total surface area, wherein the sorbent sheet comprises a sorbent material and a binder where the sorbent sheet is spiral wound to create adjacent sheet layers which allow fluid flow around and between adjacent sheet layers.

[0051] Similar to the stacked sheet arrangement, the rolled sorbent sheet product has improved performance over the sorbent material sheets alone, and has improved performance over the equivalent weight of activated carbon that is provided in pelletized or powdered form.

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[0052] The rolled arrangement results in an improved BWC for a given sheet area versus the same area for individual sheets that are not rolled. For example, each individual sorbent material sheet may have a BWC of about 12, and the rolled sorbent sheet media has a BWC that is at least about 1-10%, at least about 5-15%, at least about 2-20%, at least about 5-10%, at least about 5%, or at least about 7% higher than the sum of the BWC of the individual sheets.

[0053] Performance improvements of the rolled sorbent material sheet product of the invention can also be measured as the performance of the product having a given amount of activated carbon versus the performance of that same amount and grade of activated carbon if provided within a canister in a pelletized or powdered form. In some embodiments, the rolledsorbent sheet product has a BWC that is about 3% higher, about 5% higher, about 7% higher, about 9% higher, about 10% higher, about 12% higher, about 14% higher, and about 16% higher than the same amount and grade of activated carbon within a canister in pelletized or powdered form. Ranges based on these amounts are also contemplated, such as performance that is between about 5-14% higher, between about 5-10% higher, between about 10-16% higher, and so forth.

[0054] The rolled sorbent sheet product has a BWC at least 10% higher than the BWC of a pelletized/powdered form of the same amount by weight of the sorbent material in the sorbent sheet. The stacked sorbent sheet product has a butane working capacity greater than about 10 g/100cc. The stacked sorbent sheet product has a butane working capacity of about 7.0 g/100cc to about 30 g/100cc, or greater than about 12 g/100cc, or greater than about 13 g/100cc, or greater than about 14 g/100 cc, or greater than about 15 g/100cc, or greater than 20 g/100cc. Ranges are also contemplated, such as about 10-20 g/cc, about 10-12 g/cc, about 10-14 g/cc, about 12-14 g/cc, about 12-15 g/cc, and about 15-20 g/cc.

[0055] A rolled sorbent sheet product as described herein has a generally cylindrical shape having a length substantially greater than its diameter, although any dimension can be employed, including conical, or frustro-conical variations, as well as ellipsoids, or other shapes.

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[0056] The density of the rolled sorbent sheet product may be computed based on the formulas below:

Roll Density Calculations (US units)

$$\rho\left(\frac{lb}{ft^3}\right) = (3) * \frac{BW * L}{\left(\frac{OD^2}{4} - \frac{ID^2}{4}\right) * \pi}$$

BW: Basis Weight $\left(\frac{oz}{yd^2}\right)$ *L: Length on Roll* (yd)

OD: Outer Roll Diameter (in) *ID: Inner Roll Diameter/Core Diameter* (in)

W: Machine width or roll length (in) ρ*: Roll Density* $\left(\frac{lb}{ft^3}\right)$

Roll Density Calculations (SI units)

$$\rho\left(\frac{kg}{m^3}\right) = (1000) * \frac{BW * L}{\left(\frac{OD^2}{4} - \frac{ID^2}{4}\right) * \pi}$$

BW: Basis Weight $\left(\frac{g}{m^2}\right)$ *L: Length on Roll* (m)

OD: Outer Roll Diameter (mm) *ID: Inner Roll Diameter/Core Diameter* (mm)

W: Machine width or roll length (mm) ρ*: Roll Density* $\left(\frac{kg}{m^3}\right)$

[0057] The rolled sorbent sheet product may be wound to an average roll density of about 80-1500 kg/m^3, about 500-2000 kg/m^3, about 750-1500 kg/m^3, about 900-1200 kg/m^3, about 900-1050 kg/m^3, about 400-500 kg/m^3, about 500-600 kg/m^3, about 500-550 kg/m^3, about 600-650 kg/m^3, about 650-700 kg/m^3, and about 700-750 kg/m^3.

[0058] The rolled sorbent sheet product has a butane working capacity greater than about 10 g/100cc. In some embodiments, the rolled sorbent sheet product has a butane working capacity of about 7.0 g/100cc to about 30 g/100cc. The rolled sorbent sheet product may also have butane working capacities that are the same as the above described sorbent sheet products which are not rolled.

[0059] Similar to the discussion above with respect to the stacked sorbent material sheets, the wound or rolled sorbent material sheets may include multiple particle size distributions or populations of the adsorbent pelletized or powdered activated carbon. The same ratios are contemplated as discussed above. Similar to the discussion above, this results in greater performance because it enables a larger amount of the activated carbon to be incorporated into the sheets which are formed into the rolled sorbent sheet product.

[0060] As used herein, wound or rolled sorbent sheet products refer to any form of layering of one or more sorbent material sheets by winding, spiral winding, concentric layering of tubular (of any cross-sectional shape, e.g. round, elliptical, square, triangular, rectangle, etc.) or combination thereof. For example, a single sorbent material sheet may be spiral wound along its length to form a cylindrical-shaped rolled sorbent material sheet product. As another example, a plurality of sorbent material sheets can be stacked and then wound together to form a similar cylindrical shape. As another alternative, several sheets

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each formed into a cylinder having a slightly different diameter from the next can be arranged such that they from concentric rings in cross-section of a similarly sized cylinder. Various combinations of these and other arrangements may be used to fill the space within any shape of housing or canister, as described elsewhere herein.

As noted above with respect to the sorbent material sheets, the binder is selected from polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

[0061] The Housing

[0062] The invention also contemplates the use of a housing which partially or totally encapsulates the sorbent material sheets. The housing may be configured in a variety of shapes, for example tetrahedrons, cubes and cuboidal shapes, cylinders, spheres, hyperboloids of a single sheet, conical shapes, ellipsoidal shapes, rectangular shapes, hyperbolic paraboloid shapes, elongate bar shapes, paraboloids, and combinations of these shapes. The combinations may be selected to have different sections each of which have different shapes or portions of different shapes. The housing may also include sections which are separated and are connected by an additional part, for instance, at least one hose or tube which is designed to transfer fuel vapors as needed, or a thin portion of housing that contains the sorbent material sheets. The housing may also be configured with no shape, for example as a flexible bag or pouch containing the sorbent material sheets.

[0063] One major advantage of the invention is that the use of the sorbent material sheets are both flexible and self-supporting and can be laminated, rolled, wound, folded, or stacked in a variety of configurations within the housing to suit different mechanical requirements within the tight confines of a vehicle. In such embodiments, the housing would be designed to conform or fit the spaces that are available for the device to be stored. For instance, the housing can be sized and shaped to fit in spaces within or surrounding wheel

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wells, driveshafts, batteries for hybrid powertrains, spare tires, tire changing tools, tire patching tools, vehicle trunks or other storage spaces, vehicle bumpers and bodywork panels, exhaust systems, other emissions control equipment such as urea or other injection tanks, fuel lines, vehicle frames, suspension components, engine compartment, under passenger compartment seats, within passenger compartment seats, and other spaces which are too small or too difficult to reach to be effectively utilized for passenger or cargo space.

[0064] To further reduce weight and size and take advantage of the self-supporting sorbent material sheets, the housing can be in the form of a thin walled bag or pouch. This is possible because the sorbent material sheets have some mechanical structure and are self-supporting and so do not require a rigid outer container as in conventional canisters. The film materials that form the bag can have thicknesses of about 10 μm to about 250 μm. In other embodiments, the bag film can have thicknesses of about 20 μm to about 175 μm, and the bag film can have thicknesses of about 50 μm to about 125 μm.

[0065] The bag or pouch may be formed of any materials which are used in fuel systems, and particularly are formed of materials which are designed to withstand the chemical effects of the fuel vapors contained. Bag materials include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof. The bag is typically thermoplastic for flexibility, but can also be a combination with amounts of thermoset or can be in the form of a cured rubber or an elastomer.

[0066] The housing, bag, or pouch may also be designed to act as a vapor barrier to the adsorbed fuel vapors contained therein. This barrier property may be inherent to the polymer itself, or may be achieved through the use of at least one barrier additive and/or at least one barrier layer. Examples of barrier additives which can be formed as a layer or as a particulate filler include polymers such as epoxy, polyamide, polyamide imides, fluoropolymers, fluororubbers, and combinations of those. Barrier layers can also be made of

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metals such as aluminum, steel, titanium, and alloys of those. The metal barrier layers can be formed by conventional mechanical means, such as coextrusion or adhering with the other layers of the housing, or they can be chemically deposited, such as by chemical vapor deposition or electroplating. The metal barrier layer can be formed from a foil having a thickness of less than about 25 μm, less than about 20 μm, less than about 15 μm, less than about 10μm, or less than about 5 μm.

[0067] The housing and its materials may also be selected to be compatible with "ship in a bottle" fuel systems. In such systems, many or all of the fuel system components, including the fuel pumps, ORVR, fuel filters, valves, and other components are fitted within the vehicle fuel tank. Such systems are advantageous because they reduce assembly time and the amount of space required by the fuel system. In such systems, the housing should have materials which are capable of being immersed in the selected fuel, typically gasoline, for extended periods of time within the vehicle fuel tank, while also being able to withstand the effects of the adsorbed fuel vapors within.

[0068] The housing may also be a thin metal housing. The thin metal housing can be formed of flexible or rigid metals such as steel, aluminum, titanium, and alloys of those. The metal housing can be formed from a foil having a thickness of about 5-100 μm, or about 10-250 μm. In some embodiments, the foil may be as thick as about 1 mm. Whether the housing is flexible or rigid depends on the selection of the material, the thickness, and any treatments that have been applied to the metals, such as heat treatments or hot or cold working.

[0069] In some embodiments, the housing for the sorbent material sheets may be omitted entirely, with the sorbent material sheets being contained within the fuel tank itself. In such configurations, the sorbent materials sheets can be attached to a portion of the interior of the fuel tank that does not regularly come in contact with liquid fuel and which is free to adsorb fuel vapors. This portion is typically the top or sides of the fuel tank, or combinations of those. The fuel tank may also include a recessed portion on the top or the sides which is designed to include the sorbent material sheets and allow the sorbent material sheets to adsorb fuel vapors. Such embodiments where sorbent material sheets are attached to the interior portions of the fuel tank not only offer maximum space savings and weight savings by omitting the canister structure, but also simplify manufacturing and installation because the sheets are already installed within the fuel tank during vehicle assembly.

[0070] The housing can also be eliminated by forming a rolled or folded sorbent sheet and then selectively curing the outer sheets so that they form a durable, cured shell that acts

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as a support for the rolled or folded sorbent sheets within. Such selective curing can be accomplished thermally or with a chemical bath, or via actinic radiation, such as ultraviolet light or by electron beam curing.

[0071] In embodiments where the sorbent material sheets omit the housing and are contained within the vehicle fuel tank itself, the sorbent material sheets may be attached to the fuel tank in a variety of ways. The sorbent material sheets can be fastened using mechanical fasteners such as screws, rivets, or clamps, or the sorbent material sheets may be fastened using an adhesive backing positioned between the fuel tank wall and the sorbent material sheets. The adhesive backing may be a single layer of adhesive or a double sided adhesive tape or sheet. The adhesive used in the adhesive backing may include pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, and reactive multi-part adhesives. Adhesive compositions include acrylic and (meth)acrylic, acrylate and (meth)acrylate, epoxies in one- and two-part formulations, and urethane.

[0072] The sorbent material sheets may be applied during manufacturing in a variety of ways. In some embodiments, the fuel tank may be formed and the sorbent material sheets are applied in a separate step where the adhesive is applied followed by the application of the sorbent material sheets. In other embodiments, the sorbent material sheets are placed, with or without an adhesive backing as appropriate, on the inside of a mold and the fuel tank is injected or blow molded around the sorbent material sheets. In other embodiments, the sorbent material sheets may be coextruded with panels of material which make up the sides of the fuel tank, and the edges of those panels are adhered or welded together to seal the final tank with the sorbent material sheets on the inside.

[0073] When the sorbent material sheets are contained within the vehicle fuel tank without the housing, the fuel tank may include additional valves and ports to accommodate the adsorption and desorption of fuel vapors in the fuel tank. For example, during engine operation, air may be introduced into the fuel tank to desorb the fuel vapors which are contained in the sorbent material sheets, as well as those which are present in the tank. These desorbed fuel vapors are then sent to the engine for combustion during optimal cycles as required by the ECU.

[0074] When the sorbent material sheets are provided without a housing and are contained within a tank, such as a vehicle fuel tank, they may be positioned so that they are not regularly immersed in the volatile liquids typically contained within the tank. This ensures that the sorbent material sheets do not become prematurely saturated, and also ensures that sufficient surface area is exposed to the vapors within the fuel tank to effect the

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adsorption of the vapors. The feature contemplates that the sorbent material sheets can be placed in parts of the tank that are unfilled, such as the ullage or headspace of the tank, or near baffles which prevent the sloshing of liquids on the sorbent material sheets. The sorbent material sheets may also be places in a dedicated portion of the tank, such as a small chamber or niche, where the liquids cannot enter.

[0075] The devices of various embodiments may include a housing and the sorbent material sheets described above. The housing may be any shape and can be configured for purifying gasses or liquids. For example, in some embodiments, the housing may be any shape such as, for example, cuboidal, cubic, or cylindrical. The sorbent material sheets may be sized to fit within the housing and substantially fill a space within the housing through which the gas or liquid is passed. In some embodiments, two or more sorbent material sheets may be stacked to substantially fill the housing, and in other embodiments, the sorbent material sheets may be rolled to form a spiral wound sheet or pressed to form a stacked sheet. In some embodiments, the stacked or pressed sheets may be such that the sides of adjoining sheets are substantially contiguous. In other embodiments, stacked or pressed sheets may be positioned such that adjoining sheets are spaced. For example, in certain embodiments, the sheets may be corrugated, having sorbent material sheets that form a series or parallel ridges and furrows, and in some embodiments, corrugated sorbent material sheets may be separated by flat sorbent material sheets. The corrugated sorbent material sheets may be disposed within the housing in a stacked or rolled/spiral wound form.

[0076] In various embodiments, the void fraction may be about 30% to about 32% less than the void volume for current devices, and in some embodiments, the void fraction may be less than 10%. For example, the devices may have a void fraction of about 45% to about 2%, about 35 % to about 5%, about 25% to about 7%, or any individual void fraction or range encompassed by these example ranges. The devices of various embodiments may exhibit less flow restriction, e.g. pressure drop, than devices having granular or pelleted sorbent materials. Thus, more adsorbent material can be incorporated into such devices without reducing the flow rate of the device.

[0077] The devices of such embodiments may have butane working capacities ("BWC") of greater than about 5.0 g/100 cc, and in some embodiments, the devices may have a BWC of about 4.0 g/100 cc to about 20 g/100 cc, 5.0 g/100cc to about 18 g/100cc, about 7.0 g/100 cc to about 16 g/100cc, or about 8.0 g/100 cc to about 15 g/100 cc, or any individual BWC or range encompassed by these example ranges. The devices may exhibit a pressure drop that is at most equal to a conventional dense pack bed of powders, pellets, or

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granules of activated carbon or other activated compounds. This feature is advantageous because it ensures that the inventive sorbent material sheet product, whether stacked, rolled, wound, or otherwise configured, still has the same ability to process and transfer vapors and gases as conventional devices, despite the increased sorbent performance.

[0078] When the sorbent material product, stacked or rolled, is combined with a housing, it is useful as a vapor loss canister or other device. As noted above, the shapes and properties achieved via the stacked or rolled products allow for unique placement and improved performance.

[0079] In accordance with some embodiments, a vapor loss canister comprises a housing having at least one sidewall defining an internal space, a sorbent sheet product, such that the sorbent sheet media is sized and configured to fit within the housing and fill substantially the entire internal space within the housing, wherein the internal space is substantially free of additional internal material other than the sorbent sheet media. That is, traditional vapor loss canisters require springs, filters, support substrates, etc. to hold and maintain the loose carbon powder or pellets. Because the sorbent sheets are substantially self-supporting, these additional support structure are not needed. This allows for the inclusion of more material or the use of a smaller canister without sacrificing performance.

[0080] In some embodiments, the sorbent sheet product comprises a stacked sorbent sheet media comprising as described above. In such instances, the housing or canister can take any shape as discussed above, but in some embodiments, is relatively flat and flexible for housing stacked sorbent sheet media that has a height substantially less than its length or width. In these instances, the housing may be a flexible bag or pouch, as discussed above.

[0081] In some instances the canister is adapted for placement atop or even within a fuel tank.

[0082] In some embodiments, sorbent sheet material product comprises a rolled sorbent sheet product as described above. In some instances, at least a portion of the housing sidewall defines a filter substantially without occupying any internal canister space.

[0083] In some embodiments, a fuel tank may be provided with integral vapor adsorption. Such tanks comprise a tank structure, and at least one sorbent sheet material product, either stacked or rolled, at least one fastening device which fastens the sorbent material product to a surface of the tank that is not regularly immersed in the volatile liquids contained within the tank. The fastening device may be an adhesive layer which is formed between one surface of the sorbent material product and a wall of the tank.

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[0084] Such adhesive may be at least one of pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, reactive multi-part adhesives, acrylic and (meth)acrylic adhesives, acrylate and (meth)acrylate adhesives, epoxies adhesives in one- and two-part formulations, urethane adhesives, and copolymers and combinations thereof.

[0085] The tank may further include one or more of at least one fuel pump(s), fuel sending line(s), fuel return line(s), atmospheric vent line, port(s), valve(s), sensor(s), air inlet(s), open cell foam, baffle(s), bladder(s) and combinations of those.

[0086] In some embodiments, the tank is a fuel tank with a "ship in a bottle" configuration.

[0087] Some embodiments provide an onboard refueling vapor recovery apparatus comprising the sorbent material sheet product as described herein. The onboard refueling vapor recovery apparatus may include a vapor adsorbing canister as described herein. The onboard refueling vapor recovery apparatus may include a tank with integral vapor adsorption of claim 22.

[0088] Additional Components

[0089] The invention may include sensors such as a fuel composition sensor. The fuel composition sensor may be used to detect the mixture of gasoline and ethanol contained within the housing and the sorbent material, and this information may be communicated to the ECU so that vapors which are later released to the engine can be more precisely used during engine combustion. Other sensors include temperature sensors, vapor pressure sensors, oxygen sensors, and the like. The sensors can operate on principles of electrochemical interaction , electronic such as thermocouples, electromechanical, refractive index, infrared spectroscopy, and others depending on the type of information that is required for the ECU. The sensors can be included alone or in combination within the housing, or, if no housing is specified, within the area that contains the sorbent materials sheets. The sensors can be included in holes or notches which are cut from the sheet, or in spaces between the sheets with the sheets wrapped or folded around the sensors.

[0090] The invention may include inlets, outlets, hoses, and associated valves to control the flow of fuel vapor to and from the sorbent materials of the invention. The openings may static or they may have valves that are opened and closed as required by the ECU to control the flow of vapor into and out of the sorbent sheets of the invention. For example, during refueling, outlet valves remain closed to ensure that displaced fuel vapors do

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not escape into the atmosphere. However, when the engine operates and the ECU requests it, at least one outlet valve may open to allow the release of adsorbed vapor into the engine to allow its combustion. There may also be included a vent and valve to the atmosphere in case there is too much fuel vapor for the sorbent material sheets of the invention to safely adsorb. There may further be included an inlet and valve for air or other gases, such as inert exhaust gases, which is used to desorb the fuel vapor as it is being sent to the engine for combustion.

[0091] The invention also contemplates the inclusion of and integration with other components which make up ORVR systems and devices. These other components may include active compressors and condensers, fuel tank heaters, fuel tank heat exchanging coils for cooling enclosed fuels, fuel filler necks, fuel filler ports, including capless fuel filler ports, vents for fuel vapors, fuel lines for sending fuel, fuel return lines, vents and vehicle rollover valves, fuel pumps, and air intake or purge valves.

[0092] The invention further contemplates devices and structures which may be combined with the sorbent material sheets to improve or control the adsorption and desorption of fluids and gases. For example, fans or pumps may be included to force the fluids or vapors over the sorbent material sheets as they are assembled, allowing the sorbent material sheets to be packed or wound tighter or allowing larger devices than would otherwise be possible with the same amount of fluid diffusion over the sheets. Alternatively, the devices can include resistance element heaters, or Peltier effect heaters or coolers which are designed to heat and/or cool the fluids and thus force their movement over the sorbent material sheets of the claimed invention. For instance, heated, expanding fluid may vent upwards and draw in more fluid at the bottom of a rolled or wound article that is oriented vertically to take advantage of the effects of gravity.

[0093] Other Uses

[0094] In addition to automotive uses, the inventors contemplate that the sorbent sheets of the claimed invention can be used in any instance where a tank or other enclosed space is designed to contain volatile liquids, in particular volatile hydrocarbons such as fuels, solvents, and other volatile compounds. Examples include but are not limited to fuel tanks in aircraft, fuel tanks in ships and other marine vehicles, fuel tanks in trucks, chemical tanks in railroad cars, barges, ships, trucks, vehicles, and other bulk carriers, and stationary chemical tanks. The sorbent material sheets of the claimed invention can also be attached or adhered to the walls of confined spaces where the presence of volatile compounds would be detrimental, for example, in chemical facilities where operators and maintenance staff must

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periodically access the space. Such sorbent material sheets, when used in such combined spaces, can not only increase safety for operators and maintenance staff, but they can also reduce the need for cumbersome protective gear.

[0095] In some embodiments, the devices may not filter microscopic particles, and therefore will have utility outside the fuel vapor recovery arena. Devices containing granular or pelleted sorbent materials filter particles that are larger than about 1% of their diameter thereby removing these particles from gases or liquids that are treated using the device. Because devices containing stacked or rolled/spiral wound sorbent material sheets allow such particles to pass through without filtering, the devices of various embodiments may be useful for filtering biological fluids such as blood, where red and white blood cells and platelets and the like must pass through the filter without being physically filtered out of the blood. Other contaminates may be adsorbed onto the sorbent material sheets and removed from the blood filtrate

EXAMPLES

[0096] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

[0097] As was discussed above, BWC is a measure of the performance of activated carbon. BWC is determined for a sample by measuring the ability of the activated carbon to adsorb and desorb butane from dry air under specified conditions, and measures the difference between the butane adsorbed at saturated and the butane retained per unit volume of carbon after a specified purge. BWC can be tested in several ways, including procedures specified by ASTM International and which are known to those of skill in the art. Specifically, testing can follow ASTM D5228, which includes revisions D5228-16, D5228-92(2015), D5228-92(2005), and D5228-92(2000).

[0098] In Examples 1-4, the carbon sheets were spiral wound to yield 10% void fraction, which give about a 30% performance improvement over the activated carbon ("PAC") alone. The void fraction of comparative granular or powdered beds of activated carbon, similar to Comparative Example 1, was approximately 40% void fraction by volume. The Examples and Comparative Example are described below.

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EXAMPLE 1

[0099] Activated carbon films were made from CPL (CT#14299-8), which is an activated carbon that is wood based and which is activated using phosphoric acid. Films were also made from CPW (CT#14299-10), which is an activated carbon that is wood based and which is activated using phosphoric acid. The activated carbons were pulverized in a mechanical mortar and pestle and mixed with 9% PTFE powder. The resulting composition had a bread dough-like consistency. The composition was rolled to form sheets having thicknesses of 0.448 mm (CT#14299-8 1), 0.411 mm (CT#14299-8 2), 0.459 mm (CT#14299-10 1), and 0.439 mm (CT#14299-10 2).

EXAMPLE 2

[00100] Activated carbon sheets were prepared as described in Example 1 using BVC-11 8x25 activated carbon, which is a nutshell based activated carbon that is activated with phosphoric acid. This formed sample CT#14266-1. A sample was also formed with BVC-11 8x35, which is also a nutshell based activated carbon that is activated with phosphoric acid. This formed sample CT#14266-2. The formed sheets had a thickness of 0.330 mm (CT#14266-1 1), 0.334 mm (CT#14266-1 2), 0.327 mm (CT#14266-1 3), 0.317 mm (CT#14266-2 1), 0.307 mm (CT#14266-2 2), and 0.328 mm (CT#14266-2 3).

[00101] Butane Working Test – Examples 1 and 2

[00102] Activated carbon sheets prepared in Examples 1 and 2 were tested for butane adsorption using the butane working test. In this test, the sheets were rolled and placed in tubes. Butane was added to the tubes and butane adsorption was measured. The Tactic experiments, used to predict the BWC performance, were run on small stacks of 5 slat sheets. Results are illustrated in TABLES 1 and 2:

TABLE 1 (Example 2)

	14266-1	14266-2
Tube vol. (cc)	3.8465	3.8465
Sheet wt. (g)	6.3604	6.0009
Sheet thick. (cm)	0.033	0.0315
Sheet vol. (cc)	11.22	10.71
Sheet dens. (g/cc)	0.566881	0.566881
BWC sheet measured (g/100cc)	16.1	14.14

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BWC sheet tactic predicted (g/100cc)	16.48	15.59
BWC PAC measured (g/100cc)	12.10	12.20
BWC PAC tactic (g/100cc)	11.98	12.31

TABLE 2 (Example 1)

	CT-14299-8	CT-14299-10
Tube vol. (cc)	16.504	16.504
Sheet wt. (g)	4.10	3.16
Sheet thick. (cm)	0.411	0.439
Sheet vol. (cc)	9.92	7.90
Sheet dens. (g/cc)	0.413	0.404
BWC sheet measured (g/100cc)	12.32	12.41
BWC sheet tactic predicted (g/100cc)	12.22	12.93
BWC PAC measured (g/100cc)	7.9	9.6
BWC PAC tactic (g/100cc)	9.59	8.89

EXAMPLE 3

[00103] Activated carbon sheets were prepared as in Examples 1 and 2, but using granular activated carbon #3445-32-4. The activated carbon sheets were also not rolled as tightly as in prior Examples 1 and 2, which The resultant sheets were tested for butane adsorption using the butane working capacity test. In these two tests, two separate stacks of 20 sheets of 0.45mm thickness were cut in rectangles of 2.2cm X 7.5cm ± 10%, sealed at the side edge with double sided tape of 0.05mm thickness and 2mm width. In this configuration, tape thickness defined the average sheet spacing. Total height of each of the stacks of 20 sheets with tape spacers was 1 cm. These stacks of sheets were then placed in large 2.54cm diameter cylindrical glass tubes for butane adsorption/desorption testing. The excess volume between the rectangular stack of sheets and the walls of the cylindrical glass tube were filled with closed cell expanded foam to take up the excess volume and sealed to avoid bypass gas flow past the inserted test samples. The butane or air was forced to flow in the 0.05mm gaps between the 20 sheets. The flow rate and volume of the stacks of sheets was selected to maintain ASTM working capacity procedure. The ASTM procedure was followed with the

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exception of the use of the stack of sheets rather than a granule bed, the use of the closed cell expanded foam for sealing, and the required larger cylindrical glass tube arrangement to accommodate the rectangular stack of sheets.

[00104] During the modified ASTM procedure, butane or air was forced to flow in the 0.05 mm gaps between the 20 sheets, with the flow rate and volume of the stacks of sheets kept to ASTM specifications for working capacity. The results of Example 3 are in Table 3 below.

COMPARATIVE EXAMPLE 1

[00105] A comparative example was also prepared using the same granular activated carbon #3445-32-4 as in Example 4, but without forming the granular activated carbon as part of a sheet or roll. The granulated activated carbon was tested per ASTM procedure. The results of this test are in Table 3 below.

TABLE 3 (Example 3 and Comparative Example 1)

	Granular activated carbon (Comparative Example 1)	Stacked 0.45mm sheets (Example 3)	
	#3445-32-4	#3445-32-4-stack 1	#3445-32-4-stack 2
Tube vol. minus foam volume if present(cc)	16.7	16.4	15.5
Carbon wt. (g)	6.513	7.885	7.465
Sheet thickness (cm)	---	.045	0.045
Granular bed or Stacked sheet vol. (cc)	16.7	16.4	15.5
Granular bed or individual Sheet density (g/cc)	0.389	.534	.534
BWC (g/100cc)	9.33	10.25	10.83
BWC % improvement	---	9.9%	16.0%

[00106] Conclusion and Summary of Examples 1-3 and Comparative Example 1

[00107] A summary of relevant data appears in Table 4 below:

TABLE 4: Summary of Data

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Example	Test	Description	Sheet Thickness (cm)	Density (g/cm^3)	BWC ($g/100cm^3$)
Ex. 1	CT#14299-8	Wood based activated carbon CPL	0.411	0.413	12.32
Ex. 1	CT#14299-10	Wood based activated carbon CPW	0.439	0.404	12.41
Ex. 2	CT#14266-1	BVC-11 (nutshell) activated carbon 8x25	0.033	0.566881	16.1
Ex. 2	CT#14266-2	BVC-11 (nutshell) activated carbon 8x35	0.0315	0.566881	14.14
Ex. 3	#3445-32-4-stack 1	GAC, 20 sheet stack	0.045	0.534	10.25
Ex. 3	#3445-32-4 stack 2	GAC, 20 sheet stack	0.045	0.534	10.83
Comp. Ex. 1	#3445-32-4	Granular Activated Carbon (GAC)	N/A	0.389	9.33

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J. CLAIMS

1. A sorbent material sheet product, comprising

   at least two sorbent material sheets, each of which has a defined upper surface and lower surface which have a combined total surface area, and

   wherein each sorbent material sheet comprises a sorbent material and a binder, and

   wherein each sorbent material sheet is stacked and arranged such that adjacent upper and lower surfaces of the separate sheets are substantially parallel and are aligned to allow fluid flow at least between the adjacent upper and lower surfaces.

2. The sorbent material sheet product of claim 1, wherein the sorbent material sheet product has a BWC stacking multiplier ratio of about 1.1 to about 1.3, wherein the BWC stacking multiplier ratio is defined by the formula:

   BWC stacking multiplier ratio = [(measured BWC of entire sorbent material sheet product) / (measured BWC of individual sorbent material sheet outside of product)] / number of sorbent material sheets in the sorbent material sheet product.

3. The sorbent material sheet product of claim 1, wherein the individual sorbent material sheets, measured individually, have BWC values that are 5-15% higher than the BWC of the same weight of sorbent material in pelletized or powdered forms.

4. The sorbent material sheet product of claim 1, wherein at least one of the sorbent material sheets are configured as being flat, wound in a spiral cylinder, wound in an elliptical form, wound in an elongate rectangular bar, folded, laminated in an "S" shape, formed as concentric cylinders, formed as concentric ellipses, formed as a concentric rectangular bar, or as combinations of these forms.

5. The sorbent material sheet product of claim 1, wherein at least one of the sorbent material sheets has raised and/or depressed portions.

6. The sorbent material sheet product of claim 5, wherein the raised and/or depressed portions are present on adjacent sheets and are nested.

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7. The sorbent material sheet product of claim 5, wherein the raised and/or depressed portions are present on adjacent sheets and are not nested.

8. The sorbent material sheet product of claim 1, wherein the sorbent material sheet product has a void volume of about 10% or less.

9. The sorbent material sheet product of claim 1, wherein each individual sorbent material sheet has a density of about 0.08 g/cc to about 1.5 g/cc.

10. The sorbent material sheet product of claim 1, wherein the sorbent material sheet product has a BWC greater than about 10 g/100cc.

11. The sorbent material product of claim 1, wherein the sorbent material sheet product has a BWC of about 7.0 g/100cc to about 30 g/100cc.

12. The sorbent material sheet product of claim 1, wherein the sorbent material sheets comprise sorbent material particles having at least two populations having different average particle diameters, and wherein the average particle diameters of the two populations have ratios of about 1:2 to about 1:10.

13. The sorbent material sheet product of claim 1, wherein the amount of binder and the amount of sorbent material sheet products are present in a gradient such that the amount of binder is highest at an outer portion of the sorbent material sheet product, and that the amount of binder is lowest at an inner portion of the sorbent material sheet product.

14. The sorbent material sheet product of claim 1, wherein at least one sorbent material sheet include holes, cuts, or apertures.

15. The sorbent material sheet product of claim 1, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanesm, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented

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polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

16. A rolled sorbent material sheet product, comprising:

    a sorbent material sheet defining an upper surface and a lower surface and having a total surface area, and which comprises a sorbent material and a binder,

    wherein the sorbent material sheet is spiral wound to form adjacent sheet layers which allow fluid flow around and between adjacent sheet layers.

17. The rolled sorbent material sheet product of claim 16, wherein the sorbent material sheet in its rolled form has a BWC that is at least 10% higher than the BWC of the same sorbent material sheet in an unrolled form.

18. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheet product has a BWC that is at least 10% higher than the BWC of a pelletized or powdered form of the substantially the same amount of sorbent material in the sorbent sheet.

19. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheet product has a generally cylindrical shape having a length that is greater than its diameter.

20. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheet product is wound to an average roll density of 500-700 kg/m^3.

21. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheet product has a butane working capacity greater than about 10 g/100cc.

22. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheet product has a butane working capacity of about 7.0 g/100cc to about 30 g/100cc.

23. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheet comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters.

24. The rolled sorbent material sheet product of claim 16, wherein the rolled sorbent material sheets comprise sorbent material particles having at least two populations

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having different average particle diameters, and wherein the average particle diameters of the two populations have ratios of about 1:2 to about 1:10.

25. The rolled sorbent material sheet product of claim 16, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

26. A vapor adsorbing canister, comprising:

    the sorbent material sheet product of claim 1, and

    a housing at least partially encapsulating the sorbent material sheet product of claim 1

27. The vapor adsorbing canister of claim 26, wherein the housing is flexible.

28. The vapor adsorbing canister of claim 26, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

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29. The vapor adsorbing canister of claim 26, wherein the shape of the housing substantially conforms to the shape of the enclosed sorbent material sheet product of claim 1.

30. The vapor adsorbing canister of claim 26, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

31. A vapor adsorbing canister, comprising,

the rolled sorbent material sheet product of claim 16, and

a housing at least partially encapsulating the rolled sorbent material sheet product of claim 16.

32. The vapor absorbing canister of claim 31, wherein the housing is flexible.

33. The vapor adsorbing canister of claim 31, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

34. The vapor absorbing canister of claim 31, wherein the shape of the housing substantially conforms to the shape of the enclosed rolled sorbent material sheet product of claim 16.

35. The vapor adsorbing canister of claim 31, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

36. A tank with integral vapor adsorption, comprising:

a tank structure, and

at least one sorbent material sheet which has a defined upper surface and lower surface which have a combined total surface area, and

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wherein each sorbent material sheet comprises a sorbent material and a binder, and

at least one fastening device which fastens the sorbent material sheet to a surface of the tank that is not regularly immersed in the volatile liquids contained within the tank.

37. The tank with integral vapor adsorption of claim 36, wherein the fastening device is an adhesive layer which is formed between one surface of the sorbent material sheet and a wall of the tank.

38. The tank with integral vapor adsorption of claim 36, wherein the adhesive comprises at least one of pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, reactive multi-part adhesives, acrylic and (meth)acrylic adhesives, acrylate and (meth)acrylate adhesives, epoxy adhesives in one- or two-part formulations, urethane adhesives, and copolymers and combinations thereof.

39. The tank with integral vapor adsorption of claim 36, wherein the tank further includes at least one fuel pump(s), fuel sending line(s), fuel return line(s), atmospheric vent line, port(s), valve(s), sensor(s), air inlet(s), open cell foam, baffle(s), bladder(s) and combinations of those.

40. The tank with integral vapor adsorption of claim 36, wherein the tank is a fuel tank with a “ship in a bottle” configuration.

41. An onboard refueling vapor recovery apparatus comprising the sorbent material sheet product of claim 1.

42. An onboard refueling vapor recovery apparatus comprising the rolled sorbent material sheet product of claim 16.

43. An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of claim 26

44. An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of claim 31.

45. An onboard refueling vapor recovery apparatus comprising the tank with integral vapor adsorption of claim 36.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/016213

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 53/02; B01D 53/04; B01D 53/14 (2018.01)
CPC - B01D 53/02; B01D 53/04; B01D 53/14; B01D 53/1487 (2018.02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2016/0271555 A1 (MEADWESTVACO CORPORATION) 22 September 2016 (22.09.2016) entire document	1-5, 7-14, 26, 29, 30 --- 6, 15, 17, 18, 21, 22, 27, 28, 36-41, 43, 45
X --- Y	US 7,077,891 B2 (JAFFE et al) 18 July 2006 (18.07.2006) entire document	16, 19, 20, 23-25 --- 15, 17, 18, 21, 22, 31-33, 35, 42, 44
Y	US 6,406,523 B1 (CONNOR et al) 18 June 2002 (18.06.2002) entire document	6
Y	US 2007/0272080 A1 (ALLEN et al) 29 November 2007 (29.11.2007) entire document	27, 28, 31-33, 35, 44
Y	US 5,897,779 A (WISTED et al) 27 April 1999 (27.04.1999) entire document	36-40, 45
Y	US 8,632,334 B2 (KNUEPPEL et al) 21 January 2014 (21.01.2014) entire document	40
Y	US 8,888,901 B2 (AISAN KOGYO KABUSHIKI KAISHA) 18 November 2014 (18.11.2014) entire document	41-45
A	US 2004/0197612 A1 (KEEFER et al) 07 October 2004 (07.10.2004) entire document	1-33, 35-45
A	US 3,730,158 A (ST. AMAND) 01 May 1973 (01.05.1973) entire document	1-33, 35-45

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 March 2018	06 APR 2018
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/016213

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 34
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

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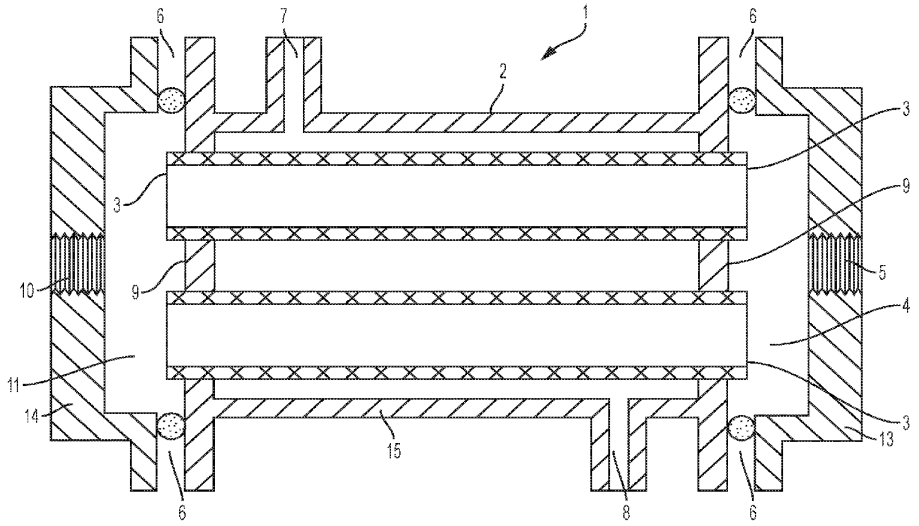


FIG. 1

(57) Abstract: Vapor Recovery Unit (VRU) includes a VRU heat exchanger and a sorbent material for the recovery of hydrocarbon vapors from the ullage of tanks. The VRU heat exchanger and sorbent material are useful in conjunction with a thermal transfer fluid to control the temperatures of the sorbent material during endothermic and exothermic reactions that occur when hydrocarbon vapors are adsorbed and desorbed, which increases performance and reduces the amount of sorbent material required to recover hydrocarbon vapors.

[Continued on next page]

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APPARATUS FOR HYDROCARBON VAPOR RECOVERY

CROSS-REFERENCE TO RELATED APPLICATIONS

[001] This application claims priority to U.S. Provisional Application Serial No. 62/713,335 filed on 1 August 2018, the entirety of which is hereby incorporated by reference.

BACKGROUND

[002] The recovery of hydrocarbon fluids, especially vapors is a well-known challenge in the chemical and transport industries. When any quantity of organic compounds such as hydrocarbon fuels are handled, stored, or transferred between tanks, the fluids trapped in the tank ullage must be accounted for. The fluids are problematic at a basic level because they can create an explosion hazard, especially if oxygen makes its way into the ullage in the tank. Prior art mitigation of these concerns by venting the trapped vapors or flaring is undesirable because doing so pollutes the environment and wastes valuable product.

[003] Another prior art approach is to adsorb the trapped ullage vapors in a bed of activated carbon which is part of a Vapor Recovery Unit (VRU or VRUs). This approach is common in fuel terminals where large quantities of gasoline are transferred from stationary tanks to on-highway trucks for delivery to gasoline filling stations. The on-highway trucks have tanks that typically hold between 5,000 and 10,000 gallons of gasoline fuel. During gasoline transfer, the gasoline vapors trapped in the tank ullage are piped to beds that contain about 5,000 lb to about 10,000 lb of activated carbon. The activated carbon may be in deep bed granular or pelleted form, and the activated carbon adsorbs the gasoline vapors from the tank ullage. After the transfer is complete and the vapors are adsorbed, a low pressure vacuum is created over the activated carbon to desorb the gasoline vapors, and the desorbed vapors are then cooled to cause the vapors to condense into a liquid. The condensed liquid is thereby recovered and may be stored for future use.

[004] The prior art VRUs also have drawbacks. The activated carbon beds are large and consume a significant footprint at the terminal or plant. The activated carbon beds also have significant thermal mass, which is challenging because the adsorption of gasoline vapors is exothermic, and the desorption is endothermic. Furthermore, the adsorption rate is limited by the temperature of the activated carbon, and higher temperatures lower the rate of adsorption. Thus, conventional VRUs limit the rate at which gasoline vapors can be adsorbed or desorbed, and also mean that a typical terminal will have at least two activated carbon

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beds, with each bed to be used in alternating fashion. This requires further equipment expenditures and grounds footprint.

[005] It would be advantageous if a VRU design could solve these and other problems of the prior art by reducing the size and weight of the VRU, controlling heat generated or required by exothermic and endothermic conditions, and enabling more rapid fuel transfer and vapor recovery.

SUMMARY

[006] Embodiment 1: A vapor recovery unit heat exchanger (VRU heat exchanger), comprising at least one sorbent material chamber that includes a sorbent material,

a heat transfer fluid chamber, a manifold in communication with the ullage space of a tank, wherein during operation, the sorbent material captures or releases fluids that originated in the ullage space of the tank.

[007] Embodiment 2: The VRU of embodiment 1, wherein the sorbent material is provided within one or more sorbent material sheets, and the sorbent material sheets further comprise a binder.

[008] Embodiment 3: The VRU of embodiments 1 or 2, wherein the binder is selected from the group consisting of polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, copolymers of any of the preceding binders, and mixtures of any preceding binders.

[009] Embodiment 4: The VRU of embodiments 1-3, wherein the amount of binder is about 2 wt.% to about 30 wt.% of a total composition of the sorbent material sheets.

[0010] Embodiment 5: The VRU of embodiments 1-4, wherein the sorbent material sheets are wound in a spiral shape or are wound in a concentric circular shape.

[0011] Embodiment 6: The VRU of embodiments 1-5, wherein the sorbent material sheets have a thickness of about 0.01 mm to about 2 mm.

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[0012] Embodiment 7: The VRU of embodiments 1-6, wherein the sorbent material is selected from the group consisting of activated carbon, natural zeolite, synthetic zeolite, silica, silica gel, alumina, zirconia, diatomaceous earths, and combinations thereof.

[0013] Embodiment 8: The VRU of embodiments 1-7, wherein the sorbent material is an activated carbon that is formed from at least one of bagasse, bamboo, coconut husks, peat, wood, lignite, coal, coal tar, petroleum pitch, asphalt and bitumen, chlorinated polymers, corn stalks and husks, wheat straw, spent grains, rice hulls and husks, and nutshells.

[0014] Embodiment 9: The VRU of embodiments 1-8, wherein the sorbent material has a BWC of about 7.0 g/100cc to about 30 g/100cc.

[0015] Embodiment 10: The VRU of embodiments 1-9, wherein the sorbent material comprises a thermally conductive filler.

[0016] Embodiment 11: The VRU of embodiments 1-10, wherein the thermally conductive filler is selected from the group consisting of transition metals, aluminum, steel, copper, silver, boron nitride, graphite, carbon black, alumina, diamond, silica, and combinations thereof.

[0017] Embodiment 12: A vapor recovery unit (VRU), comprising a first VRU heat exchanger that comprises at least one sorbent material chamber that includes a sorbent material, a heat transfer fluid chamber, a manifold in communication with the ullage space of a tank, wherein during operation, the sorbent material captures or releases fluids that originated in the ullage space of the tank; and a second VRU heat exchanger that comprises at least one sorbent material chamber that includes a sorbent material, a heat transfer fluid chamber, a manifold in communication with the ullage space of a tank, wherein during operation, the sorbent material captures or releases fluids that originated in the ullage space of the tank; and a thermal transfer fluid connection between the first VRU heat exchanger and the second VRU connection, wherein the thermal transfer fluid connection permits thermal transfer fluid to be exchanged between the first VRU heat exchanger and the second VRU heat exchanger.

[0018] Embodiment 13: The VRU of embodiment 12, further comprising a temperature control device that heats or cools the thermal transfer fluid.

[0019] Embodiment 14: The VRU of embodiments 12 or 13, further comprising a thermal transfer fluid storage medium for storing and dispensing the thermal transfer fluid to the first VRU heat exchanger, the second VRU heat exchanger, or both.

[0020] Embodiment 15: A method for operating a vapor recovery unit (VRU) wherein the VRU includes a first VRU heat exchanger and a second VRU heat exchanger, the

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method comprising operating the first VRU in an exothermic adsorption mode, thereby generating waste heat, operating the second VRU in an endothermic desorption mode, thereby cooling the second VRU; removing the waste heat by moving a heat transfer fluid through the first VRU; and dissipating at least a first portion of the waste heat by moving the heat transfer fluid through the second VRU.

[0021] Embodiment 16: The method of embodiment 15, further comprising storing heat transfer fluid until the heat transfer fluid is moved through the first VRU heat exchanger or the second VRU heat exchanger.

[0022] Embodiment 17: The method of embodiments 15 or 16, further comprising dissipating at least a second portion of the waste heat in a radiator or evaporative cooler.

DRAWINGS

[0023] Fig. 1 is a cross-sectional view of a VRU heat exchanger of the invention.

[0024] Fig. 2 is a second cross-sectional view of a VRU heat exchanger of the invention.

DETAILED DESCRIPTION

[0025] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0026] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a sorbent sheet" is a reference to "one or more sorbent sheets" and equivalents thereof known to those skilled in the art, and so forth.

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[0027] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0028] As used herein, the term "sorbent material" is meant to encompass all known materials from any source that are capable of absorbing or adsorbing liquids and/or gases. For example, sorbent materials include, but are not limited to, activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths.

[0029] The Sorbent Material

[0030] In some embodiments, the sorbent material includes one or more of activated carbon, carbon nanotubes, graphenesnatural zeolite, synthetic zeolite, silica, silica gel, alumina, zirconia, or diatomaceous earths. In some embodiments, the sorbent material is activated carbon.

[0031] One problem with prior art VRUs that are intended for recovery of flammable hydrocarbons is that high performance sorbents cannot be selected for fear of dangerous interactions. The exothermic reaction of vapor adsorption combined with the flammability of surrounding hydrocarbons means that the carbons must remain stable to protect against ignition. This means that the sorbents are selected for their stability to oxidation at all encountered temperatures, rather than their ability to adsorb and desorb butane. As an example, for activated carbon sorbents, prior art VRUs could not include activated carbons which were activated using phosphoric acid, because these could be an ignition hazard. As will be seen below, the VRU disclosed herein opens the possibility to select the highest performing sorbents, including carbons activated using chemical treatments such as phosphoric acid.

[0032] The activated carbon may be of various grades and types selected based on performance requirements, cost, and other considerations. The activated carbon may be granular from reagglomerating a powder, granular from crushing or sizing nutshells, wood, coal or pellets created by extrusion, or activated carbon in powdered form. The activated carbon may be formed by processes of carbonization and activated. The raw material, such as wood, nutshell, coal, pitch, etc. is oxidized and devolatized, with steam and/or carbon dioxide gasified to form the pore structure in the activated carbon which is useful for adsorption. The initial oxidation and devolatilization process may include a chemical

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treatment with a dehydrating chemical, such as phosphoric acid, sulfuric acid, sodium hydroxide, potassium hydroxide, and combinations of those.

[0033] A variety of activation processes are known in the art. The most useful processes for providing activated carbon for the sorbent material of the claimed invention involve a step of providing wood and/or wood byproduct, acid treating the wood and/or wood byproducts by exposure to phosphoric acid, and carbonizing the wood and/or wood byproducts using steam and/or carbon dioxide gasification. This process results in activated carbon particles having the highest butane working capacity ("BWC") according to the ASTM D5228 method which is a measure of activated carbon performance. The selection of activated carbon particles having the highest BWC means that the VRU of the invention is more compact than prior art VRUs while offering the same or higher performance.

[0034] The BWC for each sorbent material may be greater than about 10 g/100cc, and in some embodiments, the BWC may be from about 7.0 g/100cc to about 30 g/100cc, about 8.0 g/100 cc to about 25 g/100cc, about 10 g/100 cc to about 20 g/100 cc, about 10 g/100 cc to about 15 g/100 cc, about 11 g/100cc to about 15 g/100 cc, about 12 g/100cc to about 15 g/100cc or any individual BWC or range encompassed by these example ranges. In other examples, the BWC may be about 9 g/100 cc to about 15 g/100 cc, about 12 g/100 cc to about 20 g/100 cc, about 13 g/100 cc to about 20 g/100cc, about 14 g/100cc to about 20 g/100cc, or about 15 g/100cc to about 20 g/100cc. It is also contemplated that any of the endpoints of the above ranges may be combined to form new and distinct ranges.

[0035] The activated carbon may be formed from materials including bagasse, bamboo, coconut husks, peat, wood such as hardwood and softwood sources in the form of sawdust and scrap, lignite, coal and coal tar, petroleum pitch, asphalt and bitumen, chlorinated polymers, corn stalks and husks, wheat straw, spent grains, rice hulls and husks, nutshells, and combinations thereof.

[0036] The sorbent material may be provided in the form of a powder, pellets, granules, or within sorbent material sheets. The sorbent material sheets may be formed of one or more from cloth, paper, plastics, ceramics, or metals that include the above described sorbents. In some embodiments, the sorbent material sheets include plastics which may be in the form of a binder.

[0037] The sorbent material sheets include any of the sorbent materials described above including, but are not limited to, activated carbon, carbon nanotubes, graphenesnatural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths, and in

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certain embodiments, the sorbent material may be composed of activated carbon. The sorbent materials may be used alone or in combination.

[0038] In some embodiments, the sorbent material sheets are in the form of multiple, separated sheets, with sides and/or surfaces in proximity to each other. In other embodiments, the sorbent material sheet is in the form of only a single sheet that has been wound or folded over on itself to yield a stacked, wound, or otherwise constructed mass of the sheet with sides and/or surface of the sheet in proximity to each other. In still other embodiments, multiple sheets are stacked together and then wound or otherwise folded over, forming alternating layers in a single mass.

[0039] The sorbent material sheets

[0040] The sorbent material sheets may include one or more binders. Embodiments are not limited to particular binders, which can include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof. The binders can be thermoplastic or thermosetting as conditions require, and can include mixtures of thermoplastic and thermosetting compounds.

[0041] The amount of binder may be about 2 wt.% to about 40 wt.%, and in certain embodiments, the amount of binder may be about 2 wt.% to about 20 wt.%, about 2 wt.% to about 15 wt.%, about 5 wt.% to about 15 wt.%, about 2 wt.% to about 10 wt.% by weight, about 11 wt.%, or any individual amount or range encompassing these example amounts. In some embodiments, the sorbent material sheets may include a solvent, which may generally be present in small, residual, amounts of, for example, less than 10%, less than 5%, or less than 2% and greater than about 0.1 % or 0.2 % by weight. In particular, in some embodiments the sorbent material sheets may have no (0%) solvent. All amounts of binder and/or solvent are measured with respect to the total weight of the overall sorbent material.

[0042] In some embodiments, the sorbent material sheets are textured to form textured sorbent material sheets. The textured sorbent material sheets may be composed of a

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sorbent material and a binder and have a thickness sufficient to allow portions of the sheet to be compressed creating hills and valleys of desired cross-sectional size and shape.

[0043] In some embodiments, the sorbent material sheets have a thickness of less than about 2 mm, less than about 1.8 mm, less than about 1.6 mm, less than about 1.4 mm, less than about 1.2 mm, less than about 1.0 mm, about 0.01 mm to about 2 mm, about 0.01 mm to about 1.8 mm, about 0.1 mm to about 1.6 mm, about 0.01 mm to about 1.4 mm, about 0.01 mm to about 1.2 mm, about 0.01 mm to about 1.0 mm, about 0.02 mm to about 0.90 mm, about 0.05 to about 0.95 mm, about 0.05 to about 0.90 mm or any individual thickness or range encompassed by these example ranges. In some embodiments, an extra thick, *i.e.*, greater than 0.9mm, activated carbon sheet was pressed between a flat surface and the textured surface of a mold to form a textured sorbent material sheet. The overall average thickness of the sheet was reduced and texture was added to only one side of the sheet. The sheet thickness would vary with the hills and valleys of the texture pattern. This single sheet was stable with time and temperature because it has no means of relaxing to the original thick sheet. This approach was possible with the thicker activated carbon sheet material due to its malleability.

[0044] The sorbent material sheets may be textured on one or both sides. In some embodiments, the pattern and resultant channels are parallel or co-linear with the flow of the fluid through the sheets to achieve the low pressure drop. The texture may also itself form channels and flow that are not straight, such as angled, serpentine, irregular, or more complicated.

[0045] In some embodiments, the textured sorbent material sheets may have a thickness measured at a hill or peak of about 1.0 to about 1.5 mm, about 1.4 mm, about 1.3 mm, about 1.2 mm, or any individual thickness or range encompassed by any two of these values.

[0046] In some embodiments, the distance from the tip of a hill to the bottom of a valley is about 0.5 mm to about 0.1 mm. In some embodiments, the distance is about 0.4 mm, about 0.3 mm, about 0.2 mm, or any individual distance or range encompassed by any two of these values.

[0047] The sorbent material sheets of various embodiments may have a density of about 0.05 g/cc to about 2.0 g/cc, and in other embodiments, the sorbent material sheets may have a density of 0.08 g/cc to about 1.5 g/cc, about 0.1 g/cc to about 1.3 g/cc, or any density or range encompassed by these example ranges. The density is calculated first by measuring the thickness of a given square or circular piece of sheet with a micrometer, multiplying by

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the surface area to obtain the volume, and weighing the piece to obtain the density (weight / volume). The BWC for each sorbent material sheet may be greater than about 10 g/100cc, and in some embodiments, the BWC may be from about 7.0 g/100cc to about 30 g/100cc, about 8.0 g/100 cc to about 25 g/100cc, about 10 g/100 cc to about 20 g/100 cc, about 10 g/100 cc to about 15 g/100 cc, about 11 g/100cc to about 15 g/100 cc, about 12 g/100cc to about 15 g/100cc or any individual BWC or range encompassed by these example ranges. In other examples, the BWC may be about 9 g/100 cc to about 15 g/100 cc, about 12 g/100 cc to about 20 g/100 cc, about 13 g/100 cc to about 20 g/100cc, about 14 g/100cc to about 20 g/100cc, or about 15 g/100cc to about 20 g/100cc. It is also contemplated that any of the endpoints of the above ranges may be combined to form new and distinct ranges.

[0048] The sorbent material sheets of embodiments can be made by any suitable process. In some embodiments, sorbent material sheets can be made by pulverizing granular or pelletized sorbent material to a powder, mixing the powder with a binder to form a mixture, heating and blending the mixture, and rolling the mixture to form the sorbent material sheet. The step of pulverizing may produce sorbent particles having an average particle diameter of about 0.001 mm to about 0.2 mm, about 0.005 mm to about 0.1 mm, about 0.01 mm to about 0.075 mm, or any individual particle diameter or range encompassed by these example ranges, and in certain embodiments, the pulverized sorbent particles may have an average particle diameter of about 0.001 mm to about 0.01 mm. The step of mixing the powder with a binder may include mixing the sorbent particle powder with about 2% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassed by these example ranges. Heating can be carried out at any temperature sufficient to remove residual solvent such as, for example, about 50°C to about 200°C.

[0049] The sorbent material sheet may include various distributions of different sized particles to increase the packing efficiency of the powder within the sorbent material sheets. The selection of different sized particles can also improve rheological properties of the powder and surrounding binders, which allows improved mixing and uniform particle distribution before formation of the sorbent material sheets. In some embodiments, the particles of the sorbent material sheet may have a single particle size distribution, and in other embodiments, the particles may have two different particle size distributions. In further embodiments, the particle may have at least three different particle size distributions.

[0050] The mean particle sizes of at least two different particle populations, each having a particular size distribution, may be selected so that they have a ratio of between

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about 1:1 and about 1:15: In other embodiments, the mean particle sizes of the two different particle populations may have a ratio of about 1:1 to about 1:10. The mean particle sizes may also have a ratio of about 1:1 to about 1:5, or combinations of any of the above listed ratios.

[0051] In some embodiments, the sorbent material or sorbent material sheets may include a thermally conductive filler to increase the heat transfer of the sorbent material sheets. The thermally conductive filler may be a polymer, metal, or ceramic. In some embodiments, the thermally conductive filler is also electrically conductive, which reduces the risk of ignition by dissipating any accumulated electrical charge. The thermally conductive filler may be in the form of powder, wires, chopped fibers, chopped wires, platelets, and combinations of the above. The thermally conductive filler may be made of a transition metal, aluminum, steel, copper, silver, boron nitride, graphite, carbon black, alumina, diamond, silica, and combinations thereof.

[0052] The VRU

[0053] The sorbent material or sorbent material sheets described above are incorporated into a VRU. The VRU includes at least one VRU heat exchanger, and each VRU heat exchanger includes the sorbent material described above. The VRU heat exchangers are cooled or heated as needed during absorption and desorption operations. The VRU of the invention prevents the formation of zones of high temperature in the sorbent material or sorbent material sheets. The VRU also prevents formation of zones of extremely low temperature in the sorbent material or sorbent material sheets.

[0054] The VRU of the invention includes at least one VRU heat exchanger that may be used during adsorption or desorption of vapors, such as hydrocarbon vapors. The VRU heat exchanger may be a shell and tube heat exchanger, plate heat exchanger, plate and shell heat exchanger, phase change heat exchanger, helical coil heat exchangers, and spiral heat exchangers. The VRU heat exchanger is selected based on various factors including cost, size, performance, and packaging for the sorbent material sheets. The VRU heat exchanger of the VRU includes space for the inclusion of the sorbent material sheets and a separate space for a heat transfer fluid.

[0055] During the adsorption cycle, hydrocarbon vapors, such as vapors from the ullage of a storage or vehicle tank, are passed over the sorbent material or sorbent material sheets. This causes the sorbent material or sorbent material sheets to adsorb the vapors. The adsorption cycle is exothermic, generating heat as the sorbent material adsorbs the vapors. The heat transfer fluid removes this heat from the sorbent material as the sorbent material

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adsorbs the vapors. The removal of the heat maintains adsorption performance and prevents thermal runaway or ignition.

[0056] The opposite occurs during the desorption cycle. During the desorption cycle, a low pressure vacuum is created over the sorbent material, typically using a vacuum pump. This lowered pressure causes the adsorbed hydrocarbon vapors to desorb, or be removed from sorbent material. The desorption process is endothermic, and the desorbed vapors reclaimed by being condensed are returned to a storage tank so that they can be used or sold. If the desorption cycle results in process temperatures that are too cold, heat may be provided using the heat transfer fluid. This prevents freezing of compounds such as water that may be present in the VRU heat exchanger.

[0057] In one embodiment, at least one VRU heat exchanger is a shell and tube heat exchanger. In such a configuration, the sorbent material is packed within at least one cylindrical tube and a heat transfer fluid flows in the heat transfer fluid chamber between the tube and the shell of the heat exchanger. The sorbent material can be inserted within the cylindrical tube in any configuration. For example, the sorbent material can be granular and deposited as a bed within the cylindrical tube. In another example, the sorbent material is provided as a sorbent material sheet and is wound in a spiral or concentric circular shape and inserted into the tube. The tubes have various inner and outer diameters which are selected based on design space and required performance.

[0058] The inner diameter of the VRU heat exchanger tubes is not particularly limited. In some embodiments, the inner diameter of the VRU heat exchanger tubes may range from about 0.5 inches to about 6 inches. The tube diameter may be about 0.5 inches, about 1.0 inches, about 1.5 inches, about 2.0 inches, about 2.5 inches, about 3.0 inches, about 3.5 inches, about 4.0 inches, about 4.5 inches, about 5.5 inches, or about 6 inches, or any range formed from the above listed amounts. The tube may have a diameter of about 1 inch to about 5 inches, about 2 inches to about 4 inch, or about 2.5 inch to about 3.5 inches.

[0059] The selection of VRU heat exchanger tubes of the above diameter means that excellent heat transfer performance is achieved. This is especially useful during the adsorption cycle, because efficient heat conduction can be achieved across the sorbent material, and this avoids hot spots that could slow down the adsorption process or worse, cause ignition or a run-away exothermic reaction. This is because the ability of the sorbent sheets to adsorb hydrocarbons such as butane is inversely proportional to rising temperature. As temperature increases, the adsorption capacity of the sorbent material decreases. By maintaining cool temperatures in the sorbent sheets, increased adsorbent capacity is achieved.

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[0060] Further synergies are achieved when combining structure of the sorbent material sheets with the VRU heat exchanger tubes. This enables both efficient packing of the sorbent material and excellent thermal transfer through the sheets to the walls of the VRU heat exchanger tubes.

[0061] The heat transfer fluid of the VRU heat exchanger may be any fluid that is commonly used in the art, and may include air, water, nitrogen gas, oxygen gas, refrigerant, mineral oils, silicone oil, and combinations of the above. The above may be combined with additives which are included for the purposes of corrosion inhibition, freezing-point depression, freezing-point elevation, boiling-point depression, boiling-point elevation, and lubrication. Examples of such compounds include ethylene glycol, methanol, propylene glycol, glycerol, lubricant oils, and the like, which may be used alone or in combination.

[0062] In some embodiments, multiple VRU heat exchangers are be combined for even further improved, synergistic results during adsorption and desorption cycles as follows. In these embodiments, there is at least one VRU heat exchanger operating in "desorption mode" and at least one counterpart VRU heat exchanger operating in "adsorption mode." In the operation of the VRU heat exchanger in exothermic adsorption mode, waste heat is removed by the heat transfer fluid, and at least some of that waste heat may be dissipated in the VRU heat exchanger in endothermic desorption mode, preventing the overcooling situation described earlier. The remainder of the waste heat may be dissipated as needed, for instance using a radiator or evaporative cooling. Similarly, cooled heat exchange fluid resulting from the endothermic desorption mode can be used as the heat exchange fluid in the exothermic mode. These cycles may be operated simultaneously or at different times, for instance by employing a tank of stored heat transfer fluid which is held until needed for the next adsorption or desorption process.

[0063] The VRU heat exchanger can be made of a variety of materials, but is generally made of stainless steel and aluminum.

[0064] The VRU may include various seals that are designed to prevent liquids and gases from moving outside of their designated compartments. The seals may be designed and provided as is known in the art, and the seals may include gaskets, welds, adhesives, solder, brazing, and the like. The specific techniques and materials for the seals are selected depending on the mating materials and liquids and gases which are to be interfaced and/or prevented from contacting each other.

[0065] The configuration of the VRU heat exchangers depends on the expected service demands, the volume of hydrocarbons that is intended to be serviced, and other

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factors that control the amount of hydrocarbon vapors that are generated and that are desirous to recover. For example, in one embodiment that is described more fully in the Examples, a VRU includes two VRU heat exchangers, each having 60 three inch (3") diameter tubes. Each tube is 40 inches (40") in length and incorporates rolled sorbent materials sheets that include high performance activated carbon sorbent, again described in the Examples below. Larger facilities that include more tubes, where the tubes are of larger diameter, where the tubes have greater amounts of carbon, or where the tube temperatures are more aggressively controlled are possible where additional performance is required. Greater performance is often required in locations where gasoline is more rapidly purchased and consumed in surrounding filling stations. Conversely, lower performance may be required in locations where gasoline is purchased and consumed at a slower rate, thus permitting the VRU to have smaller diameter tubes, fewer tubes, and less aggressive control of tube temperatures.

[0066] Figs. 1 and 2 are cutaway views of a small scale embodiment of the invention. In Fig. 1, a shell and tube heat exchanger 1 includes shell 2. Within the shell 2 are sorbent material chambers 3 that contain sorbent materials 12. At least two manifold spaces 4 and 11 distribute vapors which are to be collected from the ullage of a tank to the sorbent tubes 3 and the sorbent materials 12 which are disposed therein. The manifold spaces 4 and 11 also permit desorption of the captured vapor from the sorbent material chambers 3 and sorbent materials 12.

[0067] The manifold spaces 4 and 11 are formed between tube sheets 9 and the respective manifold caps 13 and 14. The manifold caps 13 and 14 have respective ports 5 and 10 which is used to transfer the vapors from the tank ullage during adsorption, or to be collected during desorption. For transfer of vapors, liquids, and other compounds into and out of the manifold spaces 4 and 11, ports 5 and 10 are used.

[0068] Shell and tube heat exchanger 1 further includes tube sheets 9 which separate the heat transfer fluid chamber 15 from the interior of the sorbent material chambers 3. Manifold seals 6 are used to enclose the manifold spaces 4 and 11 and along with tube sheets 9 direct the vapors, liquids, and other compounds into and out of the sorbent tubes 3. In the depicted embodiment, the seal 6 is a gasket placed between the mating surfaces of the manifold caps 13 and 14 and the tube sheets 9. However, other seals may be placed depending on need and are not shown here. For movement of heat transfer fluid into and out of the heat transfer fluid chamber 15, inlet 7 and outlet 8 are provided. While not shown in the Figures, it is contemplated that one or more baffles may be installed within the heat

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transfer fluid chamber 15 to ensure efficient mixing and heat transfer from heat transfer fluid as it moves through the shell and tube heat exchanger 1.

[0069] In some embodiments, the sorbent material chambers 3 are tube shaped and have an inner diameter of 3 inches and a length of 40 inches. In some embodiments, ports 5 and 10 have a diameter of 1 inch, and can have a National Pipe Taper (NPT) thread. In some embodiments, ports 7 and 8 have a diameter of 0.5 inches, and can have an NPT thread.

Examples

[0070] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

EXAMPLE 1

[0071] A shell and tube heat exchanger design incorporates rolled sorbent material sheets that include an activated carbon sorbent. The rolled sorbent material sheets are packed into the tubes of a shell and tube heat exchanger. Each shell and tube heat exchanger includes 60 three inch (3") diameter tubes, each of which are 40 inches (40") in length. The tubes form the sorbent material chambers. Each shell and tube heat exchanger includes 300 lbs of sorbent material, which is high performance, 15 g/100cc BWC activated carbon. A VRU includes two such shell and tube heat exchangers, and each of the heat exchangers are connected as needed to a vacuum pump, heat transfer fluid pump, and the ullage space of a tank that has hydrocarbon vapors. This means that there is a total of 600 lbs of activated carbon required. Compared to conventional technologies which rely on beds of 5,000 to 10,000 lbs of activated carbon, this results in a 5 to 10 fold reduction in the required amount of activated carbon, and therefore a significant reduction of installed footprint and capital cost. The shell and tube heat exchanger design also reduces the required size of the associated cooling system, further reducing the installed footprint and capital cost.

EXAMPLE 2

[0072] One measurement of sorbent material performance is Butane Working Capacity (BWC), which measures the ability of an activated carbon to adsorb and desorb butane from dry air under specified conditions. BWC is a useful proxy of sorbent performance for hydrocarbon vapors, especially gasoline, because n-butane makes up a significant component of many hydrocarbon vapors, including that of gasoline. BWC is

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measured by first determining the "butane number" which is the adsorption capacity of the sorbent material at a specified temperature with a specified concentration of butane in the atmosphere. Next, the sorbent is desorbed to determine "retentivity," which results in a measured capacity at a specified desorption concentration and temperature. BWC is therefore a measurement of the total ability of a sorbent to adsorb, retain, and desorb butane vapors. In general, high vapor concentrations and low temperatures increase the capacity for adsorption (i.e., the butane number), low vapor concentrations and high temperatures increase the desorption performance (i.e., desorption or retentivity). The BWC test method is described in detail in ASTM method D5228.

[0073] Table 1 plots the simulated performance of VRU-F3, a granular coal-based activated carbon product that is sold for use in VRUs by Calgon Carbon Corporation of Moon Township, Pennsylvania. The simulation shows the sorbent capacity of a sorbent in grams of solvent per 100 ml of solvent based on temperature and the concentration of solvent in the surrounding atmosphere. In this simulation, the pressure is 1 atmosphere. Table 1 demonstrates that as temperature increases, the sorbent capacity declines. Because sorbent capacity declines with increasing temperature, better control of temperature yields significant improvements in performance. From these simulated results, we infer that the heat exchanger configuration enables adsorption at lower temperatures for a given vapor concentration of butane, which in turn yields increased BWC and therefore, increased adsorption capacity for hydrocarbon vapors.

Table 1:Simulated Performance of VRU-F3

Butane Concentration (ppmv)	**BWC (g butane/100 ml); 0°C**	**BWC (g butane/100ml); 25°C**	**BWC (g butane/100ml); 50°C**	**BWC (g butane/100 ml); 75°C**	**BWC (g butane/100 ml); 100°C**
1	1.164	0.723	0.442	0.268	0.162
10	1.875	1.241	0.812	0.524	0.335
100	2.961	2.080	1.449	0.999	0.682
1000	4.615	3.410	2.513	1.843	1.342
10000	7.145	5.515	4.263	3.294	2.539
100000	11.066	8.882	7.153	5.774	4.666
1000000	17.197	14.348	12.008	10.077	8.478

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CLAIMS:

1. A vapor recovery unit heat exchanger (VRU heat exchanger), comprising:
   at least one sorbent material chamber that includes a sorbent material,
   a heat transfer fluid chamber,
   a manifold in communication with the ullage space of a tank,
   wherein during operation, the sorbent material captures or releases fluids that originated in the ullage space of the tank.
2. The VRU of claim 1, wherein the sorbent material is provided within one or more sorbent material sheets, and the sorbent material sheets further comprise a binder.
3. The VRU of claim 2, wherein the binder is selected from the group consisting of polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, copolymers of any of the preceding binders, and mixtures of any preceding binders.
4. The VRU of claim 2, wherein the amount of binder is about 2 wt.% to about 30 wt.% of a total composition of the sorbent material sheets.
5. The VRU of claim 2, wherein the sorbent material sheets are wound in a spiral shape or are wound in a concentric circular shape.
6. The VRU of claim 2, wherein the sorbent material sheets have a thickness of about 0.01 mm to about 2 mm.
7. The VRU of claim 1, wherein the sorbent material is selected from the group consisting of activated carbon, natural zeolite, synthetic zeolite, silica, silica gel, alumina, zirconia, diatomaceous earths, and combinations thereof.
8. The VRU of claim 1, wherein the sorbent material is an activated carbon that is formed from at least one of bagasse, bamboo, coconut husks, peat, wood, lignite, coal, coal tar,

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petroleum pitch, asphalt and bitumen, chlorinated polymers, corn stalks and husks, wheat straw, spent grains, rice hulls and husks, and nutshells.

9. The VRU of claim 1, wherein the sorbent material has a BWC of about 7.0 g/100cc to about 30 g/100cc.
10. The VRU of claim 1, wherein the sorbent material comprises a thermally conductive filler.
11. The VRU of claim 10, wherein the thermally conductive filler is selected from the group consisting of transition metals, aluminum, steel, copper, silver, boron nitride, graphite, carbon black, alumina, diamond, silica, and combinations thereof.
12. A vapor recovery unit (VRU), comprising:
    a first VRU heat exchanger that comprises at least one sorbent material chamber that includes a sorbent material, a heat transfer fluid chamber, a manifold in communication with the ullage space of a tank, wherein during operation, the sorbent material captures or releases fluids that originated in the ullage space of the tank; and
    a second VRU heat exchanger that comprises at least one sorbent material chamber that includes a sorbent material, a heat transfer fluid chamber, a manifold in communication with the ullage space of a tank, wherein during operation, the sorbent material captures or releases fluids that originated in the ullage space of the tank; and
    a thermal transfer fluid connection between the first VRU heat exchanger and the second VRU connection, wherein the thermal transfer fluid connection permits thermal transfer fluid to be exchanged between the first VRU heat exchanger and the second VRU heat exchanger.
13. The VRU of claim 3, further comprising a temperature control device that heats or cools the thermal transfer fluid.
14. The VRU of claim 3, further comprising a thermal transfer fluid storage medium for storing and dispensing the thermal transfer fluid to the first VRU heat exchanger, the second VRU heat exchanger, or both.
15. A method for operating a vapor recovery unit (VRU) wherein the VRU includes a first VRU heat exchanger and a second VRU heat exchanger, the method comprising:
    operating the first VRU in an exothermic adsorption mode, thereby generating waste heat,

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operating the second VRU in an endothermic desorption mode, thereby cooling the second VRU;

removing the waste heat by moving a heat transfer fluid through the first VRU; and

dissipating at least a first portion of the waste heat by moving the heat transfer fluid through the second VRU.

16. The method of claim 15, further comprising storing heat transfer fluid until the heat transfer fluid is moved through the first VRU heat exchanger or the second VRU heat exchanger.

17. The method of claim 15, further comprising dissipating at least a second portion of the waste heat in a radiator or evaporative cooler.

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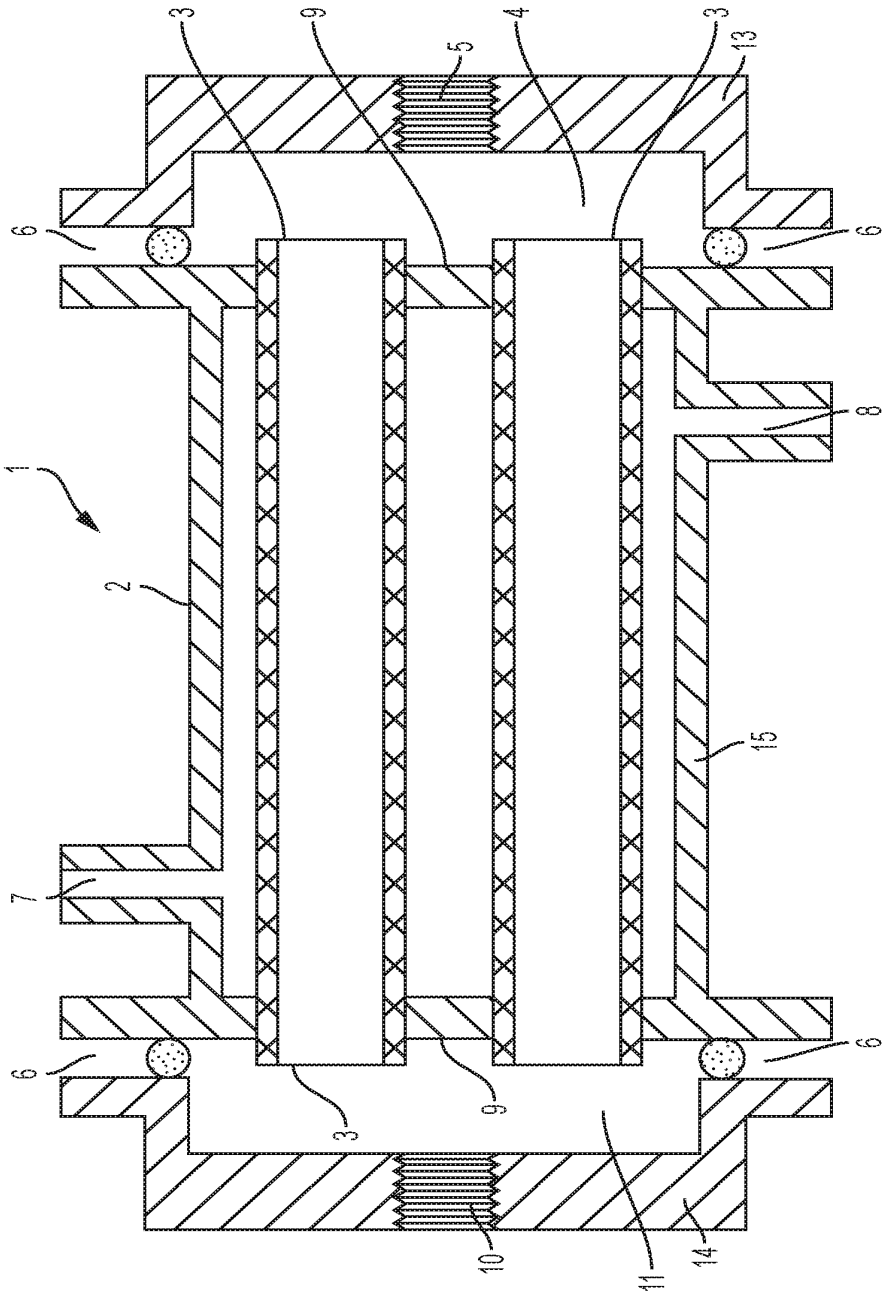


FIG. 1

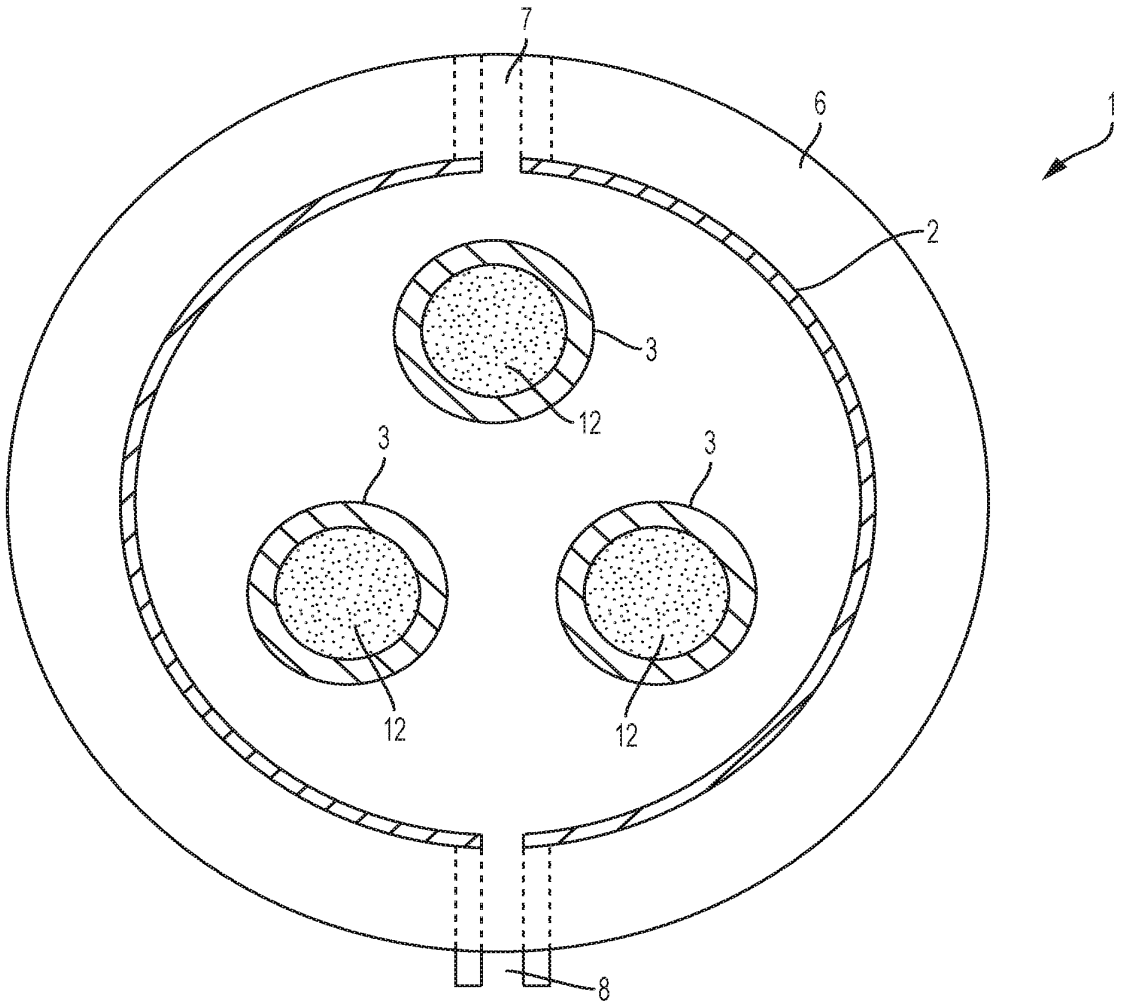


FIG. 2

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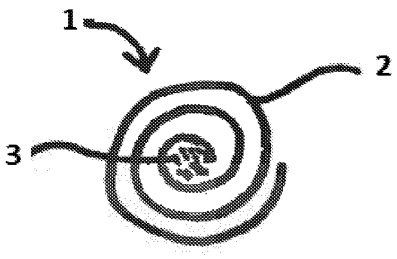


FIG. 1

(57) Abstract: Sorbent material sheets are wound around a center core of material that includes additional sorbent. This configuration further increases the packaging efficiency and performance of the sorbent material sheets as part of an overall housing or apparatus. In some embodiments, the sorbent material sheets are arranged in a stacked configuration. Configurations of the sorbent material sheets as part of a canister are also described.

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SORBENT DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/713,868 filed August 2, 2018 and U.S. Provisional Application No. 62/735,389 filed September 24, 2018. The disclosures of each of these applications are incorporated herein by reference.

BACKGROUND:

[0002] Evaporative emissions from gasoline and other liquid hydrocarbon fuels are a significant source of air pollution because the various hydrocarbons contained in the fuels can form photochemical smog on exposure to sunlight. The compounds of this smog and the hydrocarbons themselves cause degrading health effects in humans and animals as well as environmental damage. Evaporative emissions are especially problematic during vehicle refueling because the "empty" fuel tank is actually filled with fuel vapors, and the act of filling the tank with liquid fuel displaces the vapors from the tank. Evaporative emissions also occur when the fuel within the tank is heated, such as from hot ambient conditions or from nearby hot exhaust system components. Without controls, fuel vapors would be released as pollution into the atmosphere.

[0003] In the automotive sector, gasoline vapors are typically recovered during refueling by an Onboard Refueling Vapor Recovery (ORVR) canister system. These devices include multiple components which are designed to capture the displaced vapors from gasoline refueling and allow the engine to burn them at a later time. Vapors remain sealed within the fuel tank by specially designed tanks and fuel filler neck, and excess vapor is captured and adsorbed within a chemical canister. During engine operation, the Engine Control Unit (ECU) permits adsorbed vapors to be released from the canister and into the engine fuel system, burning the gasoline vapors as normal and permitting the canister to be used again.

[0004] While ORVR systems have been successful in reducing vapor emissions, they still have drawbacks. The canisters are filled with loose adsorbent particles such as activated carbon or charcoal, which can be messy to handle and package. These canisters are bulky and heavy because the adsorbent particles cannot physically support themselves, and because stringent emissions regulations now prohibit the release of even small amounts of vapor emissions, which requires higher adsorbent capacity. Manufacturing, maintenance and disposal of the canisters is also cumbersome because of the loose adsorbent particulates, and

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the complexity of ORVR devices increases the cost of each vehicle while cutting into valuable passenger and cargo space. With automakers demanding lighter weights from all components to meet increasing fuel efficiency targets, as well as cost reductions and greater passenger and cargo space, there is a need for new ORVR devices and that are smaller, lighter, simpler, and more cost effective, while still complying with stricter emissions targets.

SUMMARY

[0005] In one embodiment, the invention discloses sorbent material sheets that have improved performance over the equivalent amount of adsorbent compound provided as a powder, pellet, or granule.

[0006] In another embodiment, the invention discloses sorbent material sheets enclosed within a housing.

[0007] In another embodiment, the invention discloses sorbent material sheets that omit the housing and which are instead contained directly within a fuel tank.

[0008] In another embodiment, the invention discloses an emissions control system, such as an ORVR which includes sorbent material sheets. The sorbent material sheets within the ORVR may be enclosed within a housing or the housing may be omitted.

[0009] The invention is also directed to the embodiments listed below.

[0010]

[0011] Embodiment 1: A vapor adsorbing canister comprising a sorbent material sheet product, wherein the form of the sorbent material sheet product is selected from the group consisting of a rolled sheet that includes a sorbent and a binder, a shredded sheet that includes shredded strips of a sorbent and a binder, a cut sheet that includes cut shapes of a sorbent and a binder, strands of material formed from the fibrillation of sorbent with a binder polymer, a stacked sheet, and combinations thereof.

[0012] Embodiment 2: The vapor adsorbing canister of embodiment 1, wherein the sorbent material sheet product comprises a sorbent selected from the group consisting of activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, diatomaceous earths, and combinations thereof.

[0013] Embodiment 3: The vapor adsorbing canister of embodiments 1-2, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers

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(FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, or copolymers or combinations thereof.

[0014] Embodiment 4: The vapor adsorbing canister of embodiments 1-3, wherein the polymer binder is hydrophobic.

[0015] Embodiment 5: The vapor adsorbing canister of embodiments 1-4, wherein the form of the sorbent material sheet product is flexible and is contained within a flexible canister.

[0016] Embodiment 6: The vapor adsorbing canister of embodiments 1-5, wherein the flexible canister is in the shape of a bag, an irregular shape, a rectangular prism, a cylinder, a ellipsoid, a frustro-conical shape, or combinations thereof.

[0017] Embodiment 7: An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of embodiments 1-6.

[0018] Embodiment 8: A rolled sorbent material sheet product, comprising: a sorbent material sheet defining an upper surface and a lower surface and having a total surface area, and which comprises a sorbent material and a binder, wherein the sorbent material sheet product is spiral wound to form adjacent sheet layers which allow fluid flow around and between adjacent sheet layers; wherein the spiral wound sorbent material sheet product defines a hollow central core which houses additional sorbent material.

[0019] Embodiment 9: The rolled sorbent material sheet product of embodiment 8, wherein the rolled sorbent material sheet product has a BWC that is at least 10% higher than the BWC of a pelletized, granular, or powdered form of substantially the same amount of sorbent material in the sorbent sheet.

[0020] Embodiment 10: The rolled sorbent material sheet product of embodiments 8-9, wherein the rolled sorbent material sheet product has a generally cylindrical shape having a length that is greater than its diameter.

[0021] Embodiment 11: The rolled sorbent material sheet product of embodiments 8-10, wherein the rolled sorbent material sheet product is wound to an average roll density of 500-700 kg/m3.

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[0022] Embodiment 12: The rolled sorbent material sheet product of embodiments 8-11, wherein the rolled sorbent material sheet product has a BWC greater than about 10 g/100 cm^3.

[0023] Embodiment 13: The rolled sorbent material sheet product of embodiments 8-12, wherein the rolled sorbent material sheet product has a BWC of about 7.0 g/100 cm^3 to about 30 g/100 cm^3.

[0024] Embodiment 14: The rolled sorbent material sheet product of embodiments 8-13, wherein the rolled sorbent material sheet comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters.

[0025] Embodiment 15: The rolled sorbent material sheet product of embodiments 8-14, wherein the rolled sorbent material sheets comprise sorbent material particles having at least two populations having different average particle diameters, and wherein the average particle diameters of the two populations have ratios of about 1:1 to about 1:10.

[0026] Embodiment 16: The rolled sorbent material sheet product of embodiments 8-15, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, or copolymers or combinations thereof.

[0027] Embodiment 17: The rolled sorbent material sheet product according to embodiments 8-16, further comprising: a spacer material creating uniform spacing between adjacent surfaces.

[0028] Embodiment 18: The rolled sorbent material sheet product according to embodiments 8-17, wherein the spacer material is selected from wovens, non-wovens, fabrics, granularized sorbent material, or combinations thereof.

[0029] Embodiment 19: A vapor adsorbing canister, comprising, the sorbent material sheet product of embodiment 1, and a housing at least partially encapsulating the rolled sorbent material sheet product of embodiment 1.

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[0030] Embodiment 20: The vapor absorbing canister of embodiment 19, wherein the housing is flexible.

[0031] Embodiment 21: The vapor adsorbing canister of embodiments 19-20, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

[0032] Embodiment 22: The vapor absorbing canister of embodiments 19-21, wherein the shape of the housing substantially conforms to the shape of the enclosed sorbent material sheet product of embodiment 1.

[0033] Embodiment 23: The vapor adsorbing canister of embodiments 19-22, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

[0034] Embodiment 24 – A vapor adsorbing canister, comprising,

a. the rolled sorbent material sheet product of any of embodiments 8-18, and

b. a housing at least partially encapsulating the rolled sorbent material sheet product of any of embodiments 8-18.

[0035] Embodiment 25 – The vapor absorbing canister of embodiment 24, wherein the housing is flexible.

[0036] Embodiment 26 – The vapor adsorbing canister of embodiments 24-25, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high

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density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

[0037] Embodiment 27 – The vapor absorbing canister of embodiments 24-26, wherein the shape of the housing substantially conforms to the shape of the enclosed rolled sorbent material sheet product of embodiment 16.

[0038] Embodiment 28 – The vapor adsorbing canister of embodiments 24-27, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

[0039] Embodiment 29 – A tank with integral vapor adsorption, comprising: a tank structure, and at least one sorbent material sheet which has a defined upper surface and lower surface which have a combined total surface area, and wherein each sorbent material sheet comprises a sorbent material and a binder, and at least one fastening device which fastens the sorbent material sheet to a surface of the tank that is not regularly immersed in the volatile liquids contained within the tank.

[0040] Embodiment 30 – The tank with integral vapor adsorption of embodiment 29, wherein the fastening device is an adhesive layer which is formed between one surface of the sorbent material sheet and a wall of the tank.

[0041] Embodiment 31 – The tank with integral vapor adsorption of embodiments 29-30, wherein the adhesive comprises at least one of pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, reactive multi-part adhesives, acrylic and (meth)acrylic adhesives, acrylate and (meth)acrylate adhesives, epoxy adhesives in one- or two-part formulations, urethane adhesives, and copolymers and combinations thereof.

[0042] Embodiment 32 – The tank with integral vapor adsorption of embodiments 29-31, wherein the tank further includes at least one fuel pump(s), fuel sending line(s), fuel return line(s), atmospheric vent line, port(s), valve(s), sensor(s), air inlet(s), open cell foam, baffle(s), bladder(s) and combinations of those.

[0043] Embodiment 33 – The tank with integral vapor adsorption of embodiments 29-32, wherein the tank is a fuel tank with a “ship in a bottle” configuration.

[0044] Embodiment 34 – An onboard refueling vapor recovery apparatus comprising the sorbent material sheet product of any of embodiments 1-7.

[0045] Embodiment 35 – An onboard refueling vapor recovery apparatus comprising the rolled sorbent material sheet product of any of embodiments 8-18.

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[0046] Embodiment 36 – An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of any of embodiments 19-23.

[0047] Embodiment 37 – An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of embodiment 24-28.

[0048] Embodiment 38 – An onboard refueling vapor recovery apparatus comprising the tank with integral vapor adsorption of any of embodiments 29-33.

DESCRIPTION OF DRAWINGS

[0049] FIG. 1 depicts one embodiment of the invention utilizing a sorbent core.

[0050] FIG. 2 depicts a further embodiment of the invention utilizing a sorbent core.

[0051] FIG. 3 depicts a further embodiment of the invention utilizing spacers.

[0052] FIG. 4 depicts a further embodiment of the invention utilizing spacers.

DETAILED DESCRIPTION

[0053] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0054] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a combustion chamber" is a reference to "one or more combustion chambers" and equivalents thereof known to those skilled in the art, and so forth.

[0055] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

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[0056] As used herein, the term "sorbent material" is meant to encompass all known materials from any source that are capable of adsorbing liquids and/or gases. For example, sorbent materials include, but are not limited to, activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths.

[0057] As used herein, descriptions and claims of multiple sorbent material sheets mean that there are multiple, separated sheets, with sides and/or surfaces in proximity to each other. Alternatively, descriptions and claims of multiple sorbent material sheets mean that there is only a single sheet, but that it has been wound or folded over on itself to yield a stacked, wound, or otherwise constructed mass of sheets with sides and/or surfaces in proximity to each other. The term also envisions that multiple sheets are stacked together and then wound or otherwise folded over, forming alternating layers in a single mass.

[0058] As used in the context of the sorbent or sorbent material or sorbent material sheets, the term surface means the outer boundary of that individual component. Even more specifically, in the context of the sorbent material sheets, the term surface means the largest planar faces of the sheets, which when rolled or stacked face each other or themselves. In a sheet, the surface is the portion that is significantly larger than the thickness of the sheet.

[0059] Embodiments of the invention are directed to devices containing one or more sheets of sorbent material, sorbent material sheets, and methods for making sorbent material sheets and devices containing these sheets. In various embodiments, the sorbent material sheets may be composed of a sorbent material and a binder and have a thickness of less than about 2 mm, or less than about 1 mm. The devices of various embodiments may include a housing and one or more sorbent material sheets. In some embodiments, the devices may have a void fraction of about 10% or more of the total volume of the housing.

[0060] Finally, some embodiments are directed to sorbent devices described in U.S. Patent Application Serial No. 15/885,317 filed on January 31, 2018, the entirety of which is hereby incorporated by reference.

[0061] The Sorbent Material Sheets

[0062] The sorbent material sheets of the invention may include any of the sorbent materials described above including, but are not limited to, activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths, and in certain embodiments, the sorbent material sheets may be composed of activated carbon. The sorbents may be used alone or in combination.

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[0063] The activated carbon may be of various grades and types selected based on performance requirements, cost, and other considerations. The activated carbon may be granular from reagglomerating a powder, granular from crushing or sizing nutshells, wood, coal or pellets created by extrusion, or activated carbon in powdered form. The activated carbon may be formed by processes of carbonization and activated. The raw material, such as wood, nutshell, coal, pitch, etc. is oxidized and devolatized, with steam and/or carbon dioxide gasified to form the pore structure in the activated carbon which is useful for adsorption. The initial oxidation and devolatilization process may include a chemical treatment with a dehydrating chemical, such as phosphoric acid, sulfuric acid, sodium hydroxide, potassium hydroxide, and combinations of those.

[0064] A variety of activation processes are known in the art. The most useful processes for providing activated carbon for the sorbent material sheets of the claimed invention involve a step of providing wood and/or wood byproduct, acid treating the wood and/or wood byproducts by exposure to phosphoric acid, and carbonizing the wood and/or wood byproducts using steam and/or carbon dioxide gasification. This process results in activated carbon particles having the highest butane working capacity ("BWC"), which is a measure of activated carbon performance. More details of the BWC testing and results are described in the Examples.

[0065] The activated carbon may be formed from materials including bagasse, bamboo, coconut husks, peat, wood such as hardwood and softwood sources in the form of sawdust and scrap, lignite, synthetic polymers, coal and coal tar, petroleum pitch, asphalt and bitumen, corn stalks and husks, wheat straw, spent grains, rice hulls and husks, nutshells, and combinations thereof.

[0066] The sorbent material sheets may further include one or more binders. Embodiments are not limited to particular binders, which can include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and

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combinations thereof. The binders can be thermoplastic or thermosetting as conditions require, and can include mixtures of thermoplastic and thermosetting compounds.

[0067] The amount of binder may be about 1% to about 30% by weight of the total composition, and in certain embodiments, the amount of binder may be about 1% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassing these example amounts. The binder may be present in the amount of about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20% or any range made of any two or more of the above amounts, all of which are measured by weight of the total composition. In some embodiments, the sorbent material sheets may include a solvent, which may generally be present in small, residual, amounts of, for example, less than 10%, less than 5%, or less than 2% and greater than about 0.1 % or 0.2 % by weight. In particular, in some embodiments the sorbent material sheets may have no (0%) solvent.

[0068] In some embodiments, the sorbent material sheets have a thickness of less than about 2 mm, less than about 1.8 mm, less than about 1.6 mm, less than about 1.4 mm, less than about 1.2 mm, less than about 1.0 mm, about 0.01 mm to about 2 mm, about 0.01 mm to about 1.8 mm, about 0.1 mm to about 1.6 mm, about 0.01 mm to about 1.4 mm, about 0.01 mm to about 1.2 mm, about 0.01 mm to about 1.0 mm, about 0.02 mm to about 0.90 mm, about 0.05 to about 0.95 mm, about 0.05 to about 0.90 mm or any individual thickness or range encompassed by these example ranges. The sorbent material sheets of various embodiments may have a density of about 0.05 g/cm^3 to about 2.0 g/cm^3, and in other embodiments, the sorbent material sheets may have a density of 0.08 g/cm^3 to about 1.5 g/cm^3, about 0.1 g/cm^3 to about 1.3 g/cm^3, or any density or range encompassed by these example ranges. The density is calculated first by measuring the thickness of a given square or circular piece of sheet with a micrometer, multiplying by the surface area to obtain the volume, and weighing the piece to obtain the density (weight / volume).

[0069] The BWC for each sorbent material sheet may be greater than about 10 $g/100cm^3$, and in some embodiments, the BWC may be from about 7.0 $g/100cm^3$ to about 30 $g/100cm^3$, about 8.0 g/100 cm^3 to about 25 $g/100cm^3$, about 10 g/100 cm^3 to about 20 g/100 cm^3, about 10 g/100 cm^3 to about 15 g/100 cm^3, about 11 $g/100cm^3$ to about 15 g/100 cm^3, about 12 $g/100cm^3$ to about 15 $g/100cm^3$ or any individual BWC or range encompassed by these example ranges. In other examples, the BWC may be about 9 g/100 cm^3 to about 15 g/100 cm^3, about 12 g/100 cm^3 to about 20 g/100 cm^3, about 13 g/100 cm^3 to about 20

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$g/100cm^3$, about 14 $g/100cm^3$ to about 20 $g/100cm^3$, or about 15 $g/100cm^3$ to about 20 $g/100cm^3$. It is also contemplated that any of the endpoints of the above ranges may be combined to form new and distinct ranges.

[0070] The sorbent material sheets of the present invention have higher performance as measured by the BWC than conventional sorbent materials which are provided in powders or other particulate forms.

[0071] The sorbent material sheets of embodiments can be made by any suitable process. In some embodiments, sorbent material sheets can be made by pulverizing granular or pelletized sorbent material to a powder, mixing the powder with a binder to form a mixture, heating and blending the mixture, and rolling the mixture to form the sorbent material sheet. The step of pulverizing may produce sorbent particles having an average particle diameter of about 0.001 mm to about 0.2 mm, about 0.005 mm to about 0.1 mm, about 0.01 mm to about 0.075 mm, or any individual particle diameter or range encompassed by these example ranges, and in certain embodiments, the pulverized sorbent particles may have an average particle diameter of about 0.001 mm to about 0.01 mm. The step of mixing the powder with a binder may include mixing the sorbent particle powder with about 2% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassed by these example ranges. Heating can be carried out at any temperature sufficient to remove residual solvent such as, for example, about 50°C to about 200°C.

[0072] The sorbent material sheet of the invention may include various distributions of different sized particles to increase the packing efficiency of the powder within the sorbent material sheets. The selection of different sized particles can also improve rheological properties of the powder and surrounding binders, which allows improved mixing and uniform particle distribution before formation of the sorbent material sheets. In some embodiments, the particles of the sorbent material sheet may have a single particle size distribution, and in other embodiments, the particles may have two different particle size distributions. In further embodiments, the particle may have at least three different particle size distributions.

[0073] The mean particle sizes of at least two different particle populations, each having a particular size distribution, may be selected so that they have a ratio of between about 1:1 and about 1:15: In other embodiments, the mean particle sizes of the two different particle populations may have a ratio of about 1:2 to about 1:10. The mean particle sizes may also have a ratio of about 1:2 to about 1:5, or combinations of any of the above listed ratios.

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[0074] The sorbent material sheets have significantly higher sorbent capacity than prior art fuel vapor recovery canisters for a given volume and weight. This capability can be utilized in various ways. In some embodiments, the sorbent material sheets can provide enhanced pollution controls in jurisdictions where such high levels of control are required. In other embodiments, the overall size, cost, and weight of the ORVR can be reduced for a specific level of performance. In further embodiments, an ORVR adsorption device can be designed which has increased performance over conventional adsorption canisters, thereby allowing the designer to omit costly and complex returnless fuel pump systems which would otherwise be required to reduce evaporative emissions. Higher performance adsorption devices may also render active condensing vapor systems unnecessary, which avoids the size, weight, and cost of compressor pumps and condensate storage tanks. It should be understood, however, that the ORVR adsorption device using the sorbent material sheets of the invention can also be combined with these devices for exceptionally high performance and a minimal size, weight, and cost penalty over conventional systems.

[0075] The sorbent material sheets may be configured together in a variety of ways depending on the physical space that they must conform to, the required device performance, and the features which are included in proximity to the sheets. In some embodiments, the sheets may be corrugated, include folds, and/or include holes or apertures to increase the surface area of the sorbent material sheets that is exposed to the passing fluid, therefore increasing performance for a given total sheet surface area. The various corrugations, folds, holes, and apertures can also be sized and placed to make way for internal and external features, such as fluid channels, tubing, sensors, and valves. The folds of the sorbent material sheets may take a variety of forms, such as a spiral wrapped configuration in either a cylindrical or elliptical form. The folds may also be in the form of an "S" shape, or a convex or concave "C" shape depending on the required device dimensions and/or any other required internal or external features. The sorbent material sheets may also be stacked in a flat or curved configuration, and the stacked sheets may be square, rectangular, circular, oval, or other irregular shape as needed to fit the space intended. This, in combination with the housing features discussed below, enables devices formed from the sorbent material sheets to fit in smaller, more irregularly shaped spaces than prior art canister devices, which maximizes vehicle interior space.

[0076] In addition to the above described configurations, the sorbent material sheets may also have surface features. In some embodiments, the sorbent material sheets may include raised portions, and in other embodiments, the sorbent material sheets may include

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depressed portions. These surface features may be combined within the same sheet. The inclusion of raised and/or depressed portions in the sheets may be utilized to form various configurations between the sheets as they are stacked, wrapped, and so forth. For instance, the sheets can be aligned so that the raised and/or depressed portions nest with each other, which brings the adjacent sheets closer together. The sheets can also be aligned so that the raised and/or depressed portions do not nest with each other, which forms a gap between the adjacent sheets. The alignment can be used to form various open and closed channels for vapor adsorption between the sheets.

[0077] Sorbent sheets wound in spirals or stacked, as discussed herein, can be difficult to tune for pressure drop. Controlling the tension on a wound spiral or the pressure on a stack of sheets needs to be carefully and reproducibly done via winding or stacking techniques. However in some situations, the pressure drop requirements are not easily met by these methods.

[0078] In addition to pressure drop, other design considerations include putting sorbents with different properties in a succession of volumes or chambers in order to impart the ideal conditions for fuel tank evaporative loss applications.

[0079] Carbon sheet performance can be improved by the addition of materials prior to or during sheet processing. These materials provide beneficial properties such as enhanced porosity to reduce pressure drop; adsorption of inorganic vapors such as H_2S or other undesirable gases. Alternatively, different sorbent materials can be processed simultaneously into a single sheet with distinct sections or a performance gradient from one side of the sheet to the other. For example, in an evaporative loss canister, a sheet could have high BWC or butane adsorption capacity on one side and low BWC or adsorption capacity on the other, allowing vapor emissions from fuel tanks to pass through different performing materials as the vapors move through one part of the sheet, or stack of sheets, or spiral-wound sheet, to the other.

[0080] In order to control the pressure drop of carbon sheets, whether stacked or wound in spirals, one may control the space between the sheets or the density of the sheets, which is discussed further below. The present invention allows, instead or in addition to such techniques, for additives to the mixture prior to or during processing into sheets, which, upon further processing (e.g. thermal or chemical), creates porosity in the sheets. This provides another method to control sheet porosity and pressure drop.

[0081] Furthermore, such a methodology allows for the creation of alternative forms for the sheets than stacks and spirals, such as monoliths, that would normally be excluded due

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to high pressure drop. (Such a monolith could be used as a sorbent core for a wound sheet, discussed below.) These forms could be created by assembling (e.g. gluing or otherwise connecting) sheets together to form monoliths of various shapes, including cylinders, rectangular prisms, cones, and other shapes of benefit to the application.

[0082] Examples of additives that could provide porosity include, but are not limited to, foam-like polymer additives; water-soluble polymers, which could be rinsed to leave behind pores; friable materials with particle size greater than the intended sheet thickness, which would break up and leave behind pores, materials that are thermally labile so that the sheet can be heated and the added materials vaporize, producing pores in the sheets, and other similar processes that could impart a controlled porosity within the sorbent sheets. Any of these may be used alone or in combination.

[0083] An alternative enhancement to sorbent sheet production is to process sorbent sheets such that two or more sorbents with different properties are included in a single sheet but are segregated along the width of the sheet. For example, a high BWC sorbent could be used in the same sheet with a low BWC sorbent, such that the vapors from fuel tank emissions would contact the high BWC sorbent ahead of the low BWC sorbent, within a single chamber. That is, in some embodiments, low and high BWC sorbents could be homogeneously mixed, or in some embodiments, there could be distinct sections of low or high BWC sorbents as desired.

[0084] Another example is a high BWC sorbent for adsorption of butane, included with a sorbent that would remove H_2S or other undesirable vapors that are not normally well removed by a high BWC activated carbon, for example.

[0085] Sorbent Material Sheet Product

[0086] The sorbent material sheets described above are combined into a sorbent material sheet product. The combination of the sorbent material sheets takes advantage of one or more of the above described features, such as increased surface area/volume ratio, reduced void space, improved sorbent performance, etc. In general, the individual sorbent material sheets are arranged next to each other to form a sorbent material sheet product that comprises sheets that are stacked, rolled, wound, folded, and/or laminated such that the surfaces of the sorbent material sheets are in close proximity to, or adjacent to each other. Whatever the arrangement, the goal is to maximize the surface area of the sheets exposed to the vapor, fluid, and/or gas stream and thus the performance of the sorbent material sheets.

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[0087] *Stacked Sorbent Material Sheet Product*: The stacked sorbent material sheet product of the invention comprises two or more sorbent sheets each defining an upper surface and a lower surface, and having a known combined total surface area, wherein each sorbent sheet comprises a sorbent material and a binder; where adjacent sorbent sheets are stacked and arranged such that adjacent upper and lower surfaces are substantially congruent with each other, and aligned to allow fluid flow at least between adjacent upper and lower surfaces.

[0088] Performance improvements of the stacked sorbent material sheet product of the invention can be measured as the performance of the product having a given amount of activated carbon versus the performance of that same amount and grade of activated carbon if provided within a canister in a pelletized or powdered form. In some embodiments, the stacked sorbent sheet product has a BWC that is about 3% higher, about 5% higher, about 7% higher, about 9% higher, about 10% higher, about 12% higher, about 14% higher, and about 16% higher than the same volume and grade of activated carbon within a canister in pelletized or powdered form. Ranges based on these amounts are also contemplated, such as performance that is between about 5-14% higher, between about 5-10% higher, between about 10-16% higher, and so forth.

[0089] It should be noted that these improvements are only measured as between the volumes of the pelletized or powdered activated carbon and the stacked sorbent material sheet product, without accounting for other improvements of the stacked sorbent material sheet product. One key difference, described above, is the omission of a rigid canister body that would otherwise be required. The omission of the rigid canister body, which is needed in prior art systems involving pelletized or powdered activated carbon because the loose activated carbon cannot support itself, drives weight savings.

[0090] The stacked sorbent sheet product has a BWC at least 10% higher than the BWC of a pelletized/powdered form of the same amount by volume of the sorbent material in the sorbent sheet. The stacked sorbent sheet product has a BWC greater than about 10 $g/100cm^3$. The stacked sorbent sheet product has a BWC of about 7.0 $g/100cm^3$ to about 30 $g/100cm^3$, or greater than about 12 $g/100cm^3$, or greater than about 13 $g/100cm^3$, or greater than about 14 $g/100\ cm^3$, or greater than about 15 $g/100cm^3$, or greater than 20 $g/100cm^3$. Ranges are also contemplated, such as about 10-20 g/cm^3, about 10-12 g/cm^3, about 10-14 g/cm^3, about 12-14 g/cm^3, about 12-15 g/cm^3, and about 15-20 g/cm^3.

[0091] In some embodiments, the stacked sheets are held in a spaced apart relationship which controls one or more of void volume, flow rate, pressure drop, and other

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characteristics. Such spacing is achieved in some embodiments where at least one of the two or more sorbent material sheets is corrugated. The spacing can also be achieved with various folds in the sheets, and can also be achieved by the corresponding raised and/or depressed portions of the sheets which are aligned to form gaps between the sheet. If the sheets are arranged deliberately so that the raised and/or depressed portions of the sheets do not nest between sheets, this results in additional spacing between the sheets and permits fluid flow in those portions. If the sheets are arranged deliberately so that at least some raised and/or depressed portions nest between sheets, this results in a tighter fitting stack of sheets and decreases the spacing between the sheets, with a corresponding decrease or even stop in fluid flow. Combinations of these features can be used to form stacked sorbent sheet products with directed regions or channels for fluid flow and barriers or edge seals to prevent fluid leakage. These features for fluid flow can also include holes, cuts, or apertures through one or more of the sheets in the stacked sorbent sheet product.

[0092] Each sorbent sheet defines opposed lateral edges which are substantially parallel to fluid flow. The congruent lateral edges of adjacent sorbent sheets may be separate from each other, bound together or some combination thereof. In this manner, the edges of the stacked sorbent material sheet product may be sealed, partially sealed, or unsealed. The sealed or unsealed nature can be chosen to achieve desired results such as modifying fluid flow rate and/or patterns or other properties.

[0093] In some embodiments, the stacked sorbent material product yields a void volume of about 10% or less. In some embodiments, the void volume is about 8% or less, in some embodiments, the void volume is about 6% or less, in some embodiments, the void volume is about 4% or less. In some embodiments, the stacked sorbent material product yields a void volume of about 10% or more, about 12% or more, about 14% or more, about 15% or more, about 16% or more, about 17% or more, about 18% or more, about 19% or more, about 20% or more, about 21% or more, about 22% or more, about 23% or more, about 24% or more, about 25% or more, about 26% or more, about 27% or more, about 28% or more, about 29% or more, or about 30% or more, or any range formed by combining the above ranges. In some embodiments, the stacked sorbent material product yields a void volume of about 10%, about 12%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23%, about 24%, about 25%, about 26%, about 27%, about 28%, about 29%, or about 30%, or any range formed by combining the above ranges. In some embodiments, the stacked sorbent material product

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yields a void volume of about 10-15%, about 15-20%, about 20-25%, about 25-30%, or about 30-35%.

[0094] In some embodiments, each sorbent sheet has a density of about 0.08 g/cm^3 to about 1.5 g/cm^3.

[0095] In some instances, the sorbent material sheet product comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters. See the above description of the bimodal particle size distribution which was discussed with respect to the individual sorbent material sheets. The same distribution ratios as between populations of sorbent particles are contemplated with respect to product formed of multiple sorbent material sheets. In some instances, the density of the sorbent material particles achieved by the at least two populations is greater than the density achieved by either population alone. The inclusion of a bimodal particle size distribution can also be used to improve the mechanical properties of the sorbent material sheet product because it makes the polymeric sheets much more resistant to shear forces.

[0096] In some instances, a sorbent material sheet product comprises at least two sorbent material sheets, each of which has a defined upper surface and lower surface which have a combined total surface area, and wherein each sorbent material sheet comprises a sorbent material and a binder, and wherein each sorbent material sheet is stacked and arranged such that adjacent upper and lower surfaces of the separate sheets are substantially parallel and are aligned to allow fluid flow at least between the adjacent upper and lower surfaces.

[0097] The term substantially parallel as used in the context of a stacked sorbent material sheet product means that the sheets maintain the same distance apart over their entire area, but with exceptions made for various physical characteristics and features. These exceptions that still fall within the scope of substantially parallel include but are not limited to differences due to variations in components such as spacers, sensors, apertures, tubing, ports, valves, channels, corrugations, pleats, folds, deformation encountered during manufacturing or operation, deformation due to the shape or pressures applied by or through the external housing, different wrapping techniques such as to seal the peripheries of the sheets, and so forth.

[0098] In some embodiments, the sorbent material sheet product has a BWC value about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, and about 50% higher than the BWC of the same volume of sorbent material in pelletized or powdered forms. These can also be combined to form ranges, for

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example, between about 5-25% higher. The invention also contemplates that these amounts are the endpoints on ranges, such as at least about 40% higher.

[0099] The sorbent material sheets in the sorbent material sheet product, may be configured as being flat, wound in a spiral cylinder, wound in an elliptical form, wound in an elongate rectangular bar, folded, laminated in an "S" shape, formed as concentric cylinders, formed as concentric ellipses, formed as a concentric rectangular bar, or as combinations of these forms.

[00100] In some embodiments, the sorbent material sheet product will comprise a single sorbent material sheet that is wound or rolled to achieve the desired characteristics including, but not limited to density, void space, pressure drop, capacity, etc.

[00101] *Wound/Rolled Sorbent Material Sheet Product:* The sorbent material sheet product can also be wound or rolled as an alternative or in combination with stacked embodiments. A wound or rolled sorbent material sheet product comprises a sorbent sheet defining an upper surface and a lower surface, and combined has a known total surface area, wherein the sorbent sheet comprises a sorbent material and a binder where the sorbent sheet is spiral wound to create adjacent sheet layers which allow fluid flow around and between adjacent sheet layers.

[00102] Similar to the stacked sheet arrangement, the rolled sorbent sheet product has improved performance over the equivalent volume of activated carbon that is provided in pelletized or powdered form.

[00103] Performance improvements of the rolled sorbent material sheet product of the invention can be measured as the performance of the product having a given amount of activated carbon versus the performance of that same amount and grade of activated carbon if provided within a canister in a pelletized or powdered form. In some embodiments, the rolled sorbent sheet product has a BWC that is about 3% higher, about 5% higher, about 7% higher, about 9% higher, about 10% higher, about 12% higher, about 14% higher, and about 16% higher than the same amount and grade of activated carbon within a canister in pelletized or powdered form. Ranges based on these amounts are also contemplated, such as performance that is between about 5-14% higher, between about 5-10% higher, between about 10-16% higher, and so forth.

[00104] The rolled sorbent sheet product has a BWC at least 10% higher than the BWC of a pelletized/powdered form of the same amount by volume of the sorbent material in the sorbent sheet. The rolled sorbent sheet product has a BWC greater than about 10

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g/100cm^3. The rolled sorbent sheet product has a BWC of about 7.0 g/100cm^3 to about 30 g/100cm^3, or greater than about 12 g/100cm^3, or greater than about 13 g/100cm^3, or greater than about 14 g/100 cm^3, or greater than about 15 g/100cm^3, or greater than 20 g/100cm^3. Ranges are also contemplated, such as about 10-20 g/cm^3, about 10-12 g/cm^3, about 10-14 g/cm^3, about 12-14 g/cm^3, about 12-15 g/cm^3, and about 15-20 g/cm^3.

[00105] A rolled sorbent sheet product as described herein has a generally cylindrical shape having a length substantially greater than its diameter, although any dimension can be employed, including conical, or frustro-conical variations, as well as ellipsoids, or other shapes.

[00106] The density of the rolled sorbent sheet product may be computed based on the formulas below:

Roll Density Calculations (US units)

$$\rho\left(\frac{lb}{ft^3}\right) = (3) \times \frac{BW \times L}{\left(\frac{OD^2}{4} - \frac{ID^2}{4}\right) \times \pi}$$

BW: Basis Weight $\left(\frac{oz}{yd^2}\right)$ *L: Length on Roll (yd)*

OD: Outer Roll Diameter (in) *ID: Inner Roll Diamter/Core Diameter (in)*

W: Machine width or roll length (in) ρ*: Roll Density* $\left(\frac{lb}{ft^3}\right)$

Roll Density Calculations (SI units)

$$\rho\left(\frac{kg}{m^3}\right) = (1000) \times \frac{BW \times L}{\left(\frac{OD^2}{4} - \frac{ID^2}{4}\right) \times \pi}$$

BW: Basis Weight $\left(\frac{g}{m^2}\right)$ *L: Length on Roll (m)*

OD: Outer Roll Diameter (mm) *ID: Inner Roll Diamter/Core Diameter (mm)*

W: Machine width or roll length (mm) ρ*: Roll Density* $\left(\frac{kg}{m^3}\right)$

[00107] The rolled sorbent sheet product may be wound to an average roll density of about 80-1500 kg/m^3, about 500-2000 kg/m^3, about 750-1500 kg/m^3, about 900-1200 kg/m^3, about 900-1050 kg/m^3, about 400-500 kg/m^3, about 500-600 kg/m^3, about 500-550 kg/m^3, about 600-650 kg/m^3, about 650-700 kg/m^3, and about 700-750 kg/m^3.

[00108] The rolled sorbent sheet product has a BWC greater than about 10 g/100cm^3. In some embodiments, the rolled sorbent sheet product has a BWC of about 7.0 g/100cm^3 to about 30 g/100cm^3. The rolled sorbent sheet product may also have BWCs that are the same as the above described sorbent sheet products which are not rolled.

[00109] Similar to the discussion above with respect to the stacked sorbent material sheets, the wound or rolled sorbent material sheets may include multiple particle size distributions or populations of the adsorbent pelletized or powdered activated carbon. The same ratios are contemplated as discussed above. Similar to the discussion above, this results

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in greater performance because it enables a larger amount of the activated carbon to be incorporated into the sheets which are formed into the rolled sorbent sheet product.

[00110] As used herein, wound or rolled sorbent sheet products refer to any form of layering of one or more sorbent material sheets by winding, spiral winding, concentric layering of tubular (of any cross-sectional shape, e.g. round, elliptical, square, triangular, rectangle, etc.) or combination thereof. For example, a single sorbent material sheet may be spiral wound along its length to form a cylindrical-shaped rolled sorbent material sheet product. As another example, a plurality of sorbent material sheets can be stacked and then wound together to form a similar cylindrical shape. As another alternative, several sheets each formed into a cylinder having a slightly different diameter from the next can be arranged such that they from concentric rings in cross-section of a similarly sized cylinder. Various combinations of these and other arrangements may be used to fill the space within any shape of housing or canister, as described elsewhere herein.

[00111] As used in the context of a wound or rolled sorbent material sheet or sheets, the term substantially parallel is used to mean that at a minute, infinitely small dimension, the two sheets or portions of the same sheets are the same distance from each other in all directions. However, it is also understood that in the context of the wound or rolled sorbent material sheets, especially those that are a single sheet wound in a spiral around a center or core, that this means that the sheets are not exactly the same distance apart from each other over the entire areas that face each other. Furthermore, it is understood that in this context, similar variations in distance are contemplated between the sheet or sheets due to components such as spacers, sensors, apertures, tubing, ports, valves, channels, corrugations, pleats, folds, deformation encountered during manufacturing or operation, deformation due to the shape or pressures applied by or through the external housing, different wrapping techniques such as to seal the periphery of the sheets, and so forth.

[00112] As noted above with respect to the sorbent material sheets, the binder is selected from polytetrafluoroethylene (PTFE or TEFLON), polyvinylidene fluorides (PVF2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene

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terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

[00113] Additional embodiments are also contemplated. In one embodiment, the form of the sorbent material sheet product is a rolled sheet that includes a sorbent material sheet. In another embodiment, the form of the sorbent material sheet product is a shredded sheet that includes shredded strips of the sorbent material sheet. In another embodiment, the form of the sorbent material sheet product is cut sheets of the sorbent material sheet in various shapes. When the sheets are shredded or cut, the x and y dimensions of the sheet are larger than the thickness of the sheet.

[00114] In still other embodiments, the form of the sorbent is not as a sheet product, but is instead strands of binder and sorbent. The strands may be individual, woven, non-woven, or in other forms including rope or yarn. These forms can be achieved by fibrillating the binder with the sorbent to as to form thin strands which are then combined into other forms.

[00115] In all of the above embodiments, the sorbent is made flexible and has high surface area available for vapors and gases that are passed over it. This means that the sorbent can be made to fit in confined spaces, such as small canisters, small canister chambers, flexible tubing, curved tubing, irregular shapes, snaked or otherwise irregular tubing, and other shapes that would be difficult to fit conventional forms of sorbent. These advantages permit the sorbent material sheets to be used in a variety of configurations that are not possible with conventional powdered, granulated, or pelleted sorbent.

[00116] The rolled sheets are typically made by winding the sheets around a solid, central, cylindrical spindle. This is some solid polymer or other material. The spindle is solid and takes up volume. In other instances, the sheet is wound about an open central core, such as a rigid or semi-rigid tube. In either case, the center does not contribute to the performance of the sorbent device. This application is directed toward putting that central core to good use. The activated carbon sheet is wound around an adsorptive core material producing a spiral wound device with additional adsorptive capacity.

[00117] The center core is fabricated from sorbent material or as a structure that would serve as a core with internal volume filled with sorbent material. The advantage of this would be to increase the amount of adsorbent within the device, thereby increasing performance. The central core could take the form of an open space, a hollow tube, a perforated hollow tube, or other structure used to define a space which holds additional sorbent material. The increase in sorbent material should result in even better performance.

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[00118] The center core may include not only the sheets described above, but also the other forms of the sorbent material, such as the cut or shredded sheets, rope, yarn, and the like.

[00119] Another improvement relates to improving flow between the spiral wound sheet or sheets. Winding of carbon sheets into spirals to form an adsorber was accomplished by controlling the tension of the winding process. Because the sheets are flexible and of low tensile strength, this sometimes leads to adsorbers where the spacing between the wound sheets was inconsistent, difficult to control or non-existent. The use of spacers, for example in the form of woven or non-woven, netting or other fabric or incorporating particles into the sheet whose diameter is larger than the sheet thickness leads to higher tensile strength material with pre-defined spacing between wound layers. The sheet could also be perforated to overcome issues with inconsistent winding spacing by providing a pathway between wound layers preventing blinding off of carbon and by-pass.

[00120] A biplanar spacer can be incorporated into the spiral wound adsorber during the winding process. A separate biplanar spacer, made from either a polymer, fabric, metal, carbon fiber or activated carbon fiber or combinations thereof would be wound with the carbon sheet to form the final assembly. The spacer could be of different thicknesses to control the size and pressure drop across the adsorber. The orientation of the spacer could be used to control the flow of the fluid in a path that is not necessarily the shortest distance increasing the fluid carbon contact time. This would also increase the tensile strength of the unit.

[00121] In some embodiments, the spacer can be a non-woven porous material. Non-woven porous materials could be incorporated into the wound structure that would allow uniform spacing with a controlled pressure drop. Tensile strength would also be improved.

[00122] To increase the tensile strength of the carbon sheet, a polymer or fibrous netting could be incorporated into the carbon sheet during the roll milling process. The netting could be of various configurations and thicknesses depending on the desired properties of the final sheet. The goal is to increase the tensile strength of the material allowing for more reliable winding to maintain separation and ease of manufacture.

[00123] Some embodiments achieve similar results by incorporating perforated sheets. The wound sorbent sheets could be perforated before winding so that imperfections in the winding process would be mitigated and provide for alternate pathways for fluid flow through the adsorber.

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[00124] Rather than woven or non-woven materials, granular or pelleted activated carbon could be used as a spacer. Activated carbon or some other rigid granular material, preferably a sorbent material, can be added to the carbon sheet either before or after milling to serve as the spacer and to add adsorptive capabilities.

[00125] Any of these spacers could be used with stacked sheets as well as wound sheets with the same advantages. In either structure, the space creates uniform spacing. Texture such as corrugation or other surface features could also be employed to achieve the desired characteristics and flow.

[00126] In some embodiments, the various components such as sorbent material sheets, spacers, woven and/or non-woven materials, perforated or non-perforated sheets, additional sorbent material, and other components may be rolled in alternating fashion, which is sometimes referred to as a "jelly roll" structure as the alternating components remain parallel with each other and spiral around a core in repeating bands. This embodiment is most useful for embedding spacers or other pleated, textured, or corrugated components between sorbent sheets to precisely control the spacing in between the sheets and therefore pressure drop and performance. In still further embodiments, the components may be co-nested within each other as tubes and not wound in a spiral.

[00127] Various embodiments are shown in the Figures. FIG. 1 shows the improvement of including sorbent within a central core of wound sorbent material sheets. In FIG. 1, the wound sorbent material sheet 1 is depicted as including sorbent material sheet 2 which is wrapped around a central core of sorbent 3. In another embodiment, FIG. 2 depicts a wound sorbent material sheet 1 that includes sorbent material sheet 2, again wrapped around central core of sorbent 3. However, the embodiment of FIG. 2 further includes a tube 4 or other similar structure that surrounds the sorbent 3. The tube 4 may include perforations, tears, apertures, or other similar features (not shown) to permit at least some gas or vapor to pass between the sorbent contained in the central core and the sorbent sheet material in the outer portion.

In still further embodiments, FIG. 3 depicts a wound sorbent material sheet 1 that includes sorbent material sheet 2, and further includes a spacer 5 that is included to precisely control the spacing and therefore pressure drop and other performance characteristics of the wound sheets. FIG. 4 depicts an additional embodiment, where stacked sorbent material sheet 6 includes several stacked sorbent material sheets 2. In between each pair of sorbent material sheets 2 is a spacer 5 that is used to precisely control the spacing and therefore pressure drop and other performance characteristics of the stacked sheets.

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[00128] The Housing

[00129] The invention also contemplates the use of a housing which partially or totally encapsulates the sorbent material sheets. It should be noted that while the term "housing" is used in this specification to describe the overall outer structure that at least partially encapsulates the sorbent material sheets, it is understood that such structures are known by many other terms to those of skill in the art. For example, in automotive or other fields where emissions must be controlled, the housing may be referred to as a canister, cartridge, scrubber, or the like. It is therefore contemplated that the term "housing" broadly encompasses a variety of terms and structures including canisters, cartridges, scrubbers, flexible bags, molded polymer casings, metal casings, and so forth that are used in the field of emissions control. Furthermore the term housing may refer to an empty structure awaiting the inclusion of sorbent, i.e., an unfinished part, or a completed emissions control part that includes the sorbent contained within the canister, cartridge, scrubber, flexible bag, etc. It is contemplated that these parts may be interchanged or combined depending on design requirements.

[00130] The housing may be configured in a variety of shapes, for example tetrahedrons, cubes and cuboidal shapes, cylinders, spheres, hyperboloids of a single sheet, conical shapes, ellipsoidal shapes, rectangular shapes, hyperbolic paraboloid shapes, elongated bar shapes, paraboloids, and combinations of these shapes. The combinations may be selected to have different sections each of which have different shapes or portions of different shapes. The housing may also include sections which are separated and are connected by an additional part, for instance, at least one hose or tube which is designed to transfer fuel vapors as needed, or a thin portion of housing that contains the sorbent material sheets. The housing may also be configured with no shape, for example as a flexible bag or pouch containing the sorbent material sheets.

[00131] One major advantage of the invention is that the sorbent material sheets are both flexible and self-supporting and can be laminated, rolled, wound, folded, or stacked in a variety of configurations within the housing to suit different mechanical requirements within the tight confines of a vehicle. In such embodiments, the housing would be designed to conform or fit the spaces that are available for the device to be stored. For instance, the housing can be sized and shaped to fit in spaces within or surrounding wheel wells, driveshafts, batteries for hybrid powertrains, spare tires, tire changing tools, tire patching tools, vehicle trunks or other storage spaces, vehicle bumpers and bodywork panels, exhaust

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systems, other emissions control equipment such as urea or other injection tanks, fuel lines, vehicle frames, suspension components, engine compartment, under passenger compartment seats, within passenger compartment seats, and other spaces which are too small or too difficult to reach to be effectively utilized for passenger or cargo space.

[00132] To further reduce weight and size and take advantage of the self-supporting sorbent material sheets, the housing can be in the form of a thin walled bag or pouch. This is possible because the sorbent material sheets have some mechanical structure and are self-supporting and so do not require a rigid outer container as in conventional canisters. The film materials that form the bag can have thicknesses of about 10 μm to about 250 μm. In other embodiments, the bag film can have thicknesses of about 20 μm to about 175 μm, and the bag film can have thicknesses of about 50 μm to about 125 μm.

[00133] The bag or pouch may be formed of any materials which are used in fuel systems, and particularly are formed of materials which are designed to withstand the chemical effects of the fuel vapors contained. Bag materials include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof. The bag is typically thermoplastic for flexibility, but can also be a combination with amounts of thermoset or can be in the form of a cured rubber or an elastomer.

[00134] The housing, bag, or pouch may also be designed to act as a vapor barrier to the adsorbed fuel vapors contained therein. This barrier property may be inherent to the polymer itself, or may be achieved through the use of at least one barrier additive and/or at least one barrier layer. Examples of barrier additives which can be formed as a layer or as a particulate filler include polymers such as epoxy, polyamide, polyamide imides, fluoropolymers, fluororubbers, and combinations of those. Barrier layers can also be made of metals such as aluminum, steel, titanium, and alloys of those. The metal barrier layers can be formed by conventional mechanical means, such as coextrusion or adhering with the other

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layers of the housing, or they can be chemically deposited, such as by chemical vapor deposition or electroplating. The metal barrier layer can be formed from a foil having a thickness of less than about 25 μm, less than about 20 μm, less than about 15 μm, less than about 10μm, or less than about 5 μm.

[00135] The housing and its materials may also be selected to be compatible with "ship in a bottle" fuel systems. In such systems, many or all of the fuel system components, including the fuel pumps, ORVR, fuel filters, valves, and other components are fitted within the vehicle fuel tank. Such systems are advantageous because they reduce assembly time and the amount of space required by the fuel system. In such systems, the housing should have materials which are capable of being immersed in the selected fuel, typically gasoline, for extended periods of time within the vehicle fuel tank, while also being able to withstand the effects of the adsorbed fuel vapors within.

[00136] The housing may also be a thin metal housing. The thin metal housing can be formed of flexible or rigid metals such as steel, aluminum, titanium, and alloys of those. The metal housing can be formed from a foil having a thickness of about 5-100 μm, or about 10-250 μm. In some embodiments, the foil may be as thick as about 1 mm. Whether the housing is flexible or rigid depends on the selection of the material, the thickness, and any treatments that have been applied to the metals, such as heat treatments or hot or cold working.

[00137] In some embodiments, the housing for the sorbent material sheets may be omitted entirely, with the sorbent material sheets being contained within the fuel tank itself. In such configurations, the sorbent materials sheets can be attached to a portion of the interior of the fuel tank that does not regularly come in contact with liquid fuel and which is free to adsorb fuel vapors. This portion is typically the top or sides of the fuel tank, or combinations of those. The fuel tank may also include a recessed portion on the top or the sides which is designed to include the sorbent material sheets and allow the sorbent material sheets to adsorb fuel vapors. Such embodiments where sorbent material sheets are attached to the interior portions of the fuel tank not only offer maximum space savings and weight savings by omitting the canister structure, but also simplify manufacturing and installation because the sheets are already installed within the fuel tank during vehicle assembly.

[00138] The housing can also be eliminated by forming a rolled or folded sorbent sheet and then selectively curing the outer sheets so that they form a durable, cured shell that acts as a support for the rolled or folded sorbent sheets within. Such selective curing can be

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accomplished thermally or with a chemical bath, or via actinic radiation, such as ultraviolet light or by electron beam curing.

[00139] In embodiments where the sorbent material sheets omit the housing and are contained within the vehicle fuel tank itself, the sorbent material sheets may be attached to the fuel tank in a variety of ways. The sorbent material sheets can be fastened using mechanical fasteners such as screws, rivets, or clamps, or the sorbent material sheets may be fastened using an adhesive backing positioned between the fuel tank wall and the sorbent material sheets. The adhesive backing may be a single layer of adhesive or a double sided adhesive tape or sheet. The adhesive used in the adhesive backing may include pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, and reactive multi-part adhesives. Adhesive compositions include acrylic and (meth)acrylic, acrylate and (meth)acrylate, epoxies in one- and two-part formulations, and urethane.

[00140] The sorbent material sheets may be applied during manufacturing in a variety of ways. In some embodiments, the fuel tank may be formed and the sorbent material sheets are applied in a separate step where the adhesive is applied followed by the application of the sorbent material sheets. In other embodiments, the sorbent material sheets are placed, with or without an adhesive backing as appropriate, on the inside of a mold and the fuel tank is injected or blow molded around the sorbent material sheets. In other embodiments, the sorbent material sheets may be coextruded with panels of material which make up the sides of the fuel tank, and the edges of those panels are adhered or welded together to seal the final tank with the sorbent material sheets on the inside.

[00141] When the sorbent material sheets are contained within the vehicle fuel tank without the housing, the fuel tank may include additional valves and ports to accommodate the adsorption and desorption of fuel vapors in the fuel tank. For example, during engine operation, air may be introduced into the fuel tank to desorb the fuel vapors which are contained in the sorbent material sheets, as well as those which are present in the tank. These desorbed fuel vapors are then sent to the engine for combustion during optimal cycles as required by the ECU.

[00142] When the sorbent material sheets are provided without a housing and are contained within a tank, such as a vehicle fuel tank, they may be positioned so that they are not regularly immersed in the volatile liquids typically contained within the tank. This ensures that the sorbent material sheets do not become prematurely saturated, and also ensures that sufficient surface area is exposed to the vapors within the fuel tank to effect the adsorption of the vapors. The feature contemplates that the sorbent material sheets can be

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placed in parts of the tank that are unfilled, such as the ullage or headspace of the tank, or near baffles which prevent the sloshing of liquids on the sorbent material sheets. The sorbent material sheets may also be placed in a dedicated portion of the tank, such as a small chamber or niche, where the liquids cannot enter.

[00143] The devices of various embodiments may include a housing and the sorbent material sheets described above. The housing may be any shape and can be configured for purifying gases or liquids. For example, in some embodiments, the housing may be any shape such as, for example, cuboidal, cubic, or cylindrical. The sorbent material sheets may be sized to fit within the housing and substantially fill a space within the housing through which the gas or liquid is passed. In some embodiments, two or more sorbent material sheets may be stacked to substantially fill the housing, and in other embodiments, the sorbent material sheets may be rolled to form a spiral wound sheet or pressed to form a stacked sheet. In some embodiments, the stacked or pressed sheets may be such that the sides of adjoining sheets are substantially contiguous. In other embodiments, stacked or pressed sheets may be positioned such that adjoining sheets are spaced. For example, in certain embodiments, the sheets may be corrugated, having sorbent material sheets that form a series or parallel ridges and furrows, and in some embodiments, corrugated sorbent material sheets may be separated by flat sorbent material sheets. The corrugated sorbent material sheets may be disposed within the housing in a stacked or rolled/spiral wound form.

[00144] In various embodiments, the void fraction may be about 30% to about 32% less than the void volume for current devices, and in some embodiments, the void fraction may be as low as about 10%. For example, the devices may have a void fraction of about 45% to about 10%, about 35 % to about 10%, about 25% to about 10%, or any individual void fraction or range encompassed by these example ranges. The devices of various embodiments may exhibit less flow restriction, e.g. pressure drop, than devices having granular or pelleted sorbent materials. Thus, more adsorbent material can be incorporated into such devices without reducing the flow rate of the device.

[00145] The devices of such embodiments may have BWCs of greater than about 5.0 g/100 cm^3, and in some embodiments, the devices may have a BWC of about 4.0 g/100 cm^3 to about 20 g/100 cm^3, 5.0 g/100cm^3 to about 18 g/100cm^3, about 7.0 g/100 cm^3 to about 16 g/100cm^3, or about 8.0 g/100 cm^3 to about 15 g/100 cm^3, or any individual BWC or range encompassed by these example ranges. The devices may exhibit a pressure drop that is at most equal to a conventional dense pack bed of powders, pellets, or granules of activated carbon or other activated compounds. This feature is advantageous because it ensures that

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the inventive sorbent material sheet product, whether stacked, rolled, wound, or otherwise configured, still has the same ability to process and transfer vapors and gases as conventional devices, despite the increased sorbent performance.

[00146] When the sorbent material product, stacked or rolled, is combined with a housing, it is useful as a vapor loss canister or other device. As noted above, the shapes and properties achieved via the stacked or rolled products allow for unique placement and improved performance.

[00147] In accordance with some embodiments, a vapor loss canister comprises a housing having at least one sidewall defining an internal space, a sorbent sheet product, such that the sorbent sheet media is sized and configured to fit within the housing and fill substantially the entire internal space within the housing, wherein the internal space is substantially free of additional internal material other than the sorbent sheet media. That is, traditional vapor loss canisters require springs, filters, support substrates, etc. to hold and maintain the loose carbon powder or pellets. Because the sorbent sheets are substantially self-supporting, these additional support structures are not needed. This allows for the inclusion of more material or the use of a smaller canister without sacrificing performance.

[00148] In some embodiments, the sorbent sheet product comprises a stacked sorbent sheet media comprisedas described above. In such instances, the housing or canister can take any shape as discussed above, but in some embodiments, is relatively flat and flexible for housing stacked sorbent sheet media that has a height substantially less than its length or width. In these instances, the housing may be a flexible bag or pouch, as discussed above.

[00149] In some instances the canister is adapted for placement atop or even within a fuel tank.

[00150] In some embodiments, sorbent sheet material product comprises a rolled sorbent sheet product as described above. In some instances, at least a portion of the housing sidewall defines a filter substantially without occupying any internal canister space.

[00151] In some embodiments, a fuel tank may be provided with integral vapor adsorption. Such tanks comprise a tank structure, and at least one sorbent sheet material product, either stacked or rolled, at least one fastening device which fastens the sorbent material product to a surface of the tank that is not regularly immersed in the volatile liquids contained within the tank. The fastening device may be an adhesive layer which is formed between one surface of the sorbent material product and a wall of the tank.

[00152] Such adhesive may be at least one of pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, reactive multi-part adhesives,

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acrylic and (meth)acrylic adhesives, acrylate and (meth)acrylate adhesives, epoxies adhesives in one- and two-part formulations, urethane adhesives, and copolymers and combinations thereof.

[00153] The tank may further include one or more of at least one fuel pump(s), fuel sending line(s), fuel return line(s), atmospheric vent line, port(s), valve(s), sensor(s), air inlet(s), open cell foam, baffle(s), bladder(s) and combinations of those.

[00154] In some embodiments, the tank is a fuel tank with a "ship in a bottle" configuration.

[00155] Some embodiments provide an onboard refueling vapor recovery apparatus comprising the sorbent material sheet product as described herein. The onboard refueling vapor recovery apparatus may include a vapor adsorbing canister as described herein. The onboard refueling vapor recovery apparatus may include a tank with integral vapor adsorption as described in the specification.

[00156] Additional Components

[00157] The invention may include sensors such as a fuel composition sensor. The fuel composition sensor may be used to detect the mixture of gasoline and ethanol contained within the housing and the sorbent material, and this information may be communicated to the ECU so that vapors which are later released to the engine can be more precisely used during engine combustion. Other sensors include temperature sensors, vapor pressure sensors, oxygen sensors, and the like. The sensors can operate on principles of electrochemical interaction, electronic such as thermocouples, electromechanical, refractive index, infrared spectroscopy, and others depending on the type of information that is required for the ECU. The sensors can be included alone or in combination within the housing, or, if no housing is specified, within the area that contains the sorbent material sheets. The sensors can be included in holes or notches which are cut from the sheet, or in spaces between the sheets with the sheets wrapped or folded around the sensors.

[00158] The invention may include inlets, outlets, hoses, and associated valves to control the flow of fuel vapor to and from the sorbent materials of the invention. The openings may be static or they may have valves that are opened and closed as required by the ECU to control the flow of vapor into and out of the sorbent sheets of the invention. For example, during refueling, outlet valves remain closed to ensure that displaced fuel vapors do not escape into the atmosphere. However, when the engine operates and the ECU requests it, at least one outlet valve may open to allow the release of adsorbed vapor into the engine to allow its combustion. There may also be included a vent and valve to the atmosphere in case

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there is too much fuel vapor for the sorbent material sheets of the invention to safely adsorb. There may further be included an inlet and valve for air or other gases, such as inert exhaust gases, which is used to desorb the fuel vapor as it is being sent to the engine for combustion.

[00159] The invention also contemplates the inclusion of and integration with other components which make up ORVR systems and devices. These other components may include active compressors and condensers, fuel tank heaters, fuel tank heat exchanging coils for cooling enclosed fuels, fuel filler necks, fuel filler ports, including capless fuel filler ports, vents for fuel vapors, fuel lines for sending fuel, fuel return lines, vents and vehicle rollover valves, fuel pumps, and air intake or purge valves.

[00160] The invention further contemplates devices and structures which may be combined with the sorbent material sheets to improve or control the adsorption and desorption of fluids and gases. For example, fans or pumps may be included to force the fluids or vapors over the sorbent material sheets as they are assembled, allowing the sorbent material sheets to be packed or wound tighter or allowing larger devices than would otherwise be possible with the same amount of fluid diffusion over the sheets. Alternatively, the devices can include resistance element heaters, or Peltier effect heaters or coolers which are designed to heat and/or cool the fluids and thus force their movement over the sorbent material sheets of the claimed invention. For instance, heated, expanding fluid may vent upwards and draw in more fluid at the bottom of a rolled or wound article that is oriented vertically to take advantage of the effects of gravity.

[00161] Other Uses

[00162] In addition to automotive uses, the inventors contemplate that the sorbent sheets of the claimed invention can be used in any instance where a tank or other enclosed space is designed to contain volatile liquids, in particular volatile hydrocarbons such as fuels, solvents, and other volatile compounds. Examples include but are not limited to fuel tanks in aircraft, fuel tanks in ships and other marine vehicles, fuel tanks in trucks, chemical tanks in railroad cars, barges, ships, trucks, vehicles, and other bulk carriers, and stationary chemical tanks. The sorbent material sheets of the claimed invention can also be attached or adhered to the walls of confined spaces where the presence of volatile compounds would be detrimental, for example, in chemical facilities where operators and maintenance staff must periodically access the space. Such sorbent material sheets, when used in such combined spaces, can not only increase safety for operators and maintenance staff, but they can also reduce the need for cumbersome protective gear.

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EXAMPLES

[00163] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

[00164] As was discussed above, butane working capacity (BWC) is a measure of the performance of activated carbon. BWC is determined for a sample by measuring the ability of the activated carbon to adsorb and desorb butane from dry air under specified conditions, and measures the difference between the butane adsorbed at saturated and the butane retained per unit volume of carbon after a specified purge. BWC can be tested in several ways, including procedures specified by ASTM International and which are known to those of skill in the art. Specifically, testing can follow ASTM D5228, which includes revisions D5228-16, D5228-92(2015), D5228-92(2005), and D5228-92(2000).

[00165] In Examples 1-4, the carbon sheets were spiral wound to yield 10% void fraction, which gave about a 30% performance improvement over the activated carbon alone. The void fraction of comparative granular or powdered beds of activated carbon, similar to Comparative Example 1, was approximately 40% void fraction by volume. The Examples and Comparative Example are described below.

EXAMPLE 1

[00166] Activated carbon sheets were made from CPL (CT#14299-8), which is an activated carbon that is wood based and which is activated using phosphoric acid. Sheets were also made from CPW (CT#14299-10), which is an activated carbon that is wood based and which is activated using phosphoric acid. The activated carbons were pulverized in a mechanical mortar and pestle and mixed with 9% PTFE powder. The resulting composition had a bread dough-like consistency. The composition was rolled to form sheets having thicknesses of 0.448 mm (CT#14299-8 1), 0.411 mm (CT#14299-8 2), 0.459 mm (CT#14299-10 1), and 0.439 mm (CT#14299-10 2). As used herein, GAC is used to denote granular activated carbon, and PAC is used to denote powdered activated carbon.

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EXAMPLE 2

[00167] Activated carbon sheets were prepared as described in Example 1 using BVC-11 8x25 activated carbon, which is a nutshell based activated carbon that is activated with phosphoric acid. This formed sample CT#14266-1. A sample was also formed with BVC-11 8x35, which is also a nutshell based activated carbon that is activated with phosphoric acid. This formed sample CT#14266-2. The formed sheets had a thickness of 0.330 mm (CT#14266-1 1), 0.334 mm (CT#14266-1 2), 0.327 mm (CT#14266-1 3), 0.317 mm (CT#14266-2 1), 0.307 mm (CT#14266-2 2), and 0.328 mm (CT#14266-2 3).

[00168] Butane Working Test – Examples 1 and 2

[00169] Activated carbon sheets prepared in Examples 1 and 2 were tested for butane adsorption using the butane working test. In this test, the sheets were rolled and placed in tubes. Butane was added to the tubes and butane adsorption was measured. Results are illustrated in TABLES 1 and 2:

TABLE 1 (Example 2)

	14266-1	14266-2
Tube vol. (cm^3)	3.8485	3.8485
Sheet wt. (g)	6.3604	6.0009
Sheet thick. (mm)	0.330	0.315
Sheet vol. (cm^3)	11.22	10.71
Sheet dens. (g/cm^3)	0.567	0.567
BWC sheet measured ($g/100cm^3$)	16.10	14.14
BWC GAC measured ($g/100cm^3$)	12.10	12.20

TABLE 2 (Example 1)

	CT-14299-8	CT-14299-10
Tube vol. (cm^3)	16.504	16.504
Sheet wt. (g)	4.10	3.16
Sheet thick. (mm)	0.411	0.439
Sheet vol. (cm^3)	9.92	7.90
Sheet dens. (g/cm^3)	0.413	0.404
BWC sheet measured	12.32	12.41

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($g/100cm^3$)		
BWC PAC measured ($g/100cm^3$)	7.9	9.6

EXAMPLE 3

[00170] Activated carbon sheets were prepared as in Examples 1 and 2, but using granular activated carbon #3445-32-4. The activated carbon sheets were also not rolled as tightly as in prior Examples 1 and 2, and the resultant sheets were tested for butane adsorption using the BWC test. In these two tests, two separate stacks of 20 sheets of 0.45mm thickness were cut in rectangles of 2.2cm X 7.5cm ± 10%, sealed at the side edge with double sided tape of 0.05mm thickness and 2mm width. In this configuration, tape thickness defined the average sheet spacing. Total height of each of the stacks of 20 sheets with tape spacers was 1 cm. These stacks of sheets were then placed in large 2.54cm diameter cylindrical glass tubes for butane adsorption/desorption testing. The excess volume between the rectangular stack of sheets and the walls of the cylindrical glass tube were filled with closed cell expanded foam to take up the excess volume and sealed to avoid bypass gas flow past the inserted test samples. The butane or air was forced to flow in the 0.05mm gaps between the 20 sheets. The flow rate and volume of the stacks of sheets was selected to conform to the BWC procedure. The BWC procedure was followed with the exception of the use of the stack of sheets rather than a granular bed, the use of the closed cell expanded foam for sealing, and the required larger cylindrical glass tube arrangement to accommodate the rectangular stack of sheets.

[00171] During the modified BWC procedure, butane or air was forced to flow in the 0.05 mm gaps between the 20 sheets, with the flow rate and volume of the stacks of sheets kept to BWC procedure for working capacity. The results of Example 3 are in Table 3 below.

COMPARATIVE EXAMPLE 1

[00172] A comparative example was also prepared using the same granular activated carbon #3445-32-4 as in Example 4, but without forming the granular activated carbon as part of a sheet or roll. The granulated activated carbon was tested per BWC procedure. The results of this test are in Table 3 below.

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TABLE 3 (Example 3 and Comparative Example 1)

	Granular activated carbon (Comparative Example 1)	Stacked 0.45mm sheets (Example 3)	
	#3445-32-4	#3445-32-4-stack 1	#3445-32-4-stack 2
Tube vol. minus foam volume if present (cm^3)	16.7	16.4	15.5
Carbon wt. (g)	6.513	7.885	7.465
Sheet thickness (mm)	---	0.45	0.45
Granular bed or Stacked sheet vol. (cm^3)	16.7	16.4	15.5
Granular bed or individual Sheet density (g/ cm^3)	0.389	0.534	0.534
BWC (g/100 cm^3)	9.33	10.25	10.83
BWC % improvement	---	9.9%	16.0%

[00173] Conclusion and Summary of Examples 1-3 and Comparative Example 1

[00174] A summary of relevant data appears in Table 4 below:

TABLE 4: Summary of Data

Example	**Test**	**Description**	**Sheet Thickness (mm)**	**Density (g/cm^3)**	**BWC (g/100 cm^3)**
Ex. 1	CT#14299-8	Wood based activated carbon CPL	0.411	0.413	12.32
Ex. 1	CT#14299-10	Wood based activated carbon CPW	0.439	0.404	12.41
Ex. 2	CT#14266-1	BVC-11 (nutshell) activated carbon 8x25	0.330	0.567	16.10
Ex. 2	CT#14266-2	BVC-11 (nutshell)	0.315	0.567	14.14

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		activated carbon 8x35			
Ex. 3	#3445-32-4-stack 1	GAC, 20 sheet stack	0.45	0.534	10.25
Ex. 3	#3445-32-4 stack 2	GAC, 20 sheet stack	0.45	0.534	10.83
Comp. Ex. 1	#3445-32-4	Granular Activated Carbon (GAC)	N/A	0.389	9.33

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CLAIMS

1. A vapor adsorbing canister comprising a sorbent material sheet product, wherein the form of the sorbent material sheet product is selected from the group consisting of a rolled sheet that includes a sorbent and a binder, a shredded sheet that includes shredded strips of a sorbent and a binder, a cut sheet that includes cut shapes of a sorbent and a binder, strands of material formed from the fibrillation of sorbent with a binder polymer, a stacked sheet, and combinations thereof.
2. The vapor adsorbing canister of claim 1, wherein the sorbent material sheet product comprises a sorbent selected from the group consisting of activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, diatomaceous earths, and combinations thereof.
3. The vapor adsorbing canister of claim 1, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, or copolymers or combinations thereof.
4. The vapor adsorbing canister of claim 1, wherein the polymer binder is hydrophobic.
5. The vapor adsorbing canister of claim 1, wherein the form of the sorbent material sheet product is flexible and is contained within a flexible canister.
6. The vapor adsorbing canister of claim 5, wherein the flexible canister is in the shape of a bag, an irregular shape, a rectangular prism, a cylinder, a ellipsoid, a frustro-conical shape, or combinations thereof.
7. An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of claim 1.

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8. A rolled sorbent material sheet product, comprising:

a sorbent material sheet defining an upper surface and a lower surface and having a total surface area, and which comprises a sorbent material and a binder,

wherein the sorbent material sheet product is spiral wound to form adjacent sheet layers which allow fluid flow around and between adjacent sheet layers;

wherein the spiral wound sorbent material sheet product defines a hollow central core which houses additional sorbent material.

9. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheet product has a BWC that is at least 10% higher than the BWC of a pelletized, granular, or powdered form of substantially the same amount of sorbent material in the sorbent sheet.

10. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheet product has a generally cylindrical shape having a length that is greater than its diameter.

11. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheet product is wound to an average roll density of 500-700 kg/m^3.

12. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheet product has a BWC greater than about 10 $g/100\ cm^3$.

13. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheet product has a BWC of about 7.0 $g/100\ cm^3$ to about 30 $g/100\ cm^3$.

14. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheet comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters.

15. The rolled sorbent material sheet product of claim 8, wherein the rolled sorbent material sheets comprise sorbent material particles having at least two populations having different average particle diameters, and wherein the average particle diameters of the two populations have ratios of about 1:1 to about 1:10.

16. The rolled sorbent material sheet product of claim 8, wherein the binder comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene

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terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, or copolymers or combinations thereof.

17. The rolled sorbent material sheet product according to claim 8, further comprising:

a spacer material creating uniform spacing between adjacent surfaces.

18. The rolled sorbent material sheet product according to claim 17, wherein the spacer material is selected from wovens, non-wovens, fabrics, granularized sorbent material, or combinations thereof.

19. A vapor adsorbing canister, comprising,

the sorbent material sheet product of claim 1, and

a housing at least partially encapsulating the rolled sorbent material sheet product of claim 1.

20. The vapor absorbing canister of claim 19, wherein the housing is flexible.

21. The vapor adsorbing canister of claim 19, wherein the housing comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

22. The vapor absorbing canister of claim 19, wherein the shape of the housing substantially conforms to the shape of the enclosed sorbent material sheet product of claim 1.

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23. The vapor adsorbing canister of claim 19, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

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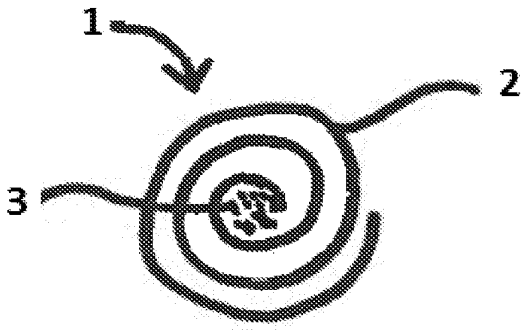


FIG. 1

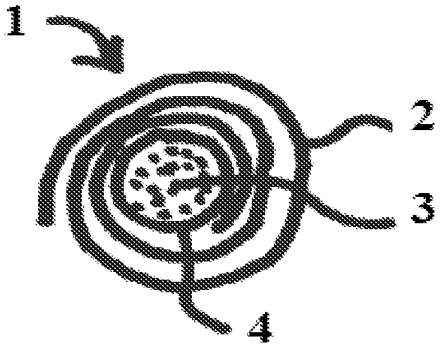


FIG.2

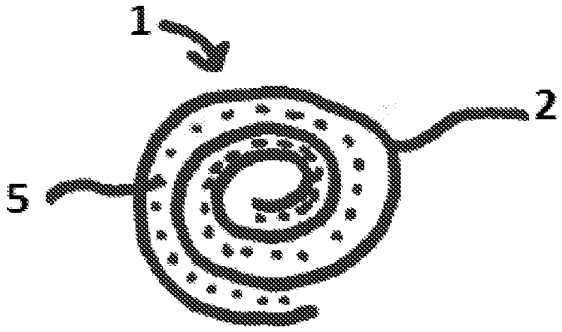


FIG. 3

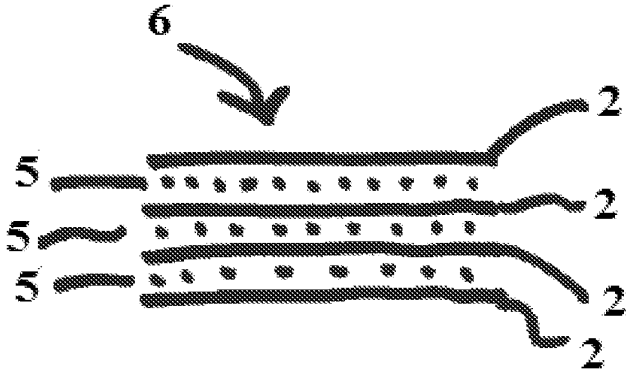


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/44958

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01D 53/02; B01D 53/04; B01D 53/14 (2019.01)
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2004/0118287 A1 (Jaffe et al.) 24 June 2004 (24.06.2004) Abstract, para [0012], [0028], [0039], [0042], [0044], [0049], [0051], and Figure 5.	1-4, 19, 23 --- 5-7, 20-22
Y	US 5,016,628 A (Lambert) 21 May 1991 (21.05.1991) Abstract; col 1 ln 58-62; col 1 ln 66-68; col 2 ln 4-5; col 2 ln 10-12; col 2 ln 51-55; and Figure 1.	5-6, 20-22
Y	US 2013/0269532 A1 (Aisan Kogyo Kabushiki Kaisha) 17 October 2013 (17.10.2013) Abstract, para [0016], [0028], and Figure 1.	7
Y	US 2002/0170436 A1 (Keefer et al.) 21 November 2002 (21.11.2002) Abstract, para [0012]-[0014], [0019], [0055], [0060], [0067]-[0068], [0129]-[0130], [0170], [0180], [0185]-[0186], [0188]-[0189], Figure 13A; Figure 14A; Figure 14C	8-18
Y	US 5,500,038 A (Dauber et al.) 19 March 1996 (19.03.1996) Abstract, col 3 ln 1-2; col 4 ln 56-60; col 5 ln 3-5; col 6 ln 47-58; col 7 ln 19-36.	8-18
A	US 6,176,897 B1 (Keefer) 23 January 2001 (23.01.2001) Entire Document.	1-23
A	US 2016/0166972 A1 (Owens et al.) 16 June 2016 (16.06.2016) Entire Document.	1-23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 October 2019	24 OCT 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US 2018/0214816 A1 (Calgon Carbon Corporation) 02 August 2018 (02.08.2018) Entire Document.	1-23

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— *with international search report (Art. 21(3))*

(54) Title: SORBENT DEVICES

(57) Abstract: Sorbent material sheets provide for enhanced performance in vapor adsorbing applications over conventional canisters and other emissions control equipment. The sorbent material sheets can be formed as part of a small, lightweight canister, or can be integrated into a fuel tank. The sorbent material sheets can also be used as part of an onboard refueling vapor recovery system to control volatile organic compound emissions from fuel tanks of gasoline vehicles, such as automobiles.

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SORBENT DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/713,894 filed August 2, 2018 and U.S. Provisional Application No. 62/735,436 filed September 24, 2018. The disclosures of each of these applications are incorporated herein by reference.

BACKGROUND

[0002] Evaporative emissions from gasoline and other liquid hydrocarbon fuels are a significant source of air pollution because the various hydrocarbons contained in the fuels can form photochemical smog on exposure to sunlight. The compounds of this smog and the hydrocarbons themselves cause degrading health effects in humans and animals as well as environmental damage. Evaporative emissions are especially problematic during vehicle refueling because the "empty" fuel tank is actually filled with fuel vapors, and the act of filling the tank with liquid fuel displaces the vapors from the tank. Evaporative emissions also occur when the fuel within the tank is heated, such as from hot ambient conditions or from nearby hot exhaust system components. Without controls, fuel vapors would be released as pollution into the atmosphere.

[0003] In the automotive sector, gasoline vapors are typically recovered during refueling by an Onboard Refueling Vapor Recovery (ORVR) canister system. These devices include multiple components which are designed to capture the displaced vapors from gasoline refueling and allow the engine to burn them at a later time. Vapors remain sealed within the fuel tank by specially designed tanks and fuel filler neck, and excess vapor is captured and adsorbed within a chemical canister. During engine operation, the Engine Control Unit (ECU) permits adsorbed vapors to be released from the canister and into the engine fuel system, burning the gasoline vapors as normal and permitting the canister to be used again.

[0004] While ORVR systems have been successful in reducing vapor emissions, they still have drawbacks. The canisters are filled with loose adsorbent particles such as activated carbon or charcoal, which can be messy to handle and package. These canisters are bulky and heavy because the adsorbent particles cannot physically support themselves, and because stringent emissions regulations now prohibit the release of even small amounts of vapor emissions, which requires higher adsorbent capacity. Manufacturing, maintenance and disposal of the canisters is also cumbersome because of the loose adsorbent particles, and the

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complexity of ORVR devices increases the cost of each vehicle while cutting into valuable passenger and cargo space. With automakers demanding lighter weights from all components to meet increasing fuel efficiency targets, as well as cost reductions and greater passenger and cargo space, there is a need for new ORVR devices and that are smaller, lighter, simpler, and more cost effective, while still complying with stricter emissions targets.

[0005] Recent stricter emissions targets are particularly challenging. In the United States, this is driven by the adoption of the Low Emission Vehicle (LEV) III standards in California and subsequent equivalent standards by the Environmental Protection Agency (EPA). Among other features, these regulations significantly lower the allowable evaporative emissions from ORVR systems, requiring not only the inclusion of a sorbent that has high overall adsorptive capacity, but also a sorbent that has high overall retention to ensure that even minute quantities of evaporative emissions are avoided. These minute quantities are known as "bleed" emissions.

[0006] The conventional solution to these emissions regulations is to include a large chamber filled with a high capacity sorbent, followed by a much smaller "scrubber" chamber that has a small amount of low retentivity carbon. The design of the smaller chamber conventionally includes delicate carbon monoliths to increase the surface area of the carbon and lower gas velocities. Examples of this approach include U.S. Patents 9,732,649 and RE38,844, both of which are hereby incorporated by reference in their entirety. There is a need for evaporative emissions controls that avoid the problems and complexity of prior art solutions while still delivering improved performance.

SUMMARY

[0007] In one embodiment, the invention discloses sorbent material sheets that have improved performance over the equivalent amount of adsorbent compound provided as a powder.

[0008] In another embodiment, the invention discloses sorbent material sheets enclosed within a housing.

[0009] In another embodiment, the invention discloses sorbent material sheets that omit the housing and which are instead contained directly within a fuel tank.

[0010] In another embodiment, the invention discloses an emissions control system, such as an ORVR which includes sorbent material sheets. The sorbent material sheets within the ORVR may be enclosed within a housing or the housing may be omitted.

[0011] The invention is also directed to the embodiments listed below:

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[0012] Embodiment 1 - A vapor adsorbing canister comprising: a first sorbent, a second sorbent, and wherein during an adsorption or a desorption operation, the linear velocity of gases is higher in the second sorbent than in the first sorbent, and wherein the first sorbent and the second sorbent each individually have an incremental adsorption capacity of greater than 35 g n-butane/L between vapor concentrations of 5 vol.% and 50 vol.% n-butane.

[0013] Embodiment 2 - The vapor adsorbing canister of embodiment 1, wherein each of the first sorbent and the second sorbent include a binder that comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, or copolymers or combinations thereof, and wherein the binder of the first and the second sorbent is the same or different.

[0014] Embodiment 3 - The vapor adsorbing canister of embodiments 1-2, wherein the first sorbent and the second sorbent each individually include less than or equal to about 20 wt.% of binder.

[0015] Embodiment 4 - The vapor adsorbing canister of embodiment 3, wherein the first sorbent and the second sorbent each individually include greater than or equal to about 80 wt.% of sorbent material.

[0016] Embodiment 5 - The vapor adsorbing canister of embodiments 1-2, wherein the first sorbent and the second sorbent each individually include less than or equal to about 10 wt.% of binder.

[0017] Embodiment 6 - The vapor adsorbing canister of embodiment 5, wherein the first sorbent and the second sorbent each individually include greater than or equal to about 90 wt.% of sorbent material.

[0018] Embodiment 7 - The vapor adsorbing canister of embodiments 1-6, wherein the second sorbent is in the form of a sheet.

[0019] Embodiment 8 - The vapor adsorbing canister of embodiments 1-6, wherein the second sorbent is in the form of a sheet that is corrugated, textured, folded, has apertures,

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wrapped in an "S" shape, in a convex "C" shape, in a concave "C" shape, rolled, has spacers between multiple sheets, and combination of the above features.

[0020] Embodiment 9 - The vapor adsorbing canister of embodiments 1-6 or 8, wherein the second sorbent is in the form of a sheet, said sheet including sorbent particles having an average particle diameter of about 0.001 mm to about 0.2 mm.

[0021] Embodiment 10 - The vapor adsorbing canister of embodiments 1-6 or 8-9, wherein the second sorbent is in the form of a sheet having raised and/or depressed portions.

[0022] Embodiment 11 - The vapor adsorbing canister of embodiment 10, wherein the raised and/or depressed portions are present on adjacent sheets and are nested.

[0023] Embodiment 12 - The vapor adsorbing canister of embodiment 10, wherein the raised and/or depressed portions are present on adjacent sheets and are not nested.

[0024] Embodiment 13 - The vapor adsorbing canister of embodiments 1-6 or 8-12, wherein the second sorbent is in the form of a sheet having a void volume of about 10% or more.

[0025] Embodiment 14 - The vapor adsorbing canister of embodiments 1-6 or 8-13, wherein the second sorbent is in the form of a sheet having a density of about 0.08 g/cm^3 to about 1.5 g/cm^3.

[0026] Embodiment 15 - The vapor adsorbing canister of embodiments 1-14, wherein the first sorbent and the second sorbent are each separately selected from the group consisting of activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, diatomaceous earths, and combinations thereof.

[0027] Embodiment 16 - The vapor adsorbing canister of embodiments 1-15, further comprising a housing.

[0028] Embodiment 17 - The vapor absorbing canister of embodiment 16, wherein the housing is flexible.

[0029] Embodiment 18 - The vapor adsorbing canister of embodiments 16-17, wherein the housing is selected from the group consisting of polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene

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(BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, copolymers thereof, and combinations thereof.

[0030] Embodiment 19 - The vapor adsorbing canister of embodiments 1-18, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

[0031] Embodiment 20 - An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of embodiments 1-19.

DETAILED DESCRIPTION

[0032] Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0033] It must also be noted that as used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a combustion chamber" is a reference to "one or more combustion chambers" and equivalents thereof known to those skilled in the art, and so forth.

[0034] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0035] As used herein, the term "sorbent material" is meant to encompass all known materials from any source that are capable of absorbing and/or adsorbing liquids and/or gases. For example, sorbent materials include, but are not limited to, activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths. As is known in the art, adsorption is the process by which molecules

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adhere to the surface of a material by chemical forces. In contrast, absorption is the process where a material is retained by another.

[0036] As used herein, descriptions and claims of multiple sorbent material sheets mean that there are multiple, separated sheets, with sides and/or surfaces in proximity to each other. Alternatively, descriptions and claims of multiple sorbent material sheets mean that there is only a single sheet, but that it has been wound or folded over on itself to yield a stacked, wound, or otherwise constructed mass of sheets with sides and/or surfaces in proximity to each other. The term also envisions that multiple sheets are stacked together and then wound or otherwise folded over, forming alternating layers in a single mass.

[0037] As used in the context of the sorbent or sorbent material or sorbent material sheets, the term surface means the outer boundary of that individual component. Even more specifically, in the context of the sorbent material sheets, the term surface means the largest planar faces of the sheets, which when rolled or stacked face each other or themselves. In a sheet, the surface is the portion that is significantly larger than the thickness of the sheet.

[0038] Embodiments of the invention are directed to devices containing one or more sheets of sorbent material, sorbent material sheets, and methods for making sorbent material sheets and devices containing these sheets. In various embodiments, the sorbent material sheets may be composed of a sorbent material and a binder and have a thickness of less than about 1 mm, or a thickness of less than about 2 mm. The devices of various embodiments may include a housing and one or more sorbent material sheets. In some embodiments, the devices may have a void fraction of about 10% or more of the total volume of the housing.

[0039] Further embodiments are directed to sorbent devices described in U.S. Patent Application Serial No. 15/885,317 filed on January 31, 2018, the entirety of which is hereby incorporated by reference.

THE SORBENT MATERIAL SHEETS

[0040] The sorbent material sheets of the invention may include any of the sorbent materials described above including, but are not limited to, activated carbon, carbon nanotubes, graphenes, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths, and in certain embodiments, the sorbent material sheets may be composed of activated carbon. The sorbents may be used alone or in combination.

[0041] The activated carbon may be of various grades and types selected based on performance requirements, cost, and other considerations. The activated carbon may be granular from reagglomerating a powder, granular from crushing or sizing nutshells, wood,

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coal or pellets created by extrusion, or activated carbon in powdered form. The activated carbon may be formed by processes of carbonization and activated. The raw material, such as wood, nutshell, coal, pitch, etc. is oxidized and devolatized, with steam and/or carbon dioxide gasified to form the pore structure in the activated carbon which is useful for adsorption. The initial oxidation and devolatilization process may include a chemical treatment with a dehydrating chemical, such as phosphoric acid, sulfuric acid, sodium hydroxide, potassium hydroxide, and combinations of those.

[0042] A variety of activation processes are known in the art. The most useful processes for providing activated carbon for the sorbent material sheets of the claimed invention involve a step of providing wood and/or wood byproduct, acid treating the wood and/or wood byproducts by exposure to phosphoric acid, and carbonizing the wood and/or wood byproducts using steam and/or carbon dioxide gasification. This process results in activated carbon particles having the highest butane working capacity ("BWC"), which is a measure of activated carbon performance. More details of the BWC testing and results are described in the Examples.

[0043] The activated carbon may be formed from materials including bagasse, bamboo, coconut husks, peat, wood such as hardwood and softwood sources in the form of sawdust and scrap, lignite, synthetic polymers, coal and coal tar, petroleum pitch, asphalt and bitumen, corn stalks and husks, wheat straw, spent grains, rice hulls and husks, nutshells, and combinations thereof.

[0044] The sorbent material sheets may further include one or more binders. Embodiments are not limited to particular binders, which can include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof. The binders can be thermoplastic or thermosetting as conditions require, and can include mixtures of thermoplastic and thermosetting compounds.

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[0045] The amount of binder may be about 1% to about 30% by weight of the total composition, and in certain embodiments, the amount of binder may be about 1% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassing these example amounts. The binder may be present in the amount of about 1%, about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20% or any range made of any two or more of the above amounts, all of which are measured by weight of the total composition. In some embodiments, the sorbent material sheets may include a solvent, which may generally be present in small, residual, amounts of, for example, less than 10%, less than 5%, or less than 2% and greater than about 0.1 % or 0.2 % by weight. In particular, in some embodiments the sorbent material sheets may have no (0%) solvent

[0046] In some embodiments, the sorbent material sheets have a thickness of less than about 2 mm, less than about 1.8 mm, less than about 1.6 mm, less than about 1.4 mm, less than about 1.2 mm, less than about 1.0 mm, about 0.01 mm to about 2 mm, about 0.01 mm to about 1.8 mm, about 0.1 mm to about 1.6 mm, about 0.01 mm to about 1.4 mm, about 0.01 mm to about 1.2 mm, about 0.01 mm to about 1.0 mm, about 0.02 mm to about 0.90 mm, about 0.05 to about 0.95 mm, about 0.05 to about 0.90 mm or any individual thickness or range encompassed by these example ranges. The sorbent material sheets of various embodiments may have a density of about 0.05 g/cm^3 to about 2.0 g/cm^3, and in other embodiments, the sorbent material sheets may have a density of 0.08 g/cm^3 to about 1.5 g/cm^3, about 0.1 g/cm^3 to about 1.3 g/cm^3, or any density or range encompassed by these example ranges. The density is calculated first by measuring the thickness of a given square or circular piece of sheet with a micrometer, multiplying by the surface area to obtain the volume, and weighing the piece to obtain the density (weight / volume).The BWC for each sorbent material sheet may be greater than about 10 $g/100cm^3$, and in some embodiments, the BWC may be from about 7.0 $g/100cm^3$ to about 30 $g/100cm^3$, about 8.0 g/100 cm^3 to about 25 $g/100cm^3$, about 10 g/100 cm^3 to about 20 g/100 cm^3, about 10 g/100 cm^3 to about 15 g/100 cm^3, about 11 $g/100cm^3$ to about 15 g/100 cm^3, about 12 $g/100cm^3$ to about 15 $g/100cm^3$ or any individual BWC or range encompassed by these example ranges. In other examples, the BWC may be about 9 g/100 cm^3 to about 15 g/100 cm^3, about 12 g/100 cm^3 to about 20 g/100 cm^3, about 13 g/100 cm^3 to about 20 $g/100cm^3$, about 14 $g/100cm^3$ to about 20 $g/100cm^3$, or about 15 $g/100cm^3$ to about 20 $g/100cm^3$. It is also contemplated that any of the endpoints of the above ranges may be combined to form new and distinct ranges.

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[0047] The sorbent material sheets of the present invention have higher performance as measured by the BWC than conventional sorbent materials which are provided in powders or other particle forms.

[0048] The sorbent material sheets of embodiments can be made by any suitable process. In some embodiments, sorbent material sheets can be made by pulverizing granular or pelletized sorbent material to a powder, mixing the powder with a binder to form a mixture, heating and blending the mixture, and rolling the mixture to form the sorbent material sheet. The step of pulverizing may produce sorbent particles having an average particle diameter of about 0.001 mm to about 0.2 mm, about 0.005 mm to about 0.1 mm, about 0.01 mm to about 0.075 mm, or any individual particle diameter or range encompassed by these example ranges, and in certain embodiments, the pulverized sorbent particles may have an average particle diameter of about 0.001 mm to about 0.01 mm. The step of mixing the powder with a binder may include mixing the sorbent particle powder with about 2% to about 20% by weight or about 2% to about 10% by weight of the total composition, or any individual amount or range encompassed by these example ranges. Heating can be carried out at any temperature sufficient to remove residual solvent such as, for example, about 50°C to about 200°C.

[0049] The sorbent material sheet of the invention may include various distributions of different sized particles to increase the packing efficiency of the powder within the sorbent material sheets. The selection of different sized particles can also improve rheological properties of the powder and surrounding binders, which allows improved mixing and uniform particle distribution before formation of the sorbent material sheets. In some embodiments, the particles of the sorbent material sheet may have a single particle size distribution, and in other embodiments, the particles may have two different particle size distributions. In further embodiments, the particle may have at least three different particle size distributions.

[0050] The mean particle sizes of at least two different particle populations, each having a particular size distribution, may be selected so that they have a ratios of between about 1:1 and about 1:15: In other embodiments, the mean particle sizes of the two different particle populations may have a ratio of about 1:2 to about 1:10. The mean particle sizes may also have a ratio of about 1:2 to about 1:5, or combinations of any of the above listed ratios.

[0051] The sorbent material sheets have significantly higher sorbent capacity than prior art fuel vapor recovery canisters for a given volume and/or weight. This capability can be utilized in various ways. In some embodiments, the sorbent material sheets can provide

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enhanced pollution controls in jurisdictions where such high levels of control are required. In other embodiments, the overall size, cost, and weight of the ORVR can be reduced for a specific level of performance. In further embodiments, an ORVR adsorption device can be designed which has increased performance over conventional adsorption canisters, thereby allowing the designer to omit costly and complex returnless fuel pump systems which would otherwise be required to reduce evaporative emissions. Higher performance adsorption devices may also render active condensing vapor systems unnecessary, which avoids the size, weight, and cost of compressor pumps and condensate storage tanks. It should be understood, however, that the ORVR adsorption device using the sorbent material sheets of the invention can also be combined with these devices for exceptionally high performance and a minimal size, weight, and cost penalty over conventional systems.

[0052] The sorbent material sheets may be configured together in a variety of ways depending on the physical space that they must conform to, the required device performance, and the features which are included in proximity to the sheets. In some embodiments, the sheets may be corrugated, include folds, and/or include holes or apertures to increase the surface area of the sorbent material sheets that is exposed to the passing fluid, therefore increasing performance for a given total sheet surface area. The various corrugations, folds, holes, and apertures can also be sized and placed to make way for internal and external features, such as fluid channels, tubing, sensors, and valves. The folds of the sorbent material sheets may take a variety of forms, such as a spiral wrapped configuration in either a cylindrical or elliptical form. The folds may also be in the form of an "S" shape, or a convex or concave "C" shape depending on the required device dimensions and/or any other required internal or external features. The sorbent material sheets may also be stacked in a flat or curved configuration, and the stacked sheets may be square, rectangular, circular, oval, or other irregular shape as needed to fit the space intended. This, in combination with the housing features discussed below, enables devices formed from the sorbent material sheets to fit in smaller, more irregularly shaped spaces than prior art canister devices, which maximizes vehicle interior space.

[0053] In addition to the above described configurations, the sorbent material sheets may also have surface features. In some embodiments, the sorbent material sheets may include raised portions, and in other embodiments, the sorbent material sheets may include depressed portions. These surface features may be combined within the same sheet. The inclusion of raised and/or depressed portions in the sheets may be utilized to form various configurations between the sheets as they are stacked, wrapped, and so forth. For instance,

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the sheets can be aligned so that the raised and/or depressed portions nest with each other, which brings the adjacent sheets closer together. The sheets can also be aligned so that the raised and/or depressed portions do not nest with each other, which forms a gap between the adjacent sheets. The alignment can be used to form various open and closed channels for vapor adsorption between the sheets.

SORBENT MATERIAL SHEET PRODUCT

[0054] The sorbent material sheets described above are combined into a sorbent material sheet product. The combination of the sorbent material sheets takes advantage of one or more of the above described features, such as increased surface area/volume ratio, reduced void space, improved sorbent performance, etc. In general, the individual sorbent material sheets are arranged next to each other to form a sorbent material sheet product that comprises sheets that are stacked, rolled, wound, folded, and/or laminated such that the surfaces of the sorbent material sheets are in close proximity to, or adjacent to each other. Whatever the arrangement, the goal is to maximize the surface area of the sheets exposed to the vapor, fluid, and/or gas stream and thus the performance of the sorbent material sheets.

[0055] *Stacked Sorbent Material Sheet Product*: The stacked sorbent material sheet product of the invention comprises two or more sorbent sheets each defining an upper surface and a lower surface, and having a known combined total surface area, wherein each sorbent sheet comprises a sorbent material and a binder; where adjacent sorbent sheets are stacked and arranged such that adjacent upper and lower surfaces are substantially congruent with each other, and aligned to allow fluid flow at least between adjacent upper and lower surfaces.

[0056] The term substantially parallel as used in the context of a stacked sorbent material sheet product means that the sheets maintain the same distance apart over their entire area, but with exceptions made for various physical characteristics and features. These exceptions that still fall within the scope of substantially parallel include but are not limited to differences due to variations in components such as spacers, sensors, apertures, tubing, ports, valves, channels, corrugations, pleats, folds, deformation encountered during manufacturing or operation, deformation due to the shape or pressures applied by or through the external housing, different wrapping techniques such as to seal the peripheries of the sheets, and so forth.

[0057] Performance improvements of the stacked sorbent material sheet product of the invention can be measured as the performance of the product having a given amount of

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activated carbon versus the performance of that same amount and grade of activated carbon if provided within a canister in a pelletized or powdered form. In some embodiments, the stacked sorbent sheet product has a BWC that is about 3% higher, about 5% higher, about 7% higher, about 9% higher, about 10% higher, about 12% higher, about 14% higher, and about 16% higher than the same volume and grade of activated carbon within a canister in pelletized or powdered form. Ranges based on these amounts are also contemplated, such as performance that is between about 5-14% higher, between about 5-10% higher, between about 10-16% higher, and so forth.

[0058] It should be noted that these improvements are only measured as between the volumes of the pelletized or powdered activated carbon and the stacked sorbent material sheet product, without accounting for other improvements of the stacked sorbent material sheet product. One key difference, described above, is the omission of a rigid canister body that would otherwise be required. The omission of the rigid canister body, which is needed in prior art systems involving pelletized or powdered activated carbon because the loose activated carbon cannot support itself, drives further weight savings and therefore even further performance for a given weight.

[0059] The stacked sorbent sheet product has a BWC at least 10% higher than the BWC of a pelletized/powdered form of the same volume of the sorbent material in the sorbent sheet. The stacked sorbent sheet product has a BWC greater than about 10 g/100cm^3. The stacked sorbent sheet product has a BWC of about 7.0 g/100cm^3 to about 30 g/100cm^3, or greater than about 12 g/100cm^3, or greater than about 13 g/100cm^3, or greater than about 14 g/100 cm^3, or greater than about 15 g/100cm^3, or greater than 20 g/100cm^3. Ranges are also contemplated, such as about 10-20 g/cm^3, about 10-12 g/cm^3, about 10-14 g/cm^3, about 12-14 g/cm^3, about 12-15 g/cm^3, and about 15-20 g/cm^3.

[0060] In some embodiments, the stacked sheets are held in a spaced apart relationship which controls one or more of void volume, flow rate, pressure drop, and other characteristics. Such spacing is achieved in some embodiments where at least one of the two or more sorbent material sheets is corrugated. The spacing can also be achieved with various folds in the sheets, and can also be achieved by the corresponding raised and/or depressed portions of the sheets which are aligned to form gaps between the sheet. If the sheets are arranged deliberately so that the raised and/or depressed portions of the sheets do not nest between sheets, this results in additional spacing between the sheets and permits fluid flow in those portions. If the sheets are arranged deliberately so that at least some raised and/or depressed portions nest between sheets, this results in a tighter fitting stack of sheets and

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decreases the spacing between the sheets, with a corresponding decrease or even stop in fluid flow. Combinations of these features can be used to form stacked sorbent sheet products with directed regions or channels for fluid flow and barriers or edge seals to prevent fluid leakage. These features for fluid flow can also include holes, cuts, or apertures through one or more of the sheets in the stacked sorbent sheet product.

[0061] Each sorbent sheet defines opposed lateral edges which are substantially parallel to fluid flow. The congruent lateral edges of adjacent sorbent sheets may be separate from each other, bound together or some combination thereof. In this manner, the edges of the stacked sorbent material sheet product may be sealed, partially sealed, or unsealed. The sealed or unsealed nature can be chosen to achieve desired results such as modifying fluid flow rate and/or patterns or other properties.

[0062] In some embodiments, the stacked sorbent material product yields a void volume of about 10% or more.

[0063] In some embodiments, each sorbent sheet has a density of about 0.08 g/cm^3 to about 1.5 g/cm^3.

[0064] In some instances, the sorbent material sheet product comprises at least two populations of sorbent material particles, wherein each of the at least two populations have different average particle diameters. See the above description of the bimodal particle size distribution which was discussed with respect to the individual sorbent material sheets. The same distribution ratios as between populations of sorbent particles are contemplated with respect to product formed of multiple sorbent material sheets. In some instances, the density of the sorbent material particles achieved by the at least two populations is greater than the density achieved by either population alone. The inclusion of a bimodal particle size distribution can also be used to improve the mechanical properties of the sorbent material sheet product because it makes the polymeric sheets much more resistant to shear forces.

[0065] In some instances, a sorbent material sheet product comprises at least two sorbent material sheets, each of which has a defined upper surface and lower surface which have a combined total surface area, and wherein each sorbent material sheet comprises a sorbent material and a binder, and wherein each sorbent material sheet is stacked and arranged such that adjacent upper and lower surfaces of the separate sheets are substantially parallel and are aligned to allow fluid flow at least between the adjacent upper and lower surfaces.

[0066] In some embodiments, the sorbent material sheet product has a BWC value of about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about

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40%, about 45%, and about 50% higher than the BWC of the same volume of sorbent material in pelletized or powdered forms. These can also be combined to form ranges, for example, between about 5-25% higher. The invention also contemplates that these amounts are the endpoints on ranges, such as at least about 40% higher.

[0067] The sorbent material sheets in the sorbent material sheet product, may be configured as being flat, wound in a spiral cylinder, wound in an elliptical form, wound in an elongate rectangular bar, folded, laminated in an "S" shape, formed as concentric cylinders, formed as concentric ellipses, formed as a concentric rectangular bar, or as combinations of these forms.

[0068] In some embodiments, the sorbent material sheet product will comprise a single sorbent material sheet that is wound or rolled to achieve the desired characteristics including, but not limited to density, void space, pressure drop, etc.

[0069] *Wound/Rolled Sorbent Material Sheet Product:* The sorbent material sheet product can also be wound or rolled as an alternative or in combination with stacked embodiments. A wound or rolled sorbent material sheet product comprises a sorbent sheet defining an upper surface and a lower surface, and combined has a known total surface area, wherein the sorbent sheet comprises a sorbent material and a binder where the sorbent sheet is spiral wound to create adjacent sheet layers which allow fluid flow around and between adjacent sheet layers.

[0070] Performance improvements of the rolled sorbent material sheet product of the invention can be measured as the performance of the product having a given amount of activated carbon versus the performance of that same amount and grade of activated carbon if provided within a canister in a pelletized or powdered form. In some embodiments, the rolled sorbent sheet product has a BWC that is about 3% higher, about 5% higher, about 7% higher, about 9% higher, about 10% higher, about 12% higher, about 14% higher, and about 16% higher than the same amount and grade of activated carbon within a canister in pelletized or powdered form. Ranges based on these amounts are also contemplated, such as performance that is between about 5-14% higher, between about 5-10% higher, between about 10-16% higher, and so forth.

[0071] The rolled sorbent sheet product has a BWC at least 10% higher than the BWC of a pelletized/powdered form of the same amount by weight of the sorbent material in the sorbent sheet. The stacked sorbent sheet product has a BWC greater than about 10 $g/100cm^3$. The stacked sorbent sheet product has a BWC of about 7.0 $g/100cm^3$ to about 30

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g/100cm^3, or greater than about 12 g/100cm^3, or greater than about 13 g/100cm^3, or greater than about 14 g/100 cm^3, or greater than about 15 g/100cm^3, or greater than 20 g/100cm^3. Ranges are also contemplated, such as about 10-20 g/cm^3, about 10-12 g/cm^3, about 10-14 g/cm^3, about 12-14 g/cm^3, about 12-15 g/cm^3, and about 15-20 g/cm^3.

[0072] A rolled sorbent sheet product as described herein has a generally cylindrical shape having a length substantially greater than its diameter, although any dimension can be employed, including conical, or frustro-conical variations, as well as ellipsoids, or other shapes.

[0073] The density of the rolled sorbent sheet product may be computed based on the formulas below:

Roll Density Calculations (US units)

$$\rho\left(\frac{lb}{ft^3}\right) = (3) \times \frac{BW \times L}{\left(\frac{OD^2}{4} - \frac{ID^2}{4}\right) \times \pi}$$

BW: Basis Weight $\left(\frac{oz}{yd^2}\right)$ *L: Length on Roll (yd)*

OD: Outer Roll Diameter (in) *ID: Inner Roll Diamter/Core Diameter (in)*

W: Machine width or roll length (in) *ρ: Roll Density* $\left(\frac{lb}{ft^3}\right)$

Roll Density Calculations (SI units)

$$\rho\left(\frac{kg}{m^3}\right) = (1000) \times \frac{BW \times L}{\left(\frac{OD^2}{4} - \frac{ID^2}{4}\right) \times \pi}$$

BW: Basis Weight $\left(\frac{g}{m^2}\right)$ *L: Length on Roll (m)*

OD: Outer Roll Diameter (mm) *ID: Inner Roll Diamter/Core Diameter (mm)*

W: Machine width or roll length (mm) *ρ: Roll Density* $\left(\frac{kg}{m^3}\right)$

[0074] The rolled sorbent sheet product may be wound to an average roll density of about 80-1500 kg/m^3, about 500-2000 kg/m^3, about 750-1500 kg/m^3, about 900-1200 kg/m^3, about 900-1050 kg/m^3, about 400-500 kg/m^3, about 500-600 kg/m^3, about 500-550 kg/m^3, about 600-650 kg/m^3, about 650-700 kg/m^3, and about 700-750 kg/m^3.

[0075] The rolled sorbent sheet product has a BWC greater than about 10 g/100cm^3. In some embodiments, the rolled sorbent sheet product has a BWC of about 7.0 g/100cm^3 to about 30 g/100cm^3. The rolled sorbent sheet product may also have BWCs that are the same as the above described sorbent sheet products which are not rolled.

[0076] Similar to the discussion above with respect to the stacked sorbent material sheets, the wound or rolled sorbent material sheets may include multiple particle size distributions or populations of the adsorbent pelletized or powdered activated carbon. The same ratios are contemplated as discussed above. Similar to the discussion above, this results in greater performance because it enables a larger amount of the activated carbon to be incorporated into the sheets which are formed into the rolled sorbent sheet product.

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[0077] As used herein, wound or rolled sorbent sheet products refer to any form of layering of one or more sorbent material sheets by winding, spiral winding, concentric layering of tubular (of any cross-sectional shape, e.g. round, elliptical, square, triangular, rectangle, etc.) or combination thereof. For example, a single sorbent material sheet may be spiral wound along its length to form a cylindrical-shaped rolled sorbent material sheet product. As another example, a plurality of sorbent material sheets can be stacked and then wound together to form a similar cylindrical shape. As another alternative, several sheets each formed into a cylinder having a slightly different diameter from the next can be arranged such that they from concentric rings in cross-section of a similarly sized cylinder. Various combinations of these and other arrangements may be used to fill the space within any shape of housing or canister, as described elsewhere herein.

[0078] As used in the context of a wound or rolled sorbent material sheet or sheets, the term substantially parallel is used to mean that at a minute, infinitely small dimension, the two sheets or portions of the same sheets are the same distance from each other in all directions. However, it is also understood that in the context of the wound or rolled sorbent material sheets, especially those that are a single sheet wound in a spiral around a center or core, that this means that the sheets are not exactly the same distance apart from each other over the entire areas that face each other. Furthermore, it is understood that in this context, similar variations in distance are contemplated between the sheet or sheets due to components such as spacers, sensors, apertures, tubing, ports, valves, channels, corrugations, pleats, folds, deformation encountered during manufacturing or operation, deformation due to the shape or pressures applied by or through the external housing, different wrapping techniques such as to seal the periphery of the sheets, and so forth.

[0079] As noted above with respect to the sorbent material sheets, the binder is selected from polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof.

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[0080] The Housing

[0081] The invention also contemplates the use of a housing which partially or totally encapsulates the sorbent material sheets. It should be noted that while the term "housing" is used in this specification to describe the overall outer structure that at least partially encapsulates the sorbent material sheets, it is understood that such structures are known by many other terms to those of skill in the art. For example, in automotive or other fields where emissions must be controlled, the housing may be referred to as a canister, cartridge, scrubber, or the like. It is therefore contemplated that the term "housing" broadly encompasses a variety of terms and structures including canisters, cartridges, scrubbers, flexible bags, molded polymer casings, metal casings, and so forth that are used in the field of emissions control. Furthermore the term housing may refer to a an empty structure awaiting the inclusion of sorbent, i.e., an unfinished part, or a completed emissions control part that includes the sorbent contained within the canister, cartridge, scrubber, flexible bag, etc. It is contemplated that these parts may be interchanged or combined depending on design requirements.

[0082] One major advantage of the invention is that the sorbent material sheets are both flexible and self-supporting and can be laminated, rolled, wound, folded, or stacked in a variety of configurations within the housing to suit different mechanical requirements within the tight confines of a vehicle. In such embodiments, the housing would be designed to conform or fit the spaces that are available for the device to be stored. For instance, the housing can be sized and shaped to fit in spaces within or surrounding wheel wells, driveshafts, batteries for hybrid powertrains, spare tires, tire changing tools, tire patching tools, vehicle trunks or other storage spaces, vehicle bumpers and bodywork panels, exhaust systems, other emissions control equipment such as urea or other injection tanks, fuel lines, vehicle frames, suspension components, engine compartment, under passenger compartment seats, within passenger compartment seats, and other spaces which are too small or too difficult to reach to be effectively utilized for passenger or cargo space.

[0083] To further reduce weight and size and take advantage of the self-supporting sorbent material sheets, the housing can be in the form of a thin walled bag or pouch. This is possible because the sorbent material sheets have some mechanical structure and are self-supporting and so do not require a rigid outer container as in conventional canisters. The film materials that form the bag can have thicknesses of about 10 μm to about 250 μm. In other

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embodiments, the bag film can have thicknesses of about 20 μm to about 175 μm, and the bag film can have thicknesses of about 50 μm to about 125 μm.

[0084] The bag or pouch may be formed of any materials which are used in fuel systems, and particularly are formed of materials which are designed to withstand the chemical effects of the fuel vapors contained. Bag materials include polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers such as perfluoroelastomers (FFKM) and tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers such as para-aramid and meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, and copolymers and combinations thereof. The bag is typically thermoplastic for flexibility, but can also be a combination with amounts of thermoset or can be in the form of a cured rubber or an elastomer.

[0085] The housing, bag, or pouch may also be designed to act as a vapor barrier to the adsorbed fuel vapors contained therein. This barrier property may be inherent to the polymer itself, or may be achieved through the use of at least one barrier additive and/or at least one barrier layer. Examples of barrier additives which can be formed as a layer or as a particle filler include polymers such as epoxy, polyamide, polyamide imides, fluoropolymers, fluororubbers, and combinations of those. Barrier layers can also be made of metals such as aluminum, steel, titanium, and alloys of those. The metal barrier layers can be formed by conventional mechanical means, such as coextrusion or adhering with the other layers of the housing, or they can be chemically deposited, such as by chemical vapor deposition or electroplating. The metal barrier layer can be formed from a foil having a thickness of less than about 25 μm, less than about 20 μm, less than about 15 μm, less than about 10μm, or less than about 5 μm.

[0086] The housing and its materials may also be selected to be compatible with "ship in a bottle" fuel systems. In such systems, many or all of the fuel system components, including the fuel pumps, ORVR, fuel filters, valves, and other components are fitted within the vehicle fuel tank. Such systems are advantageous because they reduce assembly time and the amount of space required by the fuel system. In such systems, the housing should have

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materials which are capable of being immersed in the selected fuel, typically gasoline, for extended periods of time within the vehicle fuel tank, while also being able to withstand the effects of the adsorbed fuel vapors within.

[0087] The housing may also be a thin metal housing. The thin metal housing can be formed of flexible or rigid metals such as steel, aluminum, titanium, and alloys of those. The metal housing can be formed from a foil having a thickness of about 5-100 μm, or about 10-250 μm. In some embodiments, the foil may be as thick as about 1 mm. Whether the housing is flexible or rigid depends on the selection of the material, the thickness, and any treatments that have been applied to the metals, such as heat treatments or hot or cold working.

[0088] In some embodiments, the housing for the sorbent material sheets may be omitted entirely, with the sorbent material sheets being contained within the fuel tank itself. In such configurations, the sorbent materials sheets can be attached to a portion of the interior of the fuel tank that does not regularly come in contact with liquid fuel and which is free to adsorb fuel vapors. This portion is typically the top or sides of the fuel tank, or combinations of those. The fuel tank may also include a recessed portion on the top or the sides which is designed to include the sorbent material sheets and allow the sorbent material sheets to adsorb fuel vapors. Such embodiments where sorbent material sheets are attached to the interior portions of the fuel tank not only offer maximum space savings and weight savings by omitting the canister structure, but also simplify manufacturing and installation because the sheets are already installed within the fuel tank during vehicle assembly.

[0089] The housing can also be eliminated by forming a rolled or folded sorbent sheet and then selectively curing the outer sheets so that they form a durable, cured shell that acts as a support for the rolled or folded sorbent sheets within. Such selective curing can be accomplished thermally or with a chemical bath, or via actinic radiation, such as ultraviolet light or by electron beam curing.

[0090] In embodiments where the sorbent material sheets omit the housing and are contained within the vehicle fuel tank itself, the sorbent material sheets may be attached to the fuel tank in a variety of ways. The sorbent material sheets can be fastened using mechanical fasteners such as screws, rivets, or clamps, or the sorbent material sheets may be fastened using an adhesive backing positioned between the fuel tank wall and the sorbent material sheets. The adhesive backing may be a single layer of adhesive or a double sided adhesive tape or sheet. The adhesive used in the adhesive backing may include pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives,

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and reactive multi-part adhesives. Adhesive compositions include acrylic and (meth)acrylic, acrylate and (meth)acrylate, epoxies in one- and two-part formulations, and urethane.

[0091] The sorbent material sheets may be applied during manufacturing in a variety of ways. In some embodiments, the fuel tank may be formed and the sorbent material sheets are applied in a separate step where the adhesive is applied followed by the application of the sorbent material sheets. In other embodiments, the sorbent material sheets are placed, with or without an adhesive backing as appropriate, on the inside of a mold and the fuel tank is injected or blow molded around the sorbent material sheets. In other embodiments, the sorbent material sheets may be coextruded with panels of material which make up the sides of the fuel tank, and the edges of those panels are adhered or welded together to seal the final tank with the sorbent material sheets on the inside.

[0092] When the sorbent material sheets are contained within the vehicle fuel tank without the housing, the fuel tank may include additional valves and ports to accommodate the adsorption and desorption of fuel vapors in the fuel tank. For example, during engine operation, air may be introduced into the fuel tank to desorb the fuel vapors which are contained in the sorbent material sheets, as well as those which are present in the tank. These desorbed fuel vapors are then sent to the engine for combustion during optimal cycles as required by the ECU.

[0093] When the sorbent material sheets are provided without a housing and are contained within a tank, such as a vehicle fuel tank, they may be positioned so that they are not regularly immersed in the volatile liquids typically contained within the tank. This ensures that the sorbent material sheets do not become prematurely saturated, and also ensures that sufficient surface area is exposed to the vapors within the fuel tank to effect the adsorption of the vapors. The feature contemplates that the sorbent material sheets can be placed in parts of the tank that are unfilled, such as the ullage or headspace of the tank, or near baffles which prevent the sloshing of liquids on the sorbent material sheets. The sorbent material sheets may also be placed in a dedicated portion of the tank, such as a small chamber or niche, where the liquids cannot enter.

[0094] The devices of various embodiments may include a housing and the sorbent material sheets described above. The housing may be any shape and can be configured for purifying gasses or liquids. For example, in some embodiments, the housing may be any shape such as, for example, cuboidal, cubic, or cylindrical. The sorbent material sheets may be sized to fit within the housing and substantially fill a space within the housing through which the gas or liquid is passed. In some embodiments, two or more sorbent material sheets

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may be stacked to substantially fill the housing, and in other embodiments, the sorbent material sheets may be rolled to form a spiral wound sheet or pressed to form a stacked sheet. In some embodiments, the stacked or pressed sheets may be such that the sides of adjoining sheets are substantially contiguous. In other embodiments, stacked or pressed sheets may be positioned such that adjoining sheets are spaced. For example, in certain embodiments, the sheets may be corrugated, having sorbent material sheets that form a series or parallel ridges and furrows, and in some embodiments, corrugated sorbent material sheets may be separated by flat sorbent material sheets. The corrugated sorbent material sheets may be disposed within the housing in a stacked or rolled/spiral wound form.

[0095] In various embodiments, the void fraction may be about 30% to about 32% less than the void volume for current devices, and in some embodiments, the void fraction may be less than 10%. For example, the devices may have a void fraction of about 45% to about 2%, about 35 % to about 5%, about 25% to about 7%, or any individual void fraction or range encompassed by these example ranges. The devices of various embodiments may exhibit less flow restriction, e.g. pressure drop, than devices having granular or pelleted sorbent materials. Thus, more adsorbent material can be incorporated into such devices without reducing the flow rate of the device.

[0096] The devices of such embodiments may have BWCs of greater than about 5.0 g/100 cm^3, and in some embodiments, the devices may have a BWC of about 4.0 g/100 cm^3 to about 20 g/100 cm^3, 5.0 g/100cm^3 to about 18 g/100cm^3, about 7.0 g/100 cm^3 to about 16 g/100cm^3, or about 8.0 g/100 cm^3 to about 15 g/100 cm^3, or any individual BWC or range encompassed by these example ranges. The devices may exhibit a pressure drop that is at most equal to a conventional dense pack bed of powders, pellets, or granules of activated carbon or other activated compounds. This feature is advantageous because it ensures that the inventive sorbent material sheet product, whether stacked, rolled, wound, or otherwise configured, still has the same ability to process and transfer vapors and gases as conventional devices, despite the increased sorbent performance.

[0097] When the sorbent material product, stacked or rolled, is combined with a housing, it is useful as a vapor loss canister or other device. As noted above, the shapes and properties achieved via the stacked or rolled products allow for unique placement and improved performance.

[0098] In accordance with some embodiments, a vapor loss canister comprises a housing having at least one sidewall defining an internal space, a sorbent sheet product, such that the sorbent sheet media is sized and configured to fit within the housing and fill

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substantially the entire internal space within the housing, wherein the internal space is substantially free of additional internal material other than the sorbent sheet media. That is, traditional vapor loss canisters require springs, filters, support substrates, etc. to hold and maintain the loose carbon powder or pellets. Because the sorbent sheets are substantially self-supporting, these additional support structures are not needed. This allows for the inclusion of more material or the use of a smaller canister without sacrificing performance.

[0099] In some embodiments, the sorbent sheet product comprises a stacked sorbent sheet media comprised as described above. In such instances, the housing or canister can take any shape as discussed above, but in some embodiments, is relatively flat and flexible for housing stacked sorbent sheet media that has a height substantially less than its length or width. In these instances, the housing may be a flexible bag or pouch, as discussed above.

[00100] In some instances the canister is adapted for placement atop or even within a fuel tank.

[00101] In some embodiments, sorbent sheet material product comprises a rolled sorbent sheet product as described above. In some instances, at least a portion of the housing sidewall defines a filter substantially without occupying any internal canister space.

[00102] In some embodiments, a fuel tank may be provided with integral vapor adsorption. Such tanks comprise a tank structure, and at least one sorbent sheet material product, either stacked or rolled, at least one fastening device which fastens the sorbent material product to a surface of the tank that is not regularly immersed in the volatile liquids contained within the tank. The fastening device may be an adhesive layer which is formed between one surface of the sorbent material product and a wall of the tank.

[00103] Such adhesive may be at least one of pressure sensitive adhesives, UV curing adhesives, thermally curing adhesives, hot melt adhesives, reactive multi-part adhesives, acrylic and (meth)acrylic adhesives, acrylate and (meth)acrylate adhesives, epoxies adhesives in one- and two-part formulations, urethane adhesives, and copolymers and combinations thereof.

[00104] The tank may further include one or more of at least one fuel pump(s), fuel sending line(s), fuel return line(s), atmospheric vent line, port(s), valve(s), sensor(s), air inlet(s), open cell foam, baffle(s), bladder(s) and combinations of those.

[00105] In some embodiments, the tank is a fuel tank with a "ship in a bottle" configuration.

[00106] Some embodiments provide an onboard refueling vapor recovery apparatus comprising the sorbent material sheet product as described herein. The onboard refueling

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vapor recovery apparatus may include a vapor adsorbing canister as described herein. The onboard refueling vapor recovery apparatus may include a tank with integral vapor adsorption.

SORBENT MATERIAL SHEETS TO REDUCE BLEED EMISSIONS

[00107] In some embodiments, the above sorbent materials sheets and housing are configured into a housing or canister to reduce, substantially eliminate, or eliminate bleed or breakthrough emissions that occur when vapors escape from a volume of high adsorption capacity sorbent. In these embodiments, the vapor adsorbing canister includes at least a first sorbent and a second sorbent. During an adsorption or desorption cycle that coincides with fuel storage or engine operation, the first sorbent adsorbs the majority of the fuel vapors, while the remaining vapors are scrubbed by the second sorbent. The scrubbing of the remaining vapors is key to controlling bleed emissions and achieving the low emissions targets of current and future regulations.

[00108] The first and second sorbent may each be independently formed of any sorbent, to include conventional powder, pelleted, or granular forms. However, it is most advantageous that one or both of the first and second sorbent are formed of the sorbent material sheets or the sorbent material sheet products that are described above. This enables the significant performance advantages to be used to solve the problem of bleed emissions.

[00109] In some embodiments, the first sorbent and the second sorbent may include sorbent sheets that include any of the sorbent materials described above including, but not limited to, activated carbon, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, or diatomaceous earths. In certain embodiments, the sorbent material sheets may be composed of activated carbon. The above listed sorbents may be used alone or in combination.

[00110] One advantage of the present invention is that the high surface area and high density of the carbon that is incorporated into the first and second sorbents means that a canister can be designed that has both high retentivity and high adsorptive capacity. This is because in the prior art, carbon monoliths used for the second bleed chamber relied on high binder loadings to create monoliths with greater voidage volume (i.e., the amount of unoccupied space in a volume of material) to reduce pressure drop. The disadvantage of high voidage is that it results in reduced adsorption performance and lower vapor-solid collision efficiency. While the high binder content achieved the goal of increasing voidage and thereby affording a low pressure drop, it also sacrifices adsorptive capacity because inert

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binder takes the place of otherwise adsorptive sorbent. In some prior art monoliths, the amount of activated carbon sorbent is less than 50 wt.%, for instance, which results in larger devices and low adsorptive performance. In contrast, the higher density of the present sorbent material sheets, combined with innovative arrangement of the sorbent material sheets, means that a much smaller device can be fabricated while still maintaining excellent overall adsorptive capacity with a low pressure drop.

[00111] In some embodiments, the selection of the sheet form of adsorbent material increases the apparent density versus granular, pelleted, or powdered activated carbon by up to about 35%, up to about 30%, up to about 25%, up to about 20%, up to about 15%, up to about 10%, or up to about 5%. These increases in apparent density are computed by dividing the apparent density of the sorbent material sheets over the apparent density of sorbent materials that are present in granular, pelleted, or powdered forms. The apparent densities are measured using ASTM methods D2854 and D8176.

[00112] In some embodiments, the first sorbent and the second sorbent may each have an incremental adsorption capacity of greater than about 35 g n-butane/L between vapor concentrations of 5 vol.% and 50 vol.% of n-butane. This measurement is indicative of the improved performance of the sorbent that arises in part from the greater density of sorbent material and the lesser amount of required binder. In some embodiments, the incremental adsorption capacity of the first sorbent or the second sorbent is greater than about 35 g, greater than about 36g, greater than about 37g, greater than about 38g, greater than about 39g, greater than about 40g, greater than about 41g, greater than about 42g, greater than about 43g, greater than about 44g, greater than about 45g, greater than about 46g, greater than about 47g, greater than about 48 g, greater than about 49g, greater than about 50g, greater than about 51g, greater than about 52g, greater than about 53g, greater than about 54g, greater than about 55g, greater than about 56g, greater than about 57g, greater than about 58 g, greater than about 59g, greater than about 60g, greater than about 61g, greater than about 62g, greater than about 63g, greater than about 64g, greater than about 65g, greater than about 66g, greater than about 67g, greater than about 68 g, greater than about 69g, greater than about 70g, greater than about 71g, greater than about 72g, greater than about 73g, greater than about 74g, greater than about 75g, greater than about 76g, greater than about 77g, greater than about 78 g, greater than about 79g, greater than about 80g, greater than about 81g, greater than about 82g, greater than about 83g, greater than about 84g, greater than about 85g, greater than about 86g, greater than about 87g, greater than about 88 g, greater than about 89g, greater than about 90g, greater than about 91g, greater

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than about 92g, greater than about 93g, greater than about 94g, greater than about 95g, greater than about 96g, greater than about 97g, greater than about 98 g, greater than about 99g, or greater than about 100g, all measured by weight n-butane/L or sorbent between vapor concentrations of 5 vol.% and 50 vol.% of n-butane.

[00113] In some embodiments, the first sorbent and the second sorbent may each have an effective incremental adsorption capacity of greater than about 35 g n-butane/L between vapor concentrations of 5 vol.% and 50 vol.% of n-butane. This measurement is indicative of the improved performance of the sorbent that arises in part from the greater density of sorbent material and the lesser amount of required binder. In some embodiments, the incremental adsorption capacity of the first sorbent or the second sorbent is greater than about 35 g, greater than about 36g, greater than about 37g, greater than about 38g, greater than about 39g, greater than about 40g, greater than about 41g, greater than about 42g, greater than about 43g, greater than about 44g, greater than about 45g, greater than about 46g, greater than about 47g, greater than about 48 g, greater than about 49g, greater than about 50g, greater than about 51g, greater than about 52g, greater than about 53g, greater than about 54g, greater than about 55g, greater than about 56g, greater than about 57g, greater than about 58 g, greater than about 59g, greater than about 60g, greater than about 61g, greater than about 62g, greater than about 63g, greater than about 64g, greater than about 65g, greater than about 66g, greater than about 67g, greater than about 68 g, greater than about 69g, greater than about 70g, greater than about 71g, greater than about 72g, greater than about 73g, greater than about 74g, greater than about 75g, greater than about 76g, greater than about 77g, greater than about 78 g, greater than about 79g, greater than about 80g, greater than about 81g, greater than about 82g, greater than about 83g, greater than about 84g, greater than about 85g, greater than about 86g, greater than about 87g, greater than about 88 g, greater than about 89g, greater than about 90g, greater than about 91g, greater than about 92g, greater than about 93g, greater than about 94g, greater than about 95g, greater than about 96g, greater than about 97g, greater than about 98 g, greater than about 99g, or greater than about 100g, all measured by weight n-butane/L or sorbent between vapor concentrations of 5 vol.% and 50 vol.% of n-butane.

[00114] In some embodiments, the first sorbent and the second sorbent may each have a nominal incremental adsorption capacity of greater than about 35 g n-butane/L between vapor concentrations of 5 vol.% and 50 vol.% of n-butane. This measurement is indicative of the improved performance of the sorbent that arises in part from the greater density of sorbent material and the lesser amount of required binder. In some embodiments,

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the incremental adsorption capacity of the first sorbent or the second sorbent is greater than about 35 g, greater than about 36g, greater than about 37g, greater than about 38g, greater than about 39g, greater than about 40g, greater than about 41g, greater than about 42g, greater than about 43g, greater than about 44g, greater than about 45g, greater than about 46g, greater than about 47g, greater than about 48 g, greater than about 49g, greater than about 50g, greater than about 51g, greater than about 52g, greater than about 53g, greater than about 54g, greater than about 55g, greater than about 56g, greater than about 57g, greater than about 58 g, greater than about 59g, greater than about 60g, greater than about 61g, greater than about 62g, greater than about 63g, greater than about 64g, greater than about 65g, greater than about 66g, greater than about 67g, greater than about 68 g, greater than about 69g, greater than about 70g, greater than about 71g, greater than about 72g, greater than about 73g, greater than about 74g, greater than about 75g, greater than about 76g, greater than about 77g, greater than about 78 g, greater than about 79g, greater than about 80g, greater than about 81g, greater than about 82g, greater than about 83g, greater than about 84g, greater than about 85g, greater than about 86g, greater than about 87g, greater than about 88 g, greater than about 89g, greater than about 90g, greater than about 91g, greater than about 92g, greater than about 93g, greater than about 94g, greater than about 95g, greater than about 96g, greater than about 97g, greater than about 98 g, greater than about 99g, or greater than about 100g, all measured by weight n-butane/L or sorbent between vapor concentrations of 5 vol.% and 50 vol.% of n-butane.

[00115] While the disclosure mentions first sorbents and second sorbents, it is understood that modifications and alternatives to this construction are contemplated. For example, each of the first sorbent and the second sorbent may actually include multiple bodies of sorbent in different forms or combinations. Thus, there can be first sorbents, second sorbents,, third sorbents, fourth sorbents, and so on.

ADDITIONAL COMPONENTS

[00116] The invention may include sensors such as a fuel composition sensor. The fuel composition sensor may be used to detect the mixture of gasoline and ethanol contained within the housing and the sorbent material, and this information may be communicated to the ECU so that vapors which are later released to the engine can be more precisely used during engine combustion. Other sensors include temperature sensors, vapor pressure sensors, oxygen sensors, and the like. The sensors can operate on principles of electrochemical interaction , electronic such as thermocouples, electromechanical, refractive

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index, infrared spectroscopy, and others depending on the type of information that is required for the ECU. The sensors can be included alone or in combination within the housing, or, if no housing is specified, within the area that contains the sorbent materials sheets. The sensors can be included in holes or notches which are cut from the sheet, or in spaces between the sheets with the sheets wrapped or folded around the sensors.

[00117] The invention may include inlets, outlets, hoses, and associated valves to control the flow of fuel vapor to and from the sorbent materials of the invention. The openings may be static or they may have valves that are opened and closed as required by the ECU to control the flow of vapor into and out of the sorbent sheets of the invention. For example, during refueling, outlet valves remain closed to ensure that displaced fuel vapors do not escape into the atmosphere. However, when the engine operates and the ECU requests it, at least one outlet valve may open to allow the release of adsorbed vapor into the engine to allow its combustion. There may also be included a vent and valve to the atmosphere in case there is too much fuel vapor for the sorbent material sheets of the invention to safely adsorb. There may further be included an inlet and valve for air or other gases, such as inert exhaust gases, which is used to desorb the fuel vapor as it is being sent to the engine for combustion.

[00118] The invention also contemplates the inclusion of and integration with other components which make up ORVR systems and devices. These other components may include active compressors and condensers, fuel tank heaters, fuel tank heat exchanging coils for cooling enclosed fuels, fuel filler necks, fuel filler ports, including capless fuel filler ports, vents for fuel vapors, fuel lines for sending fuel, fuel return lines, vents and vehicle rollover valves, fuel pumps, and air intake or purge valves.

[00119] The invention further contemplates devices and structures which may be combined with the sorbent material sheets to improve or control the adsorption and desorption of fluids and gases. For example, fans or pumps may be included to force the fluids or vapors over the sorbent material sheets as they are assembled, allowing the sorbent material sheets to be packed or wound tighter or allowing larger devices than would otherwise be possible with the same amount of fluid diffusion over the sheets. Alternatively, the devices can include resistance element heaters, or Peltier effect heaters or coolers which are designed to heat and/or cool the fluids and thus force their movement over the sorbent material sheets of the claimed invention. For instance, heated, expanding fluid may vent upwards and draw in more fluid at the bottom of a rolled or wound article that is oriented vertically to take advantage of the effects of gravity.

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OTHER USES

[00120] In addition to automotive uses, the inventors contemplate that the sorbent sheets of the claimed invention can be used in any instance where a tank or other enclosed space is designed to contain volatile liquids, in particular volatile hydrocarbons such as fuels, solvents, and other volatile compounds. Examples include but are not limited to fuel tanks in aircraft, fuel tanks in ships and other marine vehicles, fuel tanks in trucks, chemical tanks in railroad cars, barges, ships, trucks, vehicles, and other bulk carriers, and stationary chemical tanks. The sorbent material sheets of the claimed invention can also be attached or adhered to the walls of confined spaces where the presence of volatile compounds would be detrimental, for example, in chemical facilities where operators and maintenance staff must periodically access the space. Such sorbent material sheets, when used in such combined spaces, can not only increase safety for operators and maintenance staff, but they can also reduce the need for cumbersome protective gear.

EXAMPLES

[00121] Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

[00122] As was discussed above, BWC is a measure of the performance of activated carbon. BWC is determined for a sample by measuring the ability of the activated carbon to adsorb and desorb butane from dry air under specified conditions, and measures the difference between the butane adsorbed at saturated and the butane retained per unit volume of carbon after a specified purge. BWC can be tested in several ways, including procedures specified by ASTM International and which are known to those of skill in the art. Specifically, testing can follow ASTM D5228, which includes revisions D5228-16, D5228-92(2015), D5228-92(2005), and D5228-92(2000).

[00123] In Examples 1-4, the carbon sheets were spiral wound to yield 10% void fraction, which give about a 30% performance improvement over the activated carbons in their original, non-sheet form. The void fraction of comparative granular or powdered beds of activated carbon, similar to Comparative Example 1, was approximately 40% void fraction by volume. The Examples and Comparative Example are described below.

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EXAMPLE 1

[00124] Activated carbon sheets were made from CPL (CT#14299-8), which is an activated carbon that is wood based and which is activated using phosphoric acid. Sheets were also made from CPW (CT#14299-10), which is an activated carbon that is wood based and which is activated using phosphoric acid. The activated carbons were pulverized in a mechanical mortar and pestle and mixed with 9% PTFE powder. The resulting composition had a bread dough-like consistency. The composition was rolled to form sheets having thicknesses of 0.448 mm (CT#14299-8 1), 0.411 mm (CT#14299-8 2), 0.459 mm (CT#14299-10 1), and 0.439 mm (CT#14299-10 2).

EXAMPLE 2

[00125] Activated carbon sheets were prepared as described in Example 1 using BVC-11 8x25 activated carbon, which is a nutshell based activated carbon that is activated with phosphoric acid. This formed sample CT#14266-1. A sample was also formed with BVC-11 8x35, which is also a nutshell based activated carbon that is activated with phosphoric acid. This formed sample CT#14266-2. The formed sheets had a thickness of 0.330 mm (CT#14266-1 1), 0.334 mm (CT#14266-1 2), 0.327 mm (CT#14266-1 3), 0.317 mm (CT#14266-2 1), 0.307 mm (CT#14266-2 2), and 0.328 mm (CT#14266-2 3). As used herein, GAC is used to denote granular activated carbon, and PAC is used to denote powdered activated carbon.

[00126] Butane Working Test – Examples 1 and 2

[00127] Activated carbon sheets prepared in Examples 1 and 2 were tested for butane adsorption using the butane working test. In this test, the sheets were rolled and placed in tubes. Butane was added to the tubes and butane adsorption was measured. Results are illustrated in TABLES 1 and 2:

TABLE 1 (Example 2)

	14266-1	14266-2
Tube vol. (cm^3)	3.85	3.85
Sheet wt. (g)	6.3604	6.0009
Sheet thick. (mm)	0.330	0.315
Sheet vol. (cm^3)	11.22	10.71
Sheet dens. (g/cm^3)	0.567	0.567
BWC sheet	16.10	14.14

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measured ($g/100cm^3$)		
BWC GAC measured ($g/100cm^3$)	12.10	12.20

TABLE 2 (Example 1)

	CT-14299-8	CT-14299-10
Tube vol. (cm^3)	16.504	16.504
Sheet wt. (g)	4.10	3.16
Sheet thick. (mm)	0.411	0.439
Sheet vol. (cm^3)	9.92	7.90
Sheet dens. (g/cm^3)	0.413	0.404
BWC sheet measured ($g/100cm^3$)	12.32	12.41
BWC PAC measured ($g/100cm^3$)	7.9	9.6

EXAMPLE 3

[00128] Activated carbon sheets were prepared as in Examples 1 and 2, but using granular activated carbon #3445-32-4. The activated carbon sheets were also not rolled as tightly as in prior Examples 1 and 2, which The resultant sheets were tested for butane adsorption using the BWC test. In these two tests, two separate stacks of 20 sheets of 0.45mm thickness were cut in rectangles of 2.2cm X 7.5cm ± 10%, sealed at the side edge with double sided tape of 0.05mm thickness and 2mm width. In this configuration, tape thickness defined the average sheet spacing. Total height of each of the stacks of 20 sheets with tape spacers was 1 cm. These stacks of sheets were then placed in large 2.54cm diameter cylindrical glass tubes for butane adsorption/desorption testing. The excess volume between the rectangular stack of sheets and the walls of the cylindrical glass tube were filled with closed cell expanded foam to take up the excess volume and sealed to avoid bypass gas flow past the inserted test samples. The butane or air was forced to flow in the 0.05mm gaps between the 20 sheets. The flow rate and volume of the stacks of sheets was selected to conform to the BWC procedure. The BWC procedure was followed with the exception of the use of the stack of sheets rather than a granule bed, the use of the closed cell expanded foam

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for sealing, and the required larger cylindrical glass tube arrangement to accommodate the rectangular stack of sheets.

[00129] During the BWC procedure on the sheet stack, butane or air was forced to flow in the 0.05 mm gaps between the 20 sheets, with the flow rate and volume of the stacks of sheets kept to BWC procedure for working capacity. The results of Example 3 are in Table 3 below.

COMPARATIVE EXAMPLE 1

[00130] A comparative example was also prepared using the same granular activated carbon #3445-32-4 as in Example 4, but without forming the granular activated carbon as part of a sheet or roll. The granulated activated carbon was tested per BWC procedure. The results of this test are in Table 3 below.

TABLE 3 (Example 3 and Comparative Example 1)

	Granular activated carbon (Comparative Example 1)	Stacked 0.45mm sheets (Example 3)	
	#3445-32-4	#3445-32-4-stack 1	#3445-32-4-stack 2
Tube vol. minus foam volume if present(cm^3)	16.7	16.4	15.5
Carbon wt. (g)	6.513	7.885	7.465
Sheet thickness (mm)	---	0.45	0.45
Granular bed or Stacked sheet vol. (cm^3)	16.7	16.4	15.5
Granular bed or individual Sheet density (g/cm^3)	0.389	0.534	0.534
BWC ($g/100cm^3$)	9.33	10.25	10.83
BWC % improvement	---	9.9%	16.0%

[00131] Conclusion and Summary of Examples 1-3 and Comparative Example 1

[00132] A summary of relevant data appears in Table 4 below:

TABLE 4: Summary of Data

Example	**Test**	**Description**	**Sheet Thickness**	**Density (g/cm^3)**	**BWC ($g/100cm^3$)**

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			(mm)		
Ex. 1	CT#14299-8	Wood based activated carbon CPL	0.411	0.413	12.32
Ex. 1	CT#14299-10	Wood based activated carbon CPW	0.439	0.404	12.41
Ex. 2	CT#14266-1	BVC-11 (nutshell) activated carbon 8x25	0.330	0.567	16.10
Ex. 2	CT#14266-2	BVC-11 (nutshell) activated carbon 8x35	0.315	0.567	14.14
Ex. 3	#3445-32-4-stack 1	GAC, 20 sheet stack	0.45	0.534	10.25
Ex. 3	#3445-32-4 stack 2	GAC, 20 sheet stack	0.45	0.534	10.83
Comp. Ex. 1	#3445-32-4	Granular Activated Carbon (GAC)	N/A	0.389	9.33

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J. CLAIMS

1. A vapor adsorbing canister comprising:
   a first sorbent;
   a second sorbent; and
   wherein during an adsorption or a desorption operation, the linear velocity of gases is higher in the second sorbent than in the first sorbent; and
   wherein the first sorbent and the second sorbent each individually have an incremental adsorption capacity of greater than 35 g n-butane/L between vapor concentrations of 5 vol.% and 50 vol.% n-butane.

2. The vapor adsorbing canister of claim 1, wherein:
   each of the first sorbent and the second sorbent include a binder that comprises polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers, perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid polymers, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, or copolymers or combinations thereof, and
   wherein the binder of the first and the second sorbent is the same or different.

3. The vapor adsorbing canister of claim 1, wherein the first sorbent and the second sorbent each individually include less than or equal to about 20 wt.% of binder.

4. The vapor adsorbing canister of claim 3, wherein the first sorbent and the second sorbent each individually include greater than or equal to about 80 wt.% of sorbent material.

5. The vapor adsorbing canister of claim 1, wherein the first sorbent and the second sorbent each individually include less than or equal to about 10 wt.% of binder.

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6. The vapor adsorbing canister of claim 5, wherein the first sorbent and the second sorbent each individually include greater than or equal to about 90 wt.% of sorbent material.

7. The vapor adsorbing canister of claim 1, wherein the second sorbent is in the form of a sheet.

8. The vapor adsorbing canister of claim 1, wherein the second sorbent is in the form of a sheet that is corrugated, textured, folded, has apertures, wrapped in an "S" shape, in a convex "C" shape, in a concave "C" shape, rolled, has spacers between multiple sheets, and combination of the above features.

9. The vapor adsorbing canister of claim 1, wherein the second sorbent is in the form of a sheet, said sheet including sorbent particles having an average particle diameter of about 0.001 mm to about 0.2 mm.

10. The vapor adsorbing canister of claim 1, wherein the second sorbent is in the form of a sheet having raised and/or depressed portions.

11. The vapor adsorbing canister of claim 10, wherein the raised and/or depressed portions are present on adjacent sheets and are nested.

12. The vapor adsorbing canister of claim 10, wherein the raised and/or depressed portions are present on adjacent sheets and are not nested.

13. The vapor adsorbing canister of claim 1, wherein the second sorbent is in the form of a sheet having a void volume of about 10% or more.

14. The vapor adsorbing canister of claim 1, wherein the second sorbent is in the form of a sheet having a density of about 0.08 g/cm^3 to about 1.5 g/cm^3.

15. The vapor adsorbing canister of claim 1, wherein the first sorbent and the second sorbent are each separately selected from the group consisting of activated carbon, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, diatomaceous earths, and combinations thereof.

16. The vapor adsorbing canister of claim 1, further comprising a housing.

17. The vapor absorbing canister of claim 16, wherein the housing is flexible.

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18. The vapor adsorbing canister of claim 17, wherein the housing is selected from the group consisting of polytetrafluoroethylenes (PTFE or TEFLON), polyvinylidene fluorides (PVF_2 or PVDF), ethylene-propylene-diene (EPDM) rubbers, polyethylene oxides (PEO), UV curable acrylates, UV curable methacrylates, heat curable divinyl ethers, polybutylene terephthalate, acetal or polyoxymethylene resin, fluoroelastomers perfluoroelastomers (FFKM) and/or tetrafluoro ethylene/propylene rubbers (FEPM), aramid polymers, para-aramid, meta-aramid polymers, poly trimethylene terephthalate, ethylene acrylic elastomers, polyimide, polyamide-imides, polyurethanes, low density and high density polyethylene, polypropylene, biaxially oriented polypropylene (BoPP), polyethylene terephthalate (PET), biaxially oriented polyethylene terephthalate (BoPET), polychloroprene, copolymers thereof, and combinations thereof.

19. The vapor adsorbing canister of claim 1, further comprising at least one structure selected from tubes, inlet ports, outlet ports, sensors, valves, and fluid channels.

20. An onboard refueling vapor recovery apparatus comprising the vapor adsorbing canister of claim 1.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US19/44964

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01J 20/00, 20/02, 20/28; B01D 53/02, 53/04, 53/14 (2019.01)

CPC - B01J 20/02, 20/28, 20/2803, 20/28033, 20/28035, 20/2804, 20/2805, 20/28052; F02M 25/0854; B01D 53/04, 53/0407, 53/14, 53/1406

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2018/0030871 A1 (INGEVITY SOUTH CAROLINA, LLC.) 01 February 2018; abstract; figure 11; paragraphs [0023]-[0024], [0034], [0036], [0040], [0051], [0053], [0084], [0104]; claim 18	1-20
Y	US 8,864,877 B2 (KURARAY CHEMICAL CO., Ltd.) 21 October 2014; abstract; column 1, lines 16-21, 31-35; column 5, lines 1-5, 44-56; column 6, lines 21-29; column 7, lines 39-52; claims 2, 20	1-20
Y	US 7,077,891 B2 (JAFFE, SM et al.) 18 July 2006; abstract; figure 4; column 4, lines 51-56; column 5, lines 5-6; column 6, lines 37-51, 56-67; column 7, line 1; column 8, lines 28-33; column 10, lines 12-15, 33-37; column 11, lines 17-33	2-6, 9, 13-14
Y	US 6,406,523 B2 (CONNOR, DJ et al.) 18 June 2002; abstract; column 3, lines 21-25; claim 29	11
Y	US 2008/0308075 A1 (ALLEN, CD et al.) 18 December 2008; abstract; paragraphs [0041]-[0041]	17-18
P, Y	WO 2018/144588 A1 (CALGON CARBON CORPORATION) 09 August 2018; entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 September 2019 (17.09.2019)	18 OCT 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas Telephone No. PCT Helpdesk: 571-272-4300

Form PCT/ISA/210 (second sheet) (July 2019)

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Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
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Receipt Date:	23-NOV-2021
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Application Type:	Utility under 35 USC 111(a)

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File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	Supplemental_Information_Disclosure_Statement.pdf	21146 b4650a1a393d6fa9cceeec46cae44ad789f70bb5	no	2

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	12345013001_-_11_23_2021_-_Information_Disclosure_Statement_Fillable_PDF.pdf	1108543 bff362b9ee733e3026b4a46c87d9dab420247c8d	no	14
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Information:					
3	Foreign Reference	12345012501_-_04_02_2020_-_CA2485103A1.pdf	1096783 be9b43e5302c20a4feedeed41577ac9c590b2e70	no	34
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Information:					
4	Foreign Reference	12345003701_-_10_30_2019_-_DE3620425C1.pdf	250582 56df0731325f8b027892c75cf84ee30cb76a1b0f	no	5
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5	Foreign Reference	12345012301_-_EP0433677A1.pdf	1124581 3b84377c463a312472d9d3528503fcc085955dc0	no	20
Warnings:					
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6	Foreign Reference	12345012902_-_10_25_2019_-_EP1413348A1.pdf	346722 440beb02f7213646aff3147df1e332e576d732db	no	27
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Information:					
7	Foreign Reference	12345012301_-_GB1336241.pdf	2862835 0b14d4816c083401d83008c84bd1b51c4dff26de8	no	22
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Information:					
8	Foreign Reference	12345012301_-_11_13_2019_-_JP2008023365A.pdf	1918502 d826a5046589cba5a562eebb995a1ead9906fd1d	no	41
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Information:					

9	Foreign Reference	12345012501_-_04_02_2020_-_JPH01-058331TranslatedAbstract.pdf	268952 94e404ebad915addf4a21d2cd4ad8a33ab008315	no	4
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10	Foreign Reference	12345012301_-_WO2010042321A1.pdf	355056 28deb3f00e5a143e6f9539859dcee4f6859a95da	no	47
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11	Foreign Reference	12345012301_-_WO2011038415A2.pdf	287195 b9298a9b1f2fcb2dd13d125ee691e0336ea0a435	no	26
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Information:					
12	Foreign Reference	12345000701_-_WO2011127323A2.pdf	1232418 38b689741d11d0ce19d6dec56cd8c542c4763dc1	no	24
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Information:					
13	Foreign Reference	12345012301_-_WO2013063490A1.pdf	2435460 9362a156f4dc56e863d271b7fa4bab36cfeefa7e	no	44
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14	Foreign Reference	12345010301_-_WO2014082076A1.pdf	1892836 ab987e799654c81d89822d4d3bdd244da9692743	no	46
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Information:					
19	Foreign Reference	12345012802_-_02_12_2020_-_WO2020-028839A112802_pub.pdf	2320240 3af20e68a8c86c343a1fdd4643aef094b6efddee	no	45
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21	Non Patent Literature	12345012601_-_ChemistryofNitrogen1.pdf	673680 5bb91ed71bd9f1dcab1a8b6a8dcc5c10e9e86be8	no	16
Warnings:					
Information:					
22	Non Patent Literature	12345012301_-_Raposo879.pdf	173412 54f122f3858de58bb43c420b99739be3f853b655	no	8
Warnings:					
Information:					

23	Non Patent Literature	12345012511_-_07_29_2020_-_Sharifi8904.pdf	106158 7975cfe4c48427fbaeabc17cb30e665c7bed697e	no	2
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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Docket No.: 123450.013001
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Rebecca L. DISTEFANO et al.

Application No.: 16/839,862 | Confirmation No.: 5111

Filed: April 3, 2020 | Art Unit: OPAP

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE | Examiner: Not Yet Assigned

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT (IDS)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

Pursuant to 37 C.F.R. §§ 1.56, 1.97, and 1.98, the attention of the United States Patent and Trademark Office is hereby directed to the references listed on the attached PTO/SB/08. It is respectfully requested that the information be expressly considered during the prosecution of the above-identified application, and that the references be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

This Information Disclosure Statement is filed before the mailing date of a first Office Action on the merits (37 C.F.R. § 1.97(b)(3)).

In accordance with 37 C.F.R. § 1.98(a)(2)(ii), copies of U.S. patents and U.S. patent application publications are not submitted. Submitted herewith are copies of foreign patents and non-patent literature in accordance with 37 C.F.R. § 1.98(a)(2).

A summary/abstract translation of the non-English language references is attached.

In accordance with 37 C.F.R. § 1.97(g), the filing of this Information Disclosure Statement shall not be construed as a representation that a search has been made. In accordance with 37 C.F.R. § 1.97(h), the filing of this Information Disclosure Statement shall not be construed to be an admission that the information cited in this Information Disclosure Statement is, or is considered to be, material to patentability as defined in 37 C.F.R. § 1.56(b).

It is submitted that the Information Disclosure Statement is in compliance with 37 C.F.R. § 1.98, and the Examiner is respectfully requested to consider the listed references.

Applicant believes no fee is due with this response. However, if a fee is due, please charge our Deposit Account No. 50-0436, under Order No. 123450.013001 from which the undersigned is authorized to draw.

Dated: November 23, 2021

Respectfully submitted,

Electronic signature: /Nicholas Kokkinos/
Nicholas C. Kokkinos
Registration No.: 76,979
TROUTMAN PEPPER HAMILTON SANDERS LLP
501 Grant Street
Suite 300
Union Trust Building
Pittsburgh, Pennsylvania 15219-4429
412.454.5000
412.454.5060 (Fax)
Nicholas.Kokkinos@Troutman.com (E-Mail)

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01078

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450.013001

CONFIRMATION NO. 5111

93724
TROUTMAN PEPPER HAMILTON SANDERS LLP/Calgon
Suite 300, Union Trust Building
501 Grant Street
Pittsburgh, PA 15219-4429

PUBLICATION NOTICE

OC000000120509739

Title:PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Publication No.US-2020-0316560-A1
Publication Date:10/08/2020

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Public Records Division. The Public Records Division can be reached by telephone at (571) 272-3150 or (800) 972-6382, by facsimile at (571) 273-3250, by mail addressed to the United States Patent and Trademark Office, Public Records Division, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently https://portal.uspto.gov/pair/PublicPair. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01079

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450.013001

CONFIRMATION NO. 5111

93724
TROUTMAN PEPPER HAMILTON SANDERS LLP/Calgon
Suite 300, Union Trust Building
501 Grant Street
Pittsburgh, PA 15219-4429

POA ACCEPTANCE LETTER

OC000000119311709

Date Mailed: 08/20/2020

NOTICE OF ACCEPTANCE OF POWER OF ATTORNEY

This is in response to the Power of Attorney filed 08/17/2020.

The Power of Attorney in this application is accepted. Correspondence in this application will be mailed to the above address as provided by 37 CFR 1.33.

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/snguyen/

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01080

PTO/AIA/80 (07-12)
Approved for use through 11/30/2014. OMB 0651-0035
U.S. Patent and Trademark Office; U.S DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

POWER OF ATTORNEY TO PROSECUTE APPLICATIONS BEFORE THE USPTO

I hereby revoke all previous powers of attorney given in the application identified in the attached statement under 37 CFR 3.73(c).

I hereby appoint:

■ Practitioners associated with Customer Number: 93724

OR

☐ Practitioner(s) named below (if more than ten patent practitioners are to be named, then a customer number must be used):

Name	Registration Number	Name	Registration Number

As attorney(s) or agent(s) to represent the undersigned before the United States Patent and Trademark Office (USPTO) in connection with any and all patent applications assigned only to the undersigned according to the USPTO assignment records or assignments documents attached to this form in accordance with 37 CFR 3.73(c).

Please change the correspondence address for the application identified in the attached statement under 37 CFR 3.73(c) to:

■ The address associated with Customer Number: 93724

OR

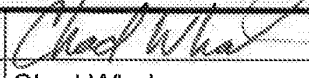
☐	Firm or Individual Name		
	Address		
	City	State	Zip
	Country		
	Telephone	Email	

Assignee Name and Address: Calgon Carbon Corporation
3000 GSK Drive
Moon Township, PA 15108

A copy of this form, together with a statement under 37 CFR 3.73(c) (Form PTO/AIA/96 or equivalent) is required to be Filed in each application in which this form is used. The statement under 37 CFR 3.73(c) may be completed by one of The practitioners appointed in this form, and must identify the application in which this Power of Attorney is to be filed.

SIGNATURE of Assignee of Record

The individual whose signature and title is supplied below is authorized to act on behalf of the assignee

Signature		Date	October 3, 2016
Name	Chad Whalen	Telephone	412-787-6787
Title	Senior Vice President, General Counsel & Secretary		

This collection of information is required by 37 CFR 1.31, 1.32 and 1.33. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/AIA/96 (08-12)
Approved for use through 01/31/2013. OMB 0651-0031
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STATEMENT UNDER 37 CFR 3.73(c)

Applicant/Patent Owner: CALGON CARBON CORPORATION

Application No./Patent No.: 16/839,862 Filed/Issue Date: April 3, 2020

Titled: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

CALGON CARBON CORPORATION, a corporation

(Name of Assignee) (Type of Assignee, e.g., corporation, partnership, university, government agency, etc.)

states that, for the patent application/patent identified above, it is (choose **one** of options 1, 2, 3 or 4 below):

1. ☑ The assignee of the entire right, title, and interest.

2. ☐ An assignee of less than the entire right, title, and interest (check applicable box):

   ☐ The extent (by percentage) of its ownership interest is _____%. Additional Statement(s) by the owners holding the balance of the interest must be submitted to account for 100% of the ownership interest.

   ☐ There are unspecified percentages of ownership. The other parties, including inventors, who together own the entire right, title and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

3. ☐ The assignee of an undivided interest in the entirety (a complete assignment from one of the joint inventors was made). The other parties, including inventors, who together own the entire right, title, and interest are:

   Additional Statement(s) by the owner(s) holding the balance of the interest must be submitted to account for the entire right, title, and interest.

4. ☐ The recipient, via a court proceeding or the like (*e.g.*, bankruptcy, probate), of an undivided interest in the entirety (a complete transfer of ownership interest was made). The certified document(s) showing the transfer is attached.

The interest identified in option 1, 2 or 3 above (not option 4) is evidenced by either (choose **one** of options A or B below):

A. ☐ An assignment from the inventor(s) of the patent application/patent identified above. The assignment was recorded in the United States Patent and Trademark Office at Reel _____, Frame _____, or for which a copy thereof is attached.

B. ☑ A chain of title from the inventor(s), of the patent application/patent identified above, to the current assignee as follows:

1. From: Rebecca L. DiStefano To: Calgon Carbon Corporation

   The document was recorded in the United States Patent and Trademark Office at

   Reel 053091, Frame 0504, or for which a copy thereof is attached.

2. From: Richard A. Mimna To: Calgon Carbon Corporation

   The document was recorded in the United States Patent and Trademark Office at

   Reel 053091, Frame 0601, or for which a copy thereof is attached.

This collection of information is required by 37 CFR 3.73(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 12 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

PTO/AIA/96 (08-12)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

STATEMENT UNDER 37 CFR 3.73(c)

3. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

4. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

5. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

6. From: _____ To: _____

The document was recorded in the United States Patent and Trademark Office at

Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet(s).

☐ As required by 37 CFR 3.73(c)(1)(i), the documentary evidence of the chain of title from the original owner to the assignee was, or concurrently is being, submitted for recordation pursuant to 37 CFR 3.11.

[NOTE: A separate copy (i.e., a true copy of the original assignment document(s)) must be submitted to Assignment Division in accordance with 37 CFR Part 3, to record the assignment in the records of the USPTO. See MPEP 302.08]

The undersigned (whose title is supplied below) is authorized to act on behalf of the assignee.

/Nicholas Kokkinos/	2020-08-17
Signature	Date
Nicholas C. Kokkinos	76,979
Printed or Typed Name	Title or Registration Number

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/AIA/01 (06-12)
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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 16/839,862

filed on April 3, 2020.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Rebecca L. DiSTEFANO Date (Optional) :

Signature:

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Privacy Act Statement

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

PTO/AIA/01 (06-12)
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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 16/839,862 filed on April 3, 2020.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Richard A. MIMNA Date (Optional): 4-27-20

Signature: 

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt

EFS ID:	40297292
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
Filer Authorized By:	Nicholas Charalambos Kokkinos
Attorney Docket Number:	123450.013001
Receipt Date:	17-AUG-2020
Filing Date:	03-APR-2020
Time Stamp:	10:16:21
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Miscellaneous Incoming Letter	123450-013001_SubmissionFormalities.pdf	15222 14978f7df2cd2cc6cbb85733e43b335bf9a1d8e9	no	1

Warnings:

Information:					
2	Power of Attorney	CCC_GeneralPOA_3000GSK.pdf	200625 4fc1820a7cf4da90aaafbcb17e3da5853cea005b	no	2
Warnings:					
Information:					
3	Assignee showing of ownership per 37 CFR 3.73	123450-013001_AssigneeStatement.pdf	126007 9bf662c0e17f85cc4fcb389ea78b331323d2b56a	no	3
Warnings:					
Information:					
4	Oath or Declaration filed	DiStefanoExecutedDeclaration.pdf	97105 fedd62b31a5a723ed5fffd0d3b3b78799fc5ddb7	no	2
Warnings:					
Information:					
5	Oath or Declaration filed	MimnaExecutedDeclaration.pdf	97878 2533e168d041c7bb2a919d05bb33f6f8c3a7ecbb	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	536837		

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Attorney Docket No.: 123450.13001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Rebecca L. DISTEFANO et al.
Application No.	:	16/839,862
Filed	:	April 3, 2020
Group Art Unit	:	1736
Confirmation No.	:	5111
Examiner	:	Not Assigned Yet

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

SUBMISSION OF POWER OF ATTORNEY, ASSIGNEE STATEMENT AND DECLARATIONS

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

Applicant respectfully submits the attached Power of Attorney, and Statement Under 3.73(c), for Calgon Carbon Corporation in the above-identified application.

Also submitted with this filing are the Declarations executed by the named inventors.

The late filing fee for the Declarations was paid on April 3, 2020; therefore, Applicant believe no fees are associated with this filing. However, please charge any shortage in fees due or credit any excess fees in connection with the filing of these papers to Deposit Account No. 50-0436.

Respectfully submitted,

/Nicholas Kokkinos/

Nicholas Kokkinos
Registration No. 76,979

Troutman Pepper Hamilton Sanders LLP
Union Trust Building
501 Grant Street, Suite 300
Pittsburgh, PA 15219-4429
Telephone: (412) 454-5000
Facsimile: (412) 454-5060
Date: August 17, 2020

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1736
Examiner Name	Not Yet Assigned
Attorney Docket Number	123450.013001

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	2	20130316433	A1	2013-11-28	Huang	

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	1	3077069	FR	A1	2019-07-26	Commissariat Energie Atomique	w/English Abstract	X
	2	2017180346	WO	A1	2017-10-19	Emerging Compounds Treatment Technologies, Inc		☐

EFS Web 2.1.18

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1736
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

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	1	JOHNSON et al., "Advanced Filtration Membranes for the Removal of Perfluoroalkyl Species from Water", American Chemical Society, ACS Omega, May 2, 2019, Vol. 4(5), pp. 8001-8006	
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INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1736
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.013001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

☒ That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2020-07-27
Name/Print	Nicholas C. Kokkinos	Registration Number	76,979

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01096

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Bibliographic data: FR3077069 (A1) — 2019-07-26

PROCEDE D'EXTRACTION DE COMPOSES ORGANIQUES FLUORES A PARTIR D'UN MILIEU AQUEUX LES CONTENANT.

Inventor(s): CARBONI MICKAEL [FR]; BOURGEOIS DAMIEN [FR]; MEYER DANIEL [FR]; SINI KARIMA [DZ] ± (CARBONI, MICKAEL, ; BOURGEOIS, DAMIEN, ; MEYER, DANIEL, ; SINI, KARIMA)

Applicant(s): COMMISSARIAT ENERGIE ATOMIQUE [FR]; UNIV DES SCIENCES ET DE LA TECHNOLOGIE HOUARI BOUMEDIENE [DZ] ± (COMMISSARIAT A L'ENERGIE ATOMIQUE ET AUX ENERGIES ALTERNATIVES, ; UNIVERSITE DES SCIENCES ET DE LA TECHNOLOGIE HOUARI BOUMEDIENE)

Classification: **- international:** ***B01D15/00; B01J20/22; C02F1/28; C02F1/58; C02F101/36***

- cooperative: **B01D17/00 (EP)**; **B01J20/22 (EP)**; **B01J20/226 (EP)**; **B01J20/3425 (EP)**; **C02F1/285 (EP)**; C02F2101/36 (EP); C02F2305/08 (EP)

Application number: FR20180050511 20180123

Priority number(s): FR20180050511 20180123

Abstract of FR3077069 (A1)

Procédé d'extraction de composés organiques fluorés, notamment perfluorés, à partir d'un milieu aqueux les contenant, comprenant au moins une étape de mise en contact au cours de laquelle on met en contact le milieu aqueux avec un composé extractant solide, dans lequel ledit composé extractant solide est choisi parmi le UiO-66, le UiO-66-(F4), le UiO-67, et leurs mélanges, moyennant quoi lesdits composés organiques fluorés sont adsorbés dans ledit composé extractant solide.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01097

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Notice

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ABSTRACT FR3077069

Process for extracting fluorinated organic compounds, in particular perfluorinated, from an aqueous medium containing them, comprising at least one contacting step during which the aqueous medium is brought into contact with a solid extracting compound, in which said solid extracting compound is chosen from UiO-66, UiO-66- (F4), UiO-67, and mixtures thereof, whereby said fluorinated organic compounds are adsorbed in said solid extracting compound.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01098

(19) RÉPUBLIQUE FRANÇAISE

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DE LA PROPRIÉTÉ INDUSTRIELLE

COURBEVOIE

(11) **N° de publication :** **3 077 069**
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(51) Int Cl[8] : ***C 02 F 1/28*** *(2018.01), B 01 D 15/00, B 01 J 20/22, C 02 F 1/58, 101/36*

(12) DEMANDE DE BREVET D'INVENTION A1

(22) **Date de dépôt :** 23.01.18.

(30) **Priorité :**

(43) **Date de mise à la disposition du public de la demande :** 26.07.19 Bulletin 19/30.

(56) **Liste des documents cités dans le rapport de recherche préliminaire :** *Se reporter à la fin du présent fascicule*

(60) **Références à d'autres documents nationaux apparentés :**

◯ **Demande(s) d'extension :**

(71) **Demandeur(s) :** *COMMISSARIAT A L'ENERGIE ATOMIQUE ET AUX ENERGIES ALTERNATIVES Etablissement public* — FR et *UNIVERSITE DES SCIENCES ET DE LA TECHNOLOGIE HOUARI BOUMEDIENE Etablissement public* — DZ.

(72) **Inventeur(s) :** CARBONI MICKAEL, BOURGEOIS DAMIEN, MEYER DANIEL et SINI KARIMA.

(73) **Titulaire(s) :** COMMISSARIAT A L'ENERGIE ATOMIQUE ET AUX ENERGIES ALTERNATIVES Etablissement public, UNIVERSITE DES SCIENCES ET DE LA TECHNOLOGIE HOUARI BOUMEDIENE Etablissement public.

(74) **Mandataire(s) :** BREVALEX Société à responsabilité limitée.

(54) PROCEDE D'EXTRACTION DE COMPOSES ORGANIQUES FLUORES A PARTIR D'UN MILIEU AQUEUX LES CONTENANT.

(57) Procédé d'extraction de composés organiques fluorés, notamment perfluorés, à partir d'un milieu aqueux les contenant, comprenant au moins une étape de mise en contact au cours de laquelle on met en contact le milieu aqueux avec un composé extractant solide, dans lequel ledit composé extractant solide est choisi parmi le UiO-66, le UiO-66-(F4), le UiO-67, et leurs mélanges, moyennant quoi lesdits composés organiques fluorés sont adsorbés dans ledit composé extractant solide.

FR 3 077 069 - A1

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01099

PROCEDE D'EXTRACTION DE COMPOSES ORGANIQUES FLUORES A PARTIR D'UN MILIEU AQUEUX LES CONTENANT.

DESCRIPTION

DOMAINE TECHNIQUE

L'invention concerne un procédé d'extraction de composés organiques fluorés, notamment perfluorés à partir d'un milieu aqueux, tel que de l'eau ou une solution aqueuse, les contenant.

Plus précisément, l'invention concerne un procédé d'extraction de polluants fluorés, notamment de polluants perfluorés à partir d'un milieu aqueux les contenant en mettant en contact ce milieu aqueux avec un composé extractant solide.

Ces composés organiques fluorés peuvent être des composés comprenant au moins un groupe alkyle fluoré, notamment un groupe alkyle perfluoré.

Ces composés qui comprennent au moins un groupe alkyle fluoré sont plus simplement appelés composés alkylfluorés.

Un groupe alkyle fluoré est un groupe alkyle dans lequel les atomes d'hydrogène de ce groupe alkyle ont été substitués partiellement, ou totalement par des atomes de fluor.

Lorsque tous les atomes d'hydrogène de ce groupe alkyle ont été substitués par des atomes de fluor alors ce groupe alkyle fluoré est appelé groupe alkyle perfluoré ou groupe perfluoroalkyle.

Plus particulièrement, lesdits composés alkylfluorés sont des composés appelés composés perfluorés, c'est-à-dire des composés comprenant un ou plusieurs groupes alkyle fluorés, tous ces groupes alkylfluorés étant des groupes alkyle perfluorés, c'est-à-dire dans lesquels tous les atomes d'hydrogène ont été remplacés par des atomes de fluor.

Ces composés perfluorés peuvent cependant comprendre des atomes d'hydrogène qui n'ont pas été remplacés par des atomes de fluor, par exemple des atomes d'hydrogène qui ne font pas partie de groupes alkyle, par exemple des atomes d'hydrogène qui font partie de groupes carboxyle, sulfonate, ou hydroxyle.

En d'autres termes, plus généralement, lorsque tous les atomes d'hydrogène d'un composé organique ont été remplacés, substitués par des atomes de fluor, alors ce

composé est appelé composé perfluoré, mais ce composé perfluoré peut cependant comprendre des atomes d'hydrogène qui n'ont pas été remplacés par des atomes de fluor, par exemple des atomes d'hydrogène qui ne font pas partie de groupes alkyle, par exemple des atomes d'hydrogène qui font partie de groupes carboxyle, sulfonate, ou hydroxyle.

Les composés perfluorés peuvent être en particulier le sulfonate de perfluorooctane (« *PerFluoroOctane Sulfonate* » ou « *PFOS* ») et l'acide perfluorooctanoïque (« *PerFluroOctanoic Acid* » ou « *PFOA* »).

Ces deux composés PFOS et PFOA sont regroupés sous le terme PFOX dans ce qui suit.

ÉTAT DE LA TECHNIQUE ANTÉRIEURE

Les composés alkylfluorés et notamment les composés perfluorés sont des molécules anthropogéniques qui sont synthétisées industriellement depuis les années 40.

Du fait de leurs résistances thermiques et chimiques élevées, ces molécules ont de nombreuses applications industrielles et domestiques diverses, par exemple dans les mousses anti-incendie, dans l'industrie textile ou encore dans l'électronique.

Parmi ces molécules, les composés les plus connus sont le sulfonate de perfluorooctane (« *PerFluoroOctane Sulfonate* » ou « *PFOS* ») et l'acide perfluorooctanoïque (« *PerFluroOctanoic Acid* » ou « *PFOA* »), regroupés sous le terme PFOX.

Ces molécules qui proviennent pour l'essentiel de la dégradation de biens de consommation les contenant, sont rejetées dans les eaux de surface, notamment par l'intermédiaire des effluents de stations d'épuration des eaux industrielles ou urbaines.

Ces molécules telles que le PFOA et le PFOS présentent un grave problème pour l'environnement et pour l'homme.

En effet, ces molécules sont très stables dans l'environnement et, du fait de leur faible volatilité et de leur solubilité dans l'eau, elles sont persistantes et très résistantes aux dégradations environnementales courantes. En outre, la biodégradation de ces molécules est très difficile à cause de la grande stabilité de la liaison C-F.

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La demi-vie des PFOX dans les écosystèmes aquatiques est de plus de 40 ans pour une dégradation par hydrolyse, et de 3,7 ans pour une dégradation par photolyse.

Comme ils se lient facilement à de nombreux matériaux, on a constaté que ces composés étaient bioaccumulatifs et qu'ils s'accumulaient en particulier dans des organes cibles (par exemple le foie) ou dans les fluides corporels, comme par exemple le sang.

Ces molécules sont très persistantes dans le corps humain, puisque la demi-vie du PFOA dans le corps humain a été estimée à presque environ 4 ans.

Ces composés sont très toxiques et ont été reliés à de nombreux problèmes de santé y compris certains cancers.

De nos jours, la présence de PFOX dans l'environnement est due principalement à des activités et à des usages antérieurs à 2002, date à laquelle la société BASF a arrêté la production de ces composés.

Une enquête sur la présence de ces composés dans les eaux destinées à la consommation humaine menée par l'ANSES en 2009 a fait ressortir que 25% des échantillons d'eau brute analysés avaient une teneur en PFOX supérieure à la limite réglementaire.

Il est estimé que de 40 à 200 tonnes de ces molécules ont été rejetées dans la nature pendant la période de production entre 1960-2002.

Il est donc nécessaire de décontaminer les rejets environnementaux dus à la production de ces molécules dans le passé ainsi que les eaux contenant ces molécules.

De nombreuses techniques ont été proposées pour éliminer ces polluants de l'eau comme l'adsorption, la séparation, la dégradation notamment biologique, l'oxydation ou la réduction.

L'extraction de ces polluants se fait majoritairement par des techniques de séparation solide/liquide du fait de leur présence dans des milieux très dilués.

Les techniques classiques comme la dégradation biologique, l'oxydation ou la réduction ne peuvent pas être utilisées à cause de la stabilité importante de ces composés, comme on l'a déjà précisé plus haut.

Cependant, il a été démontré que l'adsorption est la technique la plus efficace et la plus économique pour retirer ces polluants d'eaux usées.

La démarche la plus courante est d'utiliser des matériaux commerciaux connus pour leurs propriétés adsorbantes mais le résultat est peu efficace.

Parmi ces matériaux commerciaux connus, on peut citer le charbon actif, les résines, les matériaux minéraux, les biomatériaux et les polymères amorphes.

Le charbon actif : c'est le matériau le plus couramment utilisé comme adsorbant à cause de son faible coût. Ce matériau non polaire est très bien adapté à l'extraction de ces polluants fluorés hydrophobes. Le charbon actif a notamment été utilisé par la société 3M pour extraire le PFOS et le PFOA avec une efficacité d'extraction de 99% dans certaines conditions d'utilisation.

Un des inconvénients les plus importants du charbon actif est qu'il est très difficile à régénérer après l'adsorption.

Les résines : des résines échangeuses d'anions ou des résines neutres ont montré une efficacité d'adsorption plus importante que les charbons actifs. Cependant, les résines échangeuses d'anions ne présentent pas de sélectivité particulière, et les résines neutres, généralement basées sur des fonctionnalités fluorées, sont des matériaux coûteux. En outre, il est nécessaire d'utiliser du méthanol pour régénérer ces derniers matériaux.

Les matériaux minéraux : ces matériaux minéraux tels que les silices, zéolithes, montmorillonites..., présentent une capacité d'adsorption généralement inférieure au charbon actif. La fonctionnalisation et la mise en forme de ce type de matériau à l'aide surfactants cationiques est une technique qui est utilisée pour obtenir des matériaux extractants plus efficaces, mais qui sont alors moins sélectifs et plus coûteux.

Les matériaux « bio-sourcés » : ces matériaux, comme les chitosane et ses dérivés, ont été proposés en raison de leur grande disponibilité, mais ils présentent des performances d'extraction et de séparation médiocres.

Les polymères amorphes : ces polymères, fonctionnalisés avec des molécules capables d'extraire sélectivement les PFOX ont été également développés mais ont pour inconvénient la faible répétabilité de leurs synthèses ainsi qu'un coût élevé.

Par ailleurs, une nouvelle classe de nanomatériaux connaît un essor considérable depuis une vingtaine d'années, il s'agit des polymères de coordination (« PCs », ou « MOFs » pour *Metal-Organic Frameworks* en anglais).

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Ces matériaux cristallins sont composés de métaux ou d'amas ("*clusters*") de métaux organisés autour de ligands organiques.

Autrement dit les "*Metal–organic frameworks (MOFs)*" sont des structures tridimensionnelles construites avec un ligand organique et des nœuds contenant un métal, aussi appelés « *Secondary Building Units* », ou « *SBU* » reliés ensemble par des liaisons fortes.

Ces matériaux ont pour principaux avantages de posséder une très grande surface interne, une porosité élevée, et une grande stabilité. Ces matériaux sont robustes et ont des propriétés facilement modulables selon la nature du ligand organique.

Ces matériaux ont créé une réelle rupture technologique par rapport aux Zéolites avec des applications diverses par exemple dans le stockage ou la séparation des gaz, l'extraction de molécules ou de métaux, en catalyse ou bien encore en biologie.

En particulier, ces matériaux se sont récemment avérés être des candidats sérieux pour l'extraction de métaux ou de molécules polluantes, notamment de polluants organiques dans des milieux aqueux.

Plus précisément, un « *MOF* » particulier a récemment permis l'adsorption et la séparation du PFOA dans un milieu aqueux, à savoir une eau usée.

Ce MOF à bas de chrome, dénommé MIL-101(Cr), est obtenu par deux procédés de synthèse différents, à savoir par un procédé de synthèse directe ou par un procédé mettant en œuvre des méthodes post-synthétiques.

Dans les conditions d'utilisation, ce matériau a permis d'atteindre une capacité d'adsorption de 1,19 mmol/g de PFOA pour le matériau obtenu par un procédé de synthèse directe et de 1,89 mmol/g de PFOA pour le matériau obtenu par un procédé mettant en œuvre des méthodes post-synthétiques, avec une capacité d'adsorption rapide de 60 minutes.

Ce matériau a été utilisé trois fois de suite avec une perte totale de 10% d'efficacité.

Ce MOF présente les avantages de posséder un grand volume de cellule, une surface spécifique très importante, et des sites de chrome insaturé qui lui donnent des propriétés chélatantes intéressantes pour l'adsorption de molécules.

Mais l'utilisation de ce matériau présente l'inconvénient de pouvoir potentiellement relarguer du chrome dans l'environnement lors d'une utilisation de longue durée.

Très récemment, des MOFs basés sur des ligands imidazoles ont été utilisés pour l'extraction de PFOX, mais ils présentent une faible stabilité due à la liaison faible entre le ligand et le métal.

Il existe donc, au regard de ce qui précède, un besoin pour un procédé d'extraction de composés organiques fluorés, notamment perfluorés, à partir d'un milieu aqueux les contenant, à l'aide de composés extractants solides qui présente entre autres une grande efficacité, une sélectivité élevée, une cinétique d'extraction, adsorption rapide, et qui mette en œuvre des composés extractants solides notamment thermiquement et mécaniquement stables, non toxiques, facilement régénérables, faciles à produire à une échelle industrielle, et de préférence d'un coût peu élevé.

Le but de la présente invention est de fournir un procédé d'extraction de composés organiques fluorés, notamment perfluorés, à partir d'un milieu aqueux les contenant, à l'aide de composés extractants solides qui réponde entre autres à ce besoin.

Le but de la présente invention est encore de fournir un tel procédé qui ne présente pas les inconvénients, défauts, limitations et désavantages des procédés de l'art antérieur et qui apporte une solution aux problèmes des procédés de l'art antérieur.

EXPOSÉ DE L'INVENTION

Ce but, et d'autres encore, sont atteints, conformément à l'invention, par un procédé d'extraction de composés organiques fluorés, notamment perfluorés, à partir d'un milieu aqueux les contenant, comprenant au moins une étape de mise en contact au cours de laquelle on met en contact le milieu aqueux avec un composé extractant solide, dans lequel ledit composé extractant solide est choisi parmi le UiO-66, le UiO-66-(F4), le UiO-67, et leurs mélanges, moyennant quoi lesdits composés organiques fluorés sont adsorbés dans ledit composé extractant solide.

Le procédé selon l'invention se distingue fondamentalement des procédés de l'art antérieur en ce qu'il met en œuvre des composés extractants solides extrêmement spécifiques choisis parmi le UiO-66, le UiO-66-F4, le UiO-67, et leurs mélanges pour réaliser

l'extraction, l'adsorption de composés également très spécifiques, à savoir les composés organiques fluorés.

Le composé UiO-66, est un « *Metal Organic Framework* » « *MOF* » poreux, à base de zirconium ou plus exactement d'agrégats, « *clusters* » Zr-oxo.

Plus précisément, le composé UiO-66 est un « *MOF* » construit sur des nœuds de coordination Zirconium reliés par des ligands acide benzène 1,4-dicarboxylique (« *1,4-Benzene dicarboxylic acid* » ou « *BDC* » $C_8O_4H_6$) aussi appelé acide téréphtalique.

Autrement dit, le composé UiO-66 est un « *MOF* » comprenant des agrégats, « *clusters* », nœuds de $[Zr_6O_4(OH)_4]$ et des ligands, groupes de liaison « *linkers* », jambes(« *struts* ») BDC.

On peut considérer que le composé UiO-66 répond à la formule suivante :

$$Zr_6(BDC)_6(OH)_4(H_2O)_4.$$

Le composé UiO-66 possède une surface spécifique très élevée (plus de 1000 m^2 /g) et de grandes cavités.

Il possède une excellente capacité d'adsorption réversible de l'eau ainsi qu'une grande stabilité dans les solutions aqueuses sur une large gamme de pH.

Le composé UiO-66-(F4) est également un « *Metal Organic Framework* » MOF à base de zirconium ou plus exactement d'agrégats, « *clusters* » Zr-oxo. Ce composé est l'équivalent perfluoré du UiO-66.

La structure du composé UiO-66-(F4) est analogue à celle du composé UiO-66 sauf que les ligands BDC sont remplacés par des ligands BDC-F_4.

BDC-F_4 est l'acide tétrafluoro 2,3,5,6 – dicarboxylique aussi appelé acide tétrafluorotéréphtalique.

On peut considérer que le composé UiO-66-(F4) répond à la formule suivante :

$$Zr_6(BDC\text{-}F_4)_6(OH)_4(H_2O)_4 \text{ avec } (BDC\text{-}F_4 = C_8O_4H_2F_4).$$

La structure du composé UiO-67 est analogue à celle du composé UiO-66 sauf que les ligands BDC sont remplacés par des ligands Biphényl-4,4'-dicarboxylate (« BPDC »).

La préparation de ces composés peut être facilement réalisée à une grande échelle. De ce fait, ces composés conviennent tout à fait à une mise en œuvre industrielle.

On a montré (voir notamment exemples) que ces trois composés, et notamment les deux composés UiO-66 et UiO-66-(F4), et tout particulièrement le UiO-66-(F4), présentent d'excellentes performances, notamment des capacités d'adsorption très élevées, et une grande spécificité, sensibilité, pour l'adsorption des composés organiques fluorés et notamment des PFOX (PFOS et PFOA) .

Cela est notamment démontré par le fait que ces trois MOFs poreux et notamment le UiO-66 et le UiO-66-(F4), possèdent des capacités d'adsorption à saturation des composés organiques fluorés, et notamment des PFOX (PFOS et PFOA), pouvant atteindre jusqu'à 467 mg (composés organique fluorés)/g (MOF) dans certaines conditions (voir exemples).

En outre, il s'est avéré que la cavité perfluorée de l'UiO-66-(F4) accroîssait l'affinité de ce composé pour l'adsorption de polluants fluorés, à cause de l'interaction entre les atomes de fluor, sans modifier de manière importante la capacité de saturation par rapport au composé UiO-66 qui n'est pas fluoré.

Ce sont ainsi les propriétés hydrophobes et apolaires de l'UiO-66-(F4) qui sont mises à profit.

En résumé, les MOFs poreux, et notamment les composés UiO-66, UiO-66-(F4), mis en œuvre dans le procédé selon l'invention, possèdent une capacité d'adsorption très élevée des composés organiques fluorés, cette capacité étant plus élevée pour le UiO-66-(F4).

En outre, la cinétique d'adsorption des composés fluorés par les trois MOFs poreux mis en œuvre dans le procédé selon l'invention, et notamment par les composés UiO-66 et UiO-66-(F4) est rapide (voir exemples).

On a également montré que les trois MOFs poreux mis en œuvre dans le procédé selon l'invention, et notamment les composés UiO-66 et UiO-66-(F4) possédaient une grande stabilité chimique dans l'eau, en milieu acide et en milieu basique, à des températures pouvant atteindre 100°C. Après adsorption, la structure des trois MOFs

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poreux, et notamment des deux MOFS poreux UiO-66 et UiO-66-(F4) est conservée quelles que soient les conditions de cette adsorption.

Les trois MOFs poreux, UiO-66, UiO-67, et UiO-66-(F4) sont préparés à partir de composés non toxiques. En outre, la libération potentielle à partir de ces composés, de Zirconium, Zr, sous forme d'oxyde de Zirconium, ne présente aucun effet particulier sur la santé.

De même, les acides téréphtaliques et fluoro-téréphtaliques ne présentent pas de danger particulier dès lors qu'ils ne sont pas présents sous forme de poudre inhalable.

Enfin, le procédé selon l'invention peut être mis en œuvre avec la même efficacité et avec une capacité d'adsorption très élevée, sur de larges plages de pH, de températures, de concentrations en composés organiques fluorés.

Le procédé selon l'invention est pas ou peu affecté par la présence d'autres composés que les composés organiques fluorés, tels que des ions, même à des concentrations élevées de ces autres composés, tels que des ions (dans le milieu aqueux, comme c'est le cas par exemple dans une eau saumâtre ou une eau de mer). Les composés fluorés sont extraits sélectivement en présence de ces autres composés, tels que des ions, avec des rendements qui sont relativement peu affectés, par exemple jusqu'à 25% en moins ou en plus. Ce rendement peut donc être affecté aussi bien de manière négative que de manière positive -il est alors accru- par la présence de ces de ces autres composés, tels que des ions.

Ces ions peuvent être choisis parmi les ions halogénures tels que les ions chlorure, les ions sulfate, nitrate, phosphate, et les ions de métaux alcalins ou alcalinoterreux comme le sodium, le potassium, le calcium ou le magnésium etc.

Ces ions peuvent être présents à une concentration de 0,5 M à 0,01 M. Par exemple, le procédé selon l'invention n'est pas ou peu affecté par la présence de chlorure de sodium dans le milieu aqueux même à des concentrations élevées, par exemple supérieure à 15 g/L. Le procédé selon l'invention permet ainsi la séparation sélective des composés fluorés à partir des eaux de mer et des eaux saumâtres.

Il est totalement surprenant que les trois MOFs poreux, UiO-66, UiO-66-(F4) et UiO-67, puissent permettre avec succès, et notamment avec une capacité d'adsorption très élevée, l'extraction, adsorption, spécifiquement des composés organiques fluorés.

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En effet, l'homme du métier sait que le phénomène d'adsorption, extraction est imprévisible, et que même si un composé extractant solide a été mis en œuvre avec succès pour l'extraction d'un composé, cela ne signifie en rien que ce même composé extractant solide pourra aussi être mis en œuvre avec succès pour l'extraction d'un autre composé même voisin.

De la même manière, si un composé extractant solide tel qu'un MOF (par exemple le MIL-101(Cr) ou un MOF avec des ligands imidazoles) a été mis en œuvre avec succès pour l'extraction d'un composé, cela ne signifie en rien qu'un autre composé extractant solide même de structure voisine, par exemple un autre MOF, (comme les MOFs UiO-66, UiO-66-(F4) et UiO-67) pourra aussi être mis en œuvre avec succès pour l'extraction de ce même composé.

Le procédé selon l'invention surmonte les inconvénients, défauts, limitations et désavantages des procédés de l'art antérieur et apporte une solution aux problèmes des procédés de l'art antérieur.

Avantageusement, les composés organiques fluorés peuvent être choisis parmi les composés comprenant au moins un groupe alkyle fluoré, notamment un groupe alkyle perfluoré.

Avantageusement, les composés organiques fluorés sont choisis parmi les composés comprenant un ou plusieurs groupes alkyles fluorés, tous ces groupes alkyles fluorés étant des groupes alkyle perfluorés.

Avantageusement, les composés perfluorés sont choisis parmi le sulfonate de perfluorooctane (« *PerFluoroOctane Sulfonate* » ou « *PFOS* »), l'acide perfluorooctanoïque (« *PerFluroOctanoic Acid* » ou « *PFOA* »), et leurs mélanges.

Avantageusement, le milieu aqueux peut être de l'eau pure, une solution aqueuse, ou une suspension aqueuse.

Le milieu aqueux peut être notamment choisi parmi les eaux destinées à la consommation humaine, les eaux de mer, les eaux saumâtres, les eaux usées telles que les eaux rejetées par les égouts, les eaux issues des stations d'épuration, et les effluents industriels.

Avantageusement, la concentration en composés organiques fluorés (polluants) dans le milieu aqueux peut être de 1 mg/L jusqu'à la limite de solubilité des composés organiques fluorés (polluants) dans le milieu aqueux, par exemple dans la solution.

De préférence, la concentration en composés organiques fluorés (polluants) dans le milieu aqueux peut être de 100 à 1000 mg/L, par exemple de 500 mg/L.

Avantageusement, le milieu aqueux peut contenir, outre les composés organiques fluorés, d'autres composés tels que des ions, et les composés organiques fluorés sont extraits sélectivement par rapport à ces autres composés.

Avantageusement, le rapport m/V, masse du composé extractant solide m exprimé en mg/ volume V du milieu aqueux contenant les composés organiques fluorés exprimé en mL peut être proche de 1 ou égal à 1.

Avantageusement, l'étape de mise en contact peut être réalisée à une température de 5°C à 70°C, de préférence de 15°C à 45°C.

Avantageusement, le composé extractant solide dans lequel sont adsorbés les composés organiques fluorés peut être traité dans une étape de régénération au cours de laquelle les composés organiques fluorés adsorbés sont séparés du composé extractant solide, le composé extractant solide séparé est éventuellement recyclé dans l'étape de mise en contact et les composés organiques fluorés sont récupérés.

L'invention sera mieux comprise à la lecture de la description qui suit de modes de réalisation particuliers de l'invention, faite à titre illustratif et non limitatif au moyen d'exemples et en relation avec les dessins joints.

BRÈVE DESCRIPTION DES DESSINS

- La Figure 1 est un graphique qui montre les cinétiques d'adsorption du PFOA at du PFOS sur deux MOFs mis en œuvre selon l'invention, à savoir le UiO-66 et le UiO-66-(F4) aussi appelé MOF-F4, à une température de 25°C ± 2°C, et avec une concentration initiale en PFOX (PFOS ou PFOA) de 500 $mg.L^{-1}$ ([PFOX] = 500 $mg.L^{-1}$).

En abscisse est porté le temps (minutes), et en ordonnée est portée la capacité d'adsorption q_t (en $mg.g^{-1}$).

Les points représentés par un ● concernent l'adsorption du PFOA sur le MOF-F4.

Les points représentés par un ▼ concernent l'adsorption du PFOS sur le MOF-F4.
Les points représentés par un ■ concernent l'adsorption du PFOA sur le UiO-66.
Les points représentés par un ▲ concernent l'adsorption du PFOS sur le UiO-66.
Sur ce graphique, sont également portés, pour chaque point, les barres d'erreur correspondantes.

- La Figure 2 est un graphique qui donne les isothermes d'adsorption du PFOA et du PFOS sur deux MOFs mis en œuvre selon l'invention, à savoir le UiO-66 et le UiO-66-(F4) aussi appelé MOF-F4, à une température de 25°C, dans l'eau à un pH de 4.

En abscisse est portée la concentration en PFOX (PFOS ou PFOA) dans la solution, à l'équilibre : C_e (en $mg.L^{-1}$), et en ordonnée est portée la capacité d'absorption à saturation : q_e (en $mg.g^{-1}$).
Les points représentés par un ▲ concernent l'adsorption du PFOA sur le MOF-F4.
Les points représentés par un ■ concernent l'adsorption du PFOS sur le MOF-F4.
Les points représentés par un ▼ concernent l'adsorption du PFOA sur le UiO-66.
Les points représentés par un ● concernent l'adsorption du PFOS sur le UiO-66.
Sur ce graphique, sont également portés, pour chaque point, les barres d'erreur correspondantes. Ces barres d'erreur correspondent aux déviations standards des expériences réalisées en double.

EXPOSÉ DÉTAILLÉ DE MODES DE RÉALISATION PARTICULIERS

L'invention va maintenant être décrite en référence aux exemples suivants donnés à titre illustratif et non limitatif.

Exemple 1.

Synthèse et caractérisation des composés UiO-66 et UiO-66-(F4) et méthodes de mesure.

On s'est procuré tous les réactifs auprès de la société Aldrich® ou de la société Fisher® et ils ont été utilisés sans autre purification.

Le composé UiO-66 a été synthétisé par une réaction solvothermale classique dans du DiMéthylFormamide (DMF) à 120°C pendant 24 heures, en présence de HCl en tant que modulateur.

On a suivi le protocole de synthèse décrit dans Chem. Comm., 2013, 49, 9449.

Le composé UiO-66-(F4) est identique au composé UiO-66 à l'exception du ligand qui est totalement perfluoré.

Le composé UiO-66-(F4) ne peut pas être synthétisé par le protocole utilisé pour UiO-66, probablement à cause de la liaison polaire covalente qui change drastiquement le pKa des acides carboxyliques.

Ce composé a donc été obtenu par une synthèse hydrothermale modulée dans un mélange d'eau et d'acide acétique à 120°C pendant 24 h.

On a suivi le protocole de synthèse décrit dans Inorg. Chem., 2015, 54, 4862.

Les deux composés synthétisés ont été caractérisés par Microscopie Electronique à Balayage (MEB), Diffraction des Rayons X des poudres (DRX), Analyse thermogravimétrique (ATG), et mesures de la surface spécifique et du volume des pores par absorption d'azote en utilisant la méthode BET.

L'analyse thermogravimétrique (TGA) a été réalisée sous air en utilisant un appareil Setsys 1750 CS Evol équipé d'un creuset en platine. Après l'enregistrement d'une ligne de base en utilisant un creuset vide (100 µL), on a mesuré la perte de poids pendant un traitement thermique réalisé jusqu'à une température atteignant 650°C avec une vitesse de montée en température de 10 °C min^{-1} sous air.

Les mesures de diffraction des rayons X des poudres (DRX) ont été effectuées avec un diffractomètre Bruker® D8 θ/θ avec un rayonnement Cu-Kα (λ = 1,54178 Å).

Un microscope électronique à balayage environnemental FEI Quanta 200, équipé d'un détecteur Everhart-Thornley ("*Everhart-Thornley Detector*" ou "*ETD*") et d'un détecteur d'électrons rétrodiffusés ("*BackScattered Electron Detector*" ou "*BSED*"), a été utilisé pour enregistrer des images avec une tension d'accélération de 30 kV dans des conditions de vide poussé (« *high vacuum conditions* »).

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Les mesures de physisorption de l'azote ont été réalisées en utilisant un appareil ASAP 2020 à 77 K, après dégazage à 623 K pendant 8 heures, pour atteindre une pression inférieure à 1 mm Hg.

La surface spécifique et le volume de pores ont été calculés en utilisant la méthode BET (Brunauer, Emmett, Teller) classique.

Les mesures de spectroscopie infrarouge à transformée de Fourier ou spectroscopie IRTF (« *FTIR* », ou « *Fourier Transform InfraRed spectroscopy* » en anglais) ont été effectuées avec un appareil Perkin Elmer® Spectrum 100 en mode transmission. Les expériences d'absorption, extraction, ont été suivies par NMR ^{19}F et enregistrées sur pectromètre Bruker® à température ambiante dans l'eau.

Exemple 2.

Les deux composés synthétisés et caractérisés dans l'exemple 1 sont utilisés pour extraire, adsorber deux PFOX contenus dans un milieu aqueux, à savoir dans de l'eau ou dans des solutions aqueuses contenant, en outre, divers ions en solution.

Ces deux PFOX sont le sulfonate de perfluorooctane (« *PerFluoroOctane Sulfonate* » ou « *PFOS* ») et l'acide perfluorooctanoïque (« *PerFluroOctanoic Acid* » ou « *PFOA* »).

- Protocole de mesure.

La détermination quantitative de la concentration en PFOX en solution dans le milieu aqueux a été réalisée par RMN du ^{19}F en se basant sur le pic caractéristique du groupe CF_3 terminal (à savoir respectivement -72 ppm pour le PFOS et -80 ppm pour le PFOA) et en utilisant une courbe de calibration avec le trifluoroéthanol comme étalon, référence, interne.

La technique de RMN a une faible sensibilité mais elle a une précision suffisante pour déterminer la concentration en PFOX dans des solutions aqueuses très concentrées en PFOX (de 100 à 1000 mg/L).

La détermination quantitative a été faite en intégrant la surface du signal du PFOX et en la comparant à la surface du signal de l'étalon interne.

La fenêtre spectrale a été restreinte à de -50 ppm à – 100 ppm pour améliorer la qualité du spectre.

Des courbes d'étalonnage, calibration, ont été obtenues en utilisant 10 solutions étalons de concentrations connues de 100 à 1000 mg/L en PFOX, préparées à partir d'une solution mère de PFOX.

Les expériences d'extraction, adsorption des PFOX ont été effectuées en mettant en contact la solution aqueuse de PFOX avec l'un des deux MOFs précédemment préparés, à savoir le UiO-66, le UiO-66-(F4) et en utilisant un rapport masse de MOF sur volume m/V de 1 (c'est-à-dire 1 mL de solution aqueuse de PFOX pour 1 mg de MOF).

La solution aqueuse, avec l'un des deux MOFs, est agitée pendant 1 heure à température ambiante. Le surnageant est ensuite isolé par centrifugation et il est directement analysé par RMN du ^{19}F en présence d'un étalon interne pour déterminer la concentration précise en PFOX de la solution.

Les expériences sont réalisées deux fois.

- Cinétique d'adsorption des PFOX par les MOFs.

Le suivi cinétique est effectué en faisant varier le temps de contact à l'équilibre de 0 à 60 minutes avec une concentration en PFOX initiale de 500 mg/L et avec un rapport m/V = 1.

Sur la Figure 1, on a représenté la capacité d'adsorption q_t (en $mg.g^{-1}$) en fonction du temps (en min.) du PFOA et du PFOS par chacun des MOFS préparés dans l'exemple 1, à savoir le UiO-66 et le UiO-66-(F4) aussi appelé MOF-F4.

Pour les deux MOFs, l'adsorption peut être séparée en deux étapes. Au début, une grande quantité de PFOX est absorbée en moins de 10 minutes, puis l'adsorption devient plus faible pour atteindre l'équilibre après 60 minutes.

Toutes les autres expériences d'adsorption ont donc alors été réalisées pendant une durée de 60 minutes.

- Effet de la température sur l'adsorption des PFOX.

L'effet de la température sur l'adsorption des PFOX par le UiO-66 et le UiO-66-(F4) a été étudié sur la gamme de températures de 25°C à 40°C (298 K à 318 K).

On observe une augmentation de l'adsorption lorsque la température augmente.

- Influence du rapport m /V sur l'adsorption des PFOX.

L'influence du rapport m /V sur l'adsorption des PFOX a également été étudiée.

On a déterminé que, pour que l'adsorption soit efficace, et pour éviter les erreurs expérimentales dues à la RMN (faible sensibilité), un rapport m/V = 1 était le plus efficace pour extraire les PFOX.

- Isothermes d'adsorption.

Les isothermes d'adsorption des deux PFOX, PFOA et PFOS sur les MOFs UiO-66 et UiO-66-(F4) dans l'eau à pH 4 à 25°C sont présentées sur la Figure 2.

Ces isothermes sont obtenues en utilisant des concentrations en PFOX allant de 100 à 1000 mg/L.

On observe que l'adsorption des PFOx augmente lorsque la concentration en PFOX augmente jusqu'à ce que la saturation soit atteinte (palier, plateau).

Les données à l'équilibre ont ensuite été évaluées par le modèle de Langmuir.

Dans ce modèle, l'isotherme est exprimée par l'équation suivante :

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e}$$

où :

- q_e est la capacité d'adsorption à l'équilibre;
- q_m est la capacité d'adsorption à saturation;
- C_e est la concentration en PFOX dans la solution, à l'équilibre;
- K_l est une constante liée à l'affinité vis-à-vis des sites de liaison.

Ce modèle suppose que le processus d'adsorption ait lieu sur une surface homogène par dépôt d'une monocouche et qu'il n'y ait pas d'interaction entre les « adsorbats » sur des sites adjacents.

Les différents paramètres sont rassemblés dans le Tableau 1 ci-dessous.

Tableau 1 : Constantes d'équilibre déterminées en utilisant l'équation de Langmuir pour l'adsorption du PFOA et du PFOS sur le UiO-66 et UiO-66-(F4) aussi appelé MOF-F4.

Adsorbant	Adsorbât	Constantes de Langmuir		
		q_m ($mg.g^{-1}$)	K_L ($L.mg^{-1}$)	R^2
UiO-66	PFOA	388	1,288	0,9589
	PFOS	160	1,25	0,894
UiO-66(F4)	PFOA	467	1,05	0,969
	PFOS	254	1,06	0,961

En utilisant le modèle de Langmuir, il s'est avéré que les capacités d'adsorption des deux MOFs UiO-66 et UiO-66-(F4) sont très élevées et que les capacités d'adsorption des deux MOFs sont plus élevées pour l'adsorption du PFOA que pour l'adsorption du PFOS.

Le UiO-66-(F4) possède la meilleure capacité d'adsorption avec une capacité d'adsorption maximale de 467 $mg.g^{-1}$ de PFOA et de 254 $mg.g^{-1}$ de PFOS.

- Analyse des matériaux MOFs après adsorption des PFOX.

Les matériaux MOFs ont été analysés après adsorption des PFOX pour caractériser le polluant à l'intérieur des cavités de leurs pores.

Cette analyse a été réalisée par spectroscopie infrarouge à transformée de Fourier ou spectroscopie IRTF (« *FTIR* », ou « *Fourier Transform InfraRed spectroscopy* » en anglais) dans les conditions précisées plus haut.

Les spectres IRTF du PFOA pur, du PFOS pur, et des Zr-MOFs, c'est-à-dire du UiO-66 et du UiO-66-(F4) avant et après extraction, adsorption des PFOX ont été réalisés.

La présence des bandes C-F de BDC-F4 à 1000 cm^{-1} suggère que l'acide tétrafluorotéréphtalique a été greffé sur le UiO-66.

Les spectres des MOFs après adsorption présentent de nombreuses bandes très caractéristiques de ces matériaux ainsi que des bandes correspondant au PFOA et au PFOS. Cela confirme que les molécules de PFOX sont bien piégées dans les MOFs.

- Evaluation de la stabilité chimique des MOFs UiO-66 et UiO-66-(F4).

La stabilité chimique des matériaux est testée dans l'eau, en milieu acide (HCl 2M et 4M) et en milieu basique (NaOH, pH 10) à 25°C et à l'ébullition, pendant 24 heures.

Aucune dégradation n'a été observée dans le cas du UiO-66-(F4), tandis que quelques pics organiques (18 et 28 degrés) apparaissent pour le UIO-66, ce qui montre une interaction plus grande entre le « cluster » métallique et le ligand organique perfluoré du UiO-66-(F4).

- Influence de l'addition d'ions en solution sur le pouvoir extractant du UiO-66-(F4) vis-à-vis du PFOA.

On montre que l'addition d'un sel diminue la solubilité du PFOA en milieu aqueux.

Finalement, on étudie l'influence de l'addition d'ions en solution, en d'autres termes de la force ionique de la solution aqueuse dans laquelle se trouve le PFOA sur le pouvoir extractant du UiO-66-(F4).

Pour étudier l'influence de la force ionique de la solution aqueuse dans laquelle se trouvent le PFOA, sur le pouvoir extractant du UiO-66-(F4) en phase solide, divers ions ont été ajoutés à la solution aqueuse contenant le PFOA (Tableau 2).

La concentration en PFOA de la solution aqueuse, [PFOA], est de 1000 mg/L, la masse de UiO-66-(F4), w, est de 1 mg, et la durée de contact entre la solution et les UiO-66-(F4), est de 60 minutes.

On constate que la plupart de ces ions provoquent des interférences avec une erreur tolérable de ± 5 %. Les interférences sont causées par la présence de : Cl^- (0.1 M), K^+ (0,01 M), Ca^{2+} (0,01 M), Mg^{2+} (0,014 M) et SO_4^{2-} à une teneur pouvant aller jusqu'à 2.10^{-2} M.

Les données relatives à ces expériences sont regroupées dans le Tableau 2 ci-dessous.

Tableau 2 : Effet des ions étrangers sur l'extraction du PFOA par le UiO-66-(F4).

Composé interférant	Solution (M)	q_m ($mg.g^{-1}$)	(%) Interférence
NaCl	0,1	377	19,3
KCl	0,01	400	12,5
$CaCl_2.2H_2O$	0,01	443	1,58
$MgCl_2.6H_2O$	0,014	362	24
Na_2SO_4	0,02	277	> 20

REVENDICATIONS

1. Procédé d'extraction de composés organiques fluorés, notamment perfluorés, à partir d'un milieu aqueux les contenant, comprenant au moins une étape de mise en contact au cours de laquelle on met en contact le milieu aqueux avec un composé extractant solide, dans lequel ledit composé extractant solide est choisi parmi le UiO-66, le UiO-66-(F4), le UiO-67, et leurs mélanges, moyennant quoi lesdits composés organiques fluorés sont adsorbés dans ledit composé extractant solide.

2. Procédé selon la revendication 1, dans lequel les composés organiques fluorés sont choisis parmi les composés comprenant au moins un groupe alkyle fluoré, notamment un groupe alkyle perfluoré.

3. Procédé selon la revendication 2, dans lequel les composés organiques fluorés sont choisis parmi les composés comprenant un ou plusieurs groupes alkyles fluorés, tous ces groupes alkyles fluorés étant des groupes alkyle perfluorés.

4. Procédé selon la revendication 3, dans lequel les composés perfluorés sont choisis parmi le sulfonate de perfluorooctane (« *PerFluoroOctane Sulfonate* » ou « *PFOS* »), l'acide perfluorooctanoïque (« *PerFluroOctanoic Acid* » ou « *PFOA* »), et leurs mélanges.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le milieu aqueux est de l'eau pure, une solution aqueuse, ou une suspension aqueuse.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le milieu aqueux est choisi parmi les eaux destinées à la consommation humaine, les eaux de mer, les eaux saumâtres, les eaux usées telles que les eaux rejetées par les égouts, les eaux issues des stations d'épuration, et les effluents industriels.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la concentration en composés organiques fluorés dans le milieu aqueux est de 1 mg/L jusqu'à la limite de solubilité des composés organiques fluorés dans le milieu aqueux, de préférence de 100 à 1000 mg/L, par exemple de 500 mg/L.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le milieu aqueux contient, outre les composés organiques fluorés, d'autres composés tels que des ions, et les composés organiques fluorés sont extraits sélectivement par rapport à ces autres composés.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport m/V masse du composé extractant solide m exprimé en mg/ volume V du milieu aqueux contenant les composés organiques fluorés exprimé en mL, est proche de 1 ou égal à 1.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'étape de mise en contact est réalisée à une température de 5 à 70°C, de préférence de 15°C à 45°C.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé extractant solide dans lequel sont adsorbés les composés organiques fluorés est traité dans une étape de régénération au cours de laquelle les composés organiques fluorés adsorbés sont séparés du composé extractant solide, le composé extractant solide séparé est éventuellement recyclé dans l'étape de mise en contact et les composés organiques fluorés sont récupérés.

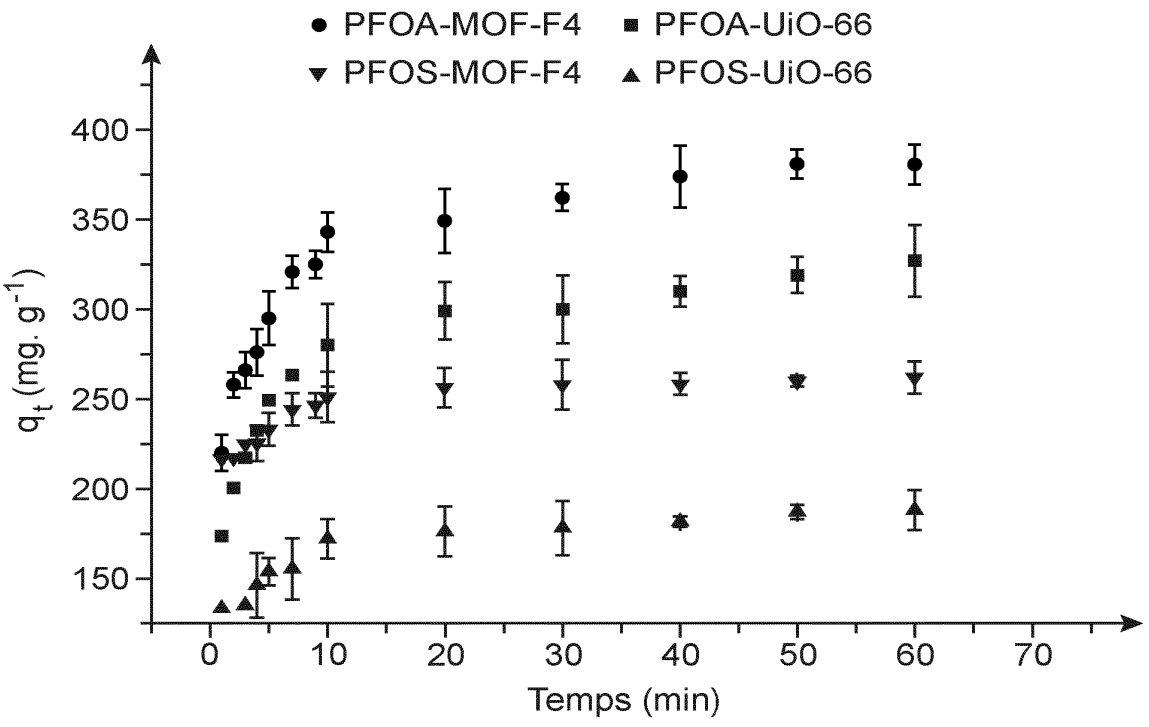

PFOA-MOF-F4
PFOA-UiO-66
PFOS-MOF-F4
PFOS-UiO-66
400
350
300
250
200
150
q_t (mg. g^{-1})
0
10
20
30
40
50
60
70
Temps (min)

FIG.1

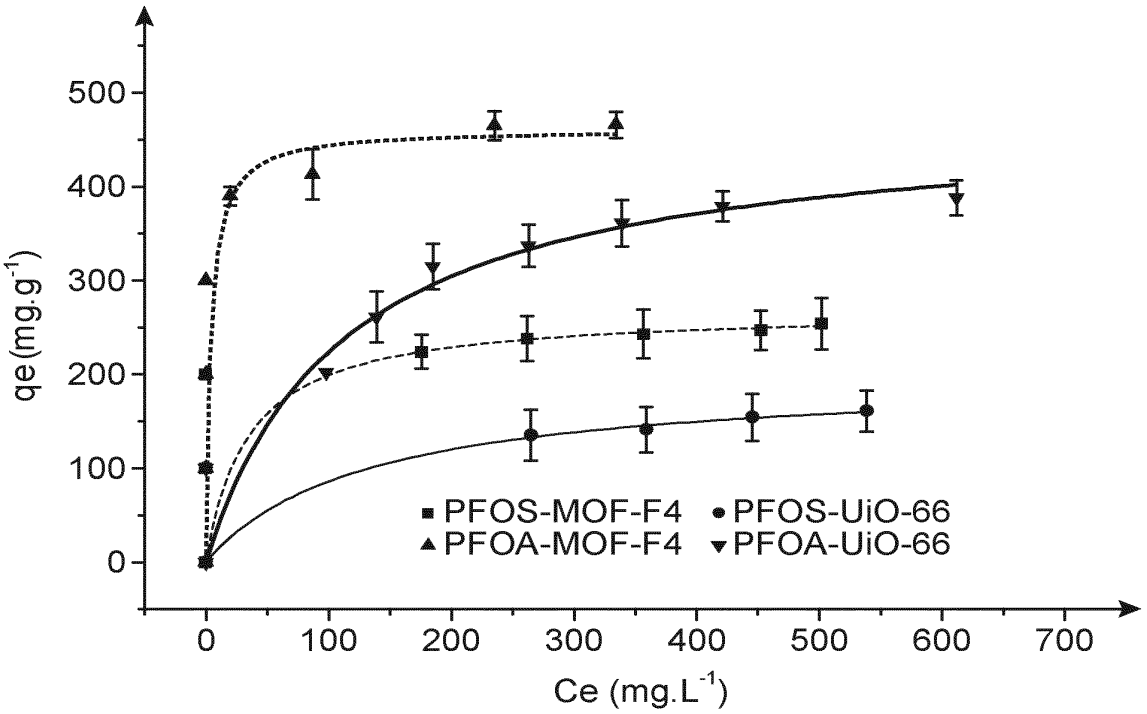

500
400
300
200
100
0
qe (mg.g-1)
0
100
200
300
400
500
600
700
Ce (mg.L-1)
PFOS-MOF-F4
PFOS-UiO-66
PFOA-MOF-F4
PFOA-UiO-66

FIG. 2

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établi sur la base des dernières revendications déposées avant le commencement de la recherche

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FA 849953
FR 1850511

DOCUMENTS CONSIDÉRÉS COMME PERTINENTS		Revendication(s) concernée(s)	Classement attribué à l'invention par l'INPI
Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes		
X	CN 107 570 116 A (UNIV ZHEJIANG OCEAN) 12 janvier 2018 (2018-01-12) * alinéas [0002], [0014] * * alinéa [0011] *	1-11	C02F1/28 C02F1/58 C02F101/36 B01D15/00 B01J20/22
X	HASAN ZUBAIR ET AL: "Removal of hazardous organics from water using metal-organic frameworks (MOFs): Plausible mechanisms for selective adsorptions", JOURNAL OF HAZARDOUS MATERIALS, ELSEVIER, AMSTERDAM, NL, vol. 283, 28 septembre 2014 (2014-09-28), pages 329-339, XP029112472, ISSN: 0304-3894, DOI: 10.1016/J.JHAZMAT.2014.09.046 * le document en entier *	1-11	
X	CHEN MENG-JIA ET AL: "Influence of crystal topology and interior surface functionality of metal-organic frameworks on PFOA sorption performance", MICROPOROUS AND MESOPOROUS MATERIALS, vol. 236, 1 septembre 2016 (2016-09-01), pages 202-210, XP029761707, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2016.08.046 * page 209 *	1-11	DOMAINES TECHNIQUES RECHERCHÉS (IPC) B01D B01J C02F

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1

Date d'achèvement de la recherche	Examinateur
24 juillet 2018	Châtellier, Xavier

CATÉGORIE DES DOCUMENTS CITÉS

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Catégorie	Citation du document avec indication, en cas de besoin, des parties pertinentes		
X	KAI LIU ET AL: "Understanding the Adsorption of PFOA on MIL-101(Cr)-Based Anionic-Exchange Metal-Organic Frameworks: Comparing DFT Calculations with Aqueous Sorption Experiments", ENVIRONMENTAL SCIENCE & TECHNOLOGY, vol. 49, no. 14, 2 juillet 2015 (2015-07-02), pages 8657-8665, XP055494790, US ISSN: 0013-936X, DOI: 10.1021/acs.est.5b00802 * page 8660 *	1-11	

X	WANG SAIHUA ET AL: "Rapid determination of small molecule pollutants using metal-organic frameworks as adsorbent and matrix of MALDI-TOF-MS", MICROPOROUS AND MESOPOROUS MATERIALS, vol. 239, 22 octobre 2016 (2016-10-22), pages 390-395, XP029822552, ISSN: 1387-1811, DOI: 10.1016/J.MICROMESO.2016.10.032 * pages 391,394 *	1-11	DOMAINES TECHNIQUES RECHERCHÉS (IPC)

1

Date d'achèvement de la recherche	Examinateur
24 juillet 2018	Châtellier, Xavier

CATÉGORIE DES DOCUMENTS CITÉS

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ANNEXE AU RAPPORT DE RECHERCHE PRÉLIMINAIRE
RELATIF A LA DEMANDE DE BREVET FRANÇAIS NO. FR 1850511 FA 849953

La présente annexe indique les membres de la famille de brevets relatifs aux documents brevets cités dans le rapport de recherche préliminaire visé ci-dessus.
Les dits membres sont contenus au fichier informatique de l'Office européen des brevets à la date du 24-07-2018
Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office européen des brevets, ni de l'Administration française

Document brevet cité au rapport de recherche	Date de publication	Membre(s) de la famille de brevet(s)	Date de publication
CN 107570116 A	12-01-2018	AUCUN	

EPO FORM P0465

Pour tout renseignement concernant cette annexe : voir Journal Officiel de l'Office européen des brevets, No.12/82

Espacenet

Bibliographic data: WO2017180346 (A1) — 2017-10-19

A SUSTAINABLE SYSTEM AND METHOD FOR REMOVING AND CONCENTRATING PER-AND POLYFLUOROALKYL SUBSTANCES (PFAS) FROM WATER

Inventor(s): NICKELSEN MICHAEL G [US]; WOODARD STEVEN E [US] ± (NICKELSEN, Michael, G, ; WOODARD, Steven, E, ; NICKELSEN, Michael, ; WOODARD, Steven)

Applicant(s): EMERGING COMPOUNDS TREAT TECH INC [US] ± (EMERGING COMPOUNDS TREATMENT TECHNOLOGIES, INC)

Classification: - international: ***C02F1/42; C02F1/58***
- cooperative: **B01J41/05 (EP, US); B01J41/12 (EP, US); B01J49/57 (EP, US); C02F1/42 (EP, US);** B01D1/00 (EP, US); B01D3/00 (EP, US); B01L1/00 (US); B01L3/00 (US); C02F2001/422 (EP, US); C02F2101/36 (EP, US); C02F2303/16 (EP, US)

Application number: WO2017US25754 20170403 Global Dossier

Priority number(s): US201715477350 20170403 ; US201662321929P 20160413

Also published as: WO2017180346 (A8) AU2017249070 (A1) AU2017249070 (B2) CA3020691 (A1) CN109195922 (A) more

Abstract of WO2017180346 (A1)

A sustainable system for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water. The system includes an anion exchange vessel having a selected anion exchange resin therein configured to remove PFAS from the water. A line coupled to the vessel introduces a flow of water contaminated with PFAS such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water. A regenerant solution line is coupled to the anion exchange vessel to introduce an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin, thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of the removed PFAS and the optimized regenerant solution. A separation and recovery subsystem recovers the

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optimized regenerant solution for reuse and separates and concentrates the removed PFAS.

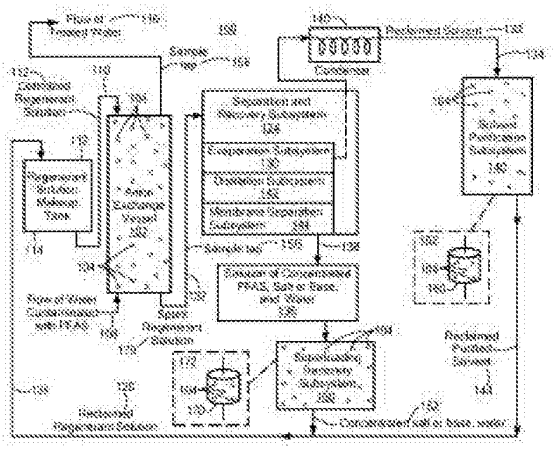


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(54) **Title**: A SUSTAINABLE SYSTEM AND METHOD FOR REMOVING AND CONCENTRATING PER-AND POLY-FLUOROALKYL SUBSTANCES (PFAS) FROM WATER

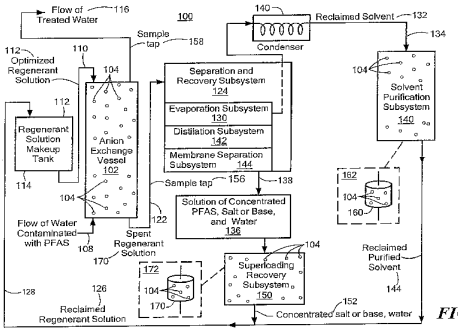


FIG. 3

(57) **Abstract**: A sustainable system for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water. The system includes an anion exchange vessel having a selected anion exchange resin therein configured to remove PFAS from the water. A line coupled to the vessel introduces a flow of water contaminated with PFAS such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water. A regenerant solution line is coupled to the anion exchange vessel to introduce an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin, thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of the removed PFAS and the optimized regenerant solution. A separation and recovery subsystem recovers the optimized regenerant solution for reuse and separates and concentrates the removed PFAS.

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A SUSTAINABLE SYSTEM AND METHOD FOR REMOVING AND CONCENTRATING PER- AND POLYFLUOROALKYL SUBSTANCES (PFAS) FROM WATER

RELATED APPLICATIONS

This application claims benefit of and priority to U.S. Patent Application Serial No. 15/477,350 filed April 3, 2017 under §§119, 120, 363, 365, and 37 C.F.R. §1.55 and §1.78, and that application and this application also claim benefit of and priority to U.S. Provisional Application Serial No. 62/321,929 filed April 13, 2016, under 35 U.S.C. §§119, 120, 363, 365, and 37 C.F.R. §1.55 and §1.78, and each of U.S. Patent Application Serial No. 15/477,350 and U.S. Provisional Application Serial No. 62/321,929 is incorporated herein by this reference.

FIELD OF THE INVENTION

This invention relates to a sustainable system and method for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water.

BACKGROUND OF THE INVENTION

Per- and polyfluoroalkyl substances (PFAS) are a class of man-made compounds that have been used to manufacture consumer products and industrial chemicals, including, *inter alia*, aqueous film forming foams (AFFFs). AFFFs have been the product of choice for firefighting at military and municipal fire training sites around the world. AFFFs have also been used extensively at oil and gas refineries for both fire training and firefighting exercises. AFFFs work by blanketing spilled

oil/fuel, cooling the surface, and preventing re-ignition. PFAS in AFFFs have contaminated the groundwater at many of these sites and refineries, including more than 100 U.S. Air Force sites.

PFAS may be used as surface treatment/coatings in consumer products such as carpets, upholstery, stain resistant apparel, cookware, paper, packaging, and the like, and may also be found in chemicals used for chemical plating, electrolytes, lubricants, and the like, which may eventually end up in the water supply.

PFAS are bio-accumulative in wildlife and humans because they typically remain in the body for extended periods of time. Laboratory PFAS exposure studies on animals have shown problems with growth and development, reproduction, and liver damage. In 2016, the U.S. Environmental Protection Agency (EPA) issued the following health advisories (HAs) for perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA): 0.07 μg/L for both the individual constituents and the sum of PFOS and PFOA concentrations, respectively. Additionally, PFAS are highly water soluble in water, result in large, dilute plumes, and have a low volatility.

PFAS are very difficult to treat largely because they are extremely stable compounds which include carbon-fluorine bonds. Carbon-fluorine bonds are the strongest known bonds in nature and are highly resistant to breakdown.

The vast majority of available conventional water treatment systems and methods to remove PFAS from water have proven to be ineffective. *See e.g.*, Rahman, et al., *Behaviour and Fate of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Drinking Water Treatment,* Water Research 50, pp. 318-340 (2014), incorporated by reference herein. Conventional activated carbon adsorption system and methods to remove PFAS from water have shown to be somewhat effective on

the longer-chain PFAS, but have difficulty in removing branched and shorter chain compounds, *see e.g.* Dudley, Master's Thesis: *Removal of Perfluorinated Compounds by Powdered Activated Carbon, Superfine Powdered Activated Carbon, and Anion Exchange Resins,* North Carolina State University (2012), incorporated by reference herein.

Appleman et al., *Treatment of Poly- and Perfluoroalkly Substances in U.S. Full-Scale Treatment Systems*, Water Research 51, pp. 246-255 (2014), incorporated by reference herein, reported that, similar to activated carbon, some conventional anion exchange resins may be more effective at treating longer chain PFAS than the shorter chain compounds. Other conventional anion exchange resins have shown some success in removing a broader range of PFAS, including the shorter-chain compounds, *see e.g.*, Dudley, *cited supra*.

Conventional anion exchange treatment systems and methods typically utilize anion exchange resin where positively charged anion exchange resin beads are disposed in a lead vessel which receives a flow of water contaminated with anionic contaminants, such as PFAS. The negatively charged contaminants are trapped by the positively charged resin beads and clean water flows out of the lead anion exchange vessel into a lag vessel, also containing anion exchange resin beads. A sample tap is frequently used to determine when the majority of the anion exchange beads in the lead exchange vessel have become saturated with contaminants. When saturation of the resin anion exchange beads is approached, a level of contaminants will be detected in the effluent tap. When this happens, the lead vessel is taken off line and the contaminated water continues flowing to the lag vessel which now becomes the lead vessel. The lead-lag vessel configuration ensures that a high level of treatment is

maintained at all times.

As discussed above, some conventional anion exchange resins can also be used to remove PFAS from water. A number of known methods exist to regenerate the anion exchange beads in the anion exchange vessel. Some known methods rely on flushing the resin with a brine or caustic solution. Other known methods may include the addition of solvents, such as methanol or ethanol, to enhance the removal of the PFAS trapped on the anion exchange beads. Effective resin regeneration has been demonstrated by passing a solvent (e.g., methanol or ethanol), blended with a sodium chloride or sodium hydroxide solution, through the resin. *See e.g.*, Deng et al., *Removal of Perfluorooctane Sulfonate from Wastewater by Anion Exchange Resins: Effects of Resin Properties and Solution Chemistry*, Water Research 44, pp. 5188-5195 (2010) and Chularueangaksorn et al., *Regeneration and Reusability of Anion Exchange Resin Used in Perfluorooctane Sulfonate Removal by Batch Experiments,* Journal of Applied Polymer Science, 10.1002, pp. 884-890 (2013), both incorporated by reference herein. However, such methods may generate a large amount of toxic regenerant solution which must be disposed of at significant expense.

Du et al., *Adsorption Behavior and Mechanism of Perfluorinated Compounds on Various Adsorbents – A Review*, J. Haz. Mat. 274, pp. 443-454 (2014), incorporated by reference herein, discloses a need to further treat the waste regenerant solution to concentrate the PFAS and reduce the volume of waste. This is a key step, because resin regeneration produces a significant volume of toxic waste.

The known methods for removing PFAS from water discussed above typically do not optimize the anion exchange resin and may have limited capacity for removing PFAS mass. Such known methods may also incompletely regenerate the anion

exchange resin by attempting to desorb the PFAS from the resin. Such known methods may incompletely regenerate the anion exchange resin which may lead to a loss of capacity, otherwise known as active sites, during each successive loading and regeneration cycle. This cumulative buildup of PFAS on the ion exchange resin is often referenced to as a "heel," and results in reduced treatment effectiveness as the heel builds up over time. Such known methods may also not reclaim and reuse the spent regenerant solution which may increase the amount spent regenerant solution with removed PFAS therein. This increases the amount of toxic spent regenerant solution with PFAS, which must be disposed of at significant expense.

Conventional systems and methods for attempting to remove PFAS also include biological treatment, air stripping, reverse osmosis, and advanced oxidation. All of these conventional techniques are ineffective and/or extremely expensive.

BRIEF SUMMARY OF THE INVENTION

In one aspect, a sustainable system for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water is featured. The system includes an anion exchange vessel including a selected anion exchange resin therein configured to remove PFAS from the water. A line coupled to the vessel is configured to introduce a flow of water contaminated with PFAS such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water. A regenerant solution line coupled to the anion exchange vessel is configured to introduce an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of the removed PFAS and the optimized regenerant solution. A separation

and recovery subsystem is configured to recover the optimized regenerant solution for reuse and separate and concentrate the removed PFAS.

In one embodiment, the PFAS may be removed from the anion exchange resin by a dual mechanism including desorption and anion exchange. The desorption may include providing the optimized regenerant solution having a predetermined concentration of a solvent configured to displace adsorbed hydrophobic tails of PFAS from the backbone of the anion exchange resin with the solvent and providing a predetermined concentration of salt or base configured to displace hydrophilic heads of PFAS with inorganic anions. The optimized regenerant solution may include a mixture of a salt or a base, a solvent, and water. The solvent may include an alcohol. The optimized regenerant solution may include about 50% to about 90% methanol by volume, about 10% to about 50% water by volume, and about 1% to about 5% salt or base by weight. The optimized regenerant solution may include about 70% methanol by volume, about 28% water by volume, and about 2% salt or base by weight. The selected anion exchange resin may include a macroporous, strong base, anion exchange resin. The separation and recovery subsystem may include one or more of: an evaporation subsystem, a distillation subsystem and/or a membrane separation subsystem. The system may include a condenser coupled to the evaporation or distillation unit configured to condense the reclaimed regenerant solution. The separation and recovery subsystem may include a solvent purification subsystem configured to remove carryover PFAS from the separation and recovery subsystem and to provide a purified, reclaimed solvent for reuse. The solvent purification subsystem may include anionic exchange resin housed in a vessel. The separation and recovery subsystem may include a super-loading recovery subsystem configured to

create an ultra-concentrated PFAS waste product and a solution of concentrated salt or base and water for reuse. The super-loading recovery subsystem may include an anionic exchange resin housed in a vessel. The super-loading recovery subsystem may be configured to provide purified reclaimed water and purified reclaimed salt or base for reuse.

In another aspect, a sustainable method for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water is featured. The method includes selecting an anion exchange resin configured to remove PFAS and provide treated water, adding the selected anion exchange resin to an anion exchange vessel, introducing a flow of water contaminated with PFAS to a vessel such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water, introducing an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of removed PFAS and the optimized regenerant solution, and subjecting the spent regenerant solution to a separation and recovery process to recover the optimized regenerant solution for reuse and separate and concentrate the removed PFAS.

In one embodiment, the PFAS may be removed from the anion exchange resin by a dual mechanism including desorption and anion exchange. The desorption may include providing a predetermined concentration of a solvent configured to displace hydrophobic tails of the PFAS on the backbone of the anion exchange resin with the solvent and providing a predetermined concentration of anions configured to displace hydrophilic heads of the PFAS with the anions. The optimized regenerant solution may include a mixture of a salt or a base, a solvent, and water. The solvent may

include an alcohol. The optimized regenerant solution may include about 50% to about 70% methanol by volume, about 2% to about 28% water by volume, and about 1% to about 5% salt or base by weight. The optimized regenerant solution may include about 70% methanol by volume, about 28% water by volume, and about 2% salt or base by weight.

The selected anion exchange resin may include a macro-porous, strong base, anion exchange resin. The separation and recovery process may be configured to maximize recovery of optimized regenerant solution and minimize volume of concentrated desorbed PFAS. The separation and recovery process may include one or more of evaporation, distillation and membrane separation. The evaporation or vacuum distillation may include condensing the spent regenerant solution. The separation and recovery process may include removing carryover PFAS to provide a purified reclaimed solvent for reuse. The separation and recovery subsystem may include creating an ultra-concentrated PFAS waste product and a solution of concentrated salt or base and water for reuse.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

Other objects, features and advantages will occur to those skilled in the art from the following description of a preferred embodiment and the accompanying drawings, in which:

Fig. 1 shows an example of a typical PFAS with a hydrophobic non-ionic tail and an anionic head;

Fig. 2 shows a three-dimensional view depicting the complex three-dimensional structure of a typical anion exchange resin bead showing examples of

positively charged exchange sites of the resin bead binding to negatively charged hydrophilic heads of PFAS molecules, and the hydrophobic carbon-fluorine tails of the PFAS adsorbing to the hydrophobic backbone of the resin bead;

Fig. 3 is a schematic block diagram showing the primary embodiments of one embodiment of sustainable system and method for removing and concentrating PFAS from water; and

Fig. 4 is a block diagram showing the primary steps of one embodiment of the sustainable method for removing and concentrating PFAS from water.

DETAILED DESCRIPTION OF THE INVENTION

Aside from the preferred embodiment or embodiments disclosed below, this invention is capable of other embodiments and of being practiced or being carried out in various ways. Thus, it is to be understood that the invention is not limited in its application to the details of construction and the arrangements of components set forth in the following description or illustrated in the drawings. If only one embodiment is described herein, the claims hereof are not to be limited to that embodiment. Moreover, the claims hereof are not to be read restrictively unless there is clear and convincing evidence manifesting a certain exclusion, restriction, or disclaimer.

As discussed in the Background section, anion exchange resins are highly effective at removing PFAS from water because of the multiple removal methods involved. The molecular structure of most PFAS compounds can be broken into two functional units including the hydrophobic non-ionic "tail," comprised of the fluorinated carbon chain and the hydrophilic anionic "head," having a negative charge. Fig. 1 shows an example of a typical PFAS 10 with hydrophobic non-ionic

tail 12 and hydrophilic anionic head 14, in this example, a sulfonate group, although anionic head 14 may be a carboxylate group or similar type group.

Anion exchange resins are essentially adsorbents with anion exchange functionality. The resin beads are typically composed of neutral copolymers (plastics) that have positively charged exchange sites. Fig. 2 shows an example of the complex three-dimensional structure of a typical anion exchange resin bead 16 with positively charged exchange sites exemplarily indicated at 18. Anion exchange resins tend to be effective at removing PFAS from water because they take advantage of the unique properties of both the anion exchange resin bead and the perfluorinated contaminants, or PFAS, using a dual mechanism of adsorption and anion exchange. For example, hydrophobic carbon-fluorine tail 12, Figs. 1 and 2, of PFAS 10 adsorbs to the hydrophobic backbone on anion exchange resin 16, Fig. 2, comprised of cross-linked polystyrene polymer chains, exemplarily indicated at 20 and divinylbenzene cross-links exemplarily indicated at 22. The negatively-charged hydrophilic heads 24 (sulfonate groups) or 26 (carboxylate groups) of PFAS 10 are attracted to positively-charged anion exchange sites 18 on anion exchange resin bead 16. The negatively charged heads 24, 26 of PFAS 10 displaces exchangeable inorganic counter ion 38, e.g., a chloride ion which is provided on anion exchange bead 18 when it is manufactured. The hydrophobic, uncharged carbon-fluorine tails 12 are adsorbed to the uncharged hydrophobic backbone comprised of polystyrene polymer chain 20 and divinylbenzene crosslink 22 via Van der Waals forces as shown.

Depending on the specific properties of both resin bead 16 and the PFAS 10, this dual mechanism of removal may be highly effective at removing PFAS from water and certain anion exchange resins have very high removal capacity for PFAS

from water.

While the dual mechanism of PFAS removal discussed above may be highly effective at removing PFAS from water because the adsorption of the hydrophobic tails of the PFAS to the hydrophobic backbone of the anion resin exchange bead, it also makes resin regeneration and reuse more difficult. A high concentration of a brine or base solution, e.g., a solution of a salt, such as NaCl, and water, or a solution of a base, such as NaOH and water, may be used to effectively displace the anionic head of the PFAS from the anion exchange site of the anion exchange resin bead, but the hydrophobic carbon-fluorine tail tends to stay adsorbed to the resin backbone. Similarly, an organic solvent, e.g., methanol or ethanol, may be used to effectively desorb the hydrophobic tail from the backbone, but then the anionic head of the PFAS stays attached to the resin anion exchange site. Research to date has demonstrated that effective regeneration techniques must overcome both mechanisms of attraction. Solutions combining organic solvents and a salt or base, such as NaCl or NaOH, have shown the most successful results to date, e.g., as disclosed in Deng et al., 2010, and Chularueangaksorn et al., 2013, discussed in the Background section. Other research has focused on using combinations of ammonium salts, including ammonium hydroxide and ammonium chloride, e.g., as disclosed by Conte et al., *Polyfluorinated Organic Micropollutants Removal from Water by Ion Exchange and Adsorption*, Chemical Engineering Transactions, Vol. 43 (2015), incorporated by reference herein.

There is shown in Fig. 3, one embodiment of sustainable system 100 for removing and concentrating PFAS from water. System 100 includes anion exchange vessel 102 including a selected anion exchange resin therein, exemplarily indicated at 104, configured to remove PFAS from flow of water 106 contaminated with PFAS.

System 100 also includes line 108 which is configured to introduce flow of water 108 contaminated with PFAS into anion exchange vessel 102 such that the PFAS binds to selected anion exchange resin 104 and are removed from the water to provide flow of treated water 116. In one example, selected anion exchange resin 104 is preferably configured to be small, e.g., about 0.5 mm to about 1 mm diameter beads made of an organic polymer substrate or similar material which is preferably porous and provides a high surface area. Exemplary selected anion exchange resins may include Dow® AMBERLITE™, IRA958 Cl, DOWEX™ PSR-2, Dow® XUS-43568.00, and similar type anion exchange resins.

System 100 also includes regenerant solution line 110 coupled to anion exchange vessel 102 configured to introduce optimized regenerant solution 112 into anion exchange vessel 102 to remove the PFAS from anion exchange resin 104 to regenerate anion exchange resin 104 and generate spent regenerant solution 120 in line 122 comprised of removed PFAS and optimized regenerant solution. In one example, optimized regenerant solution 112 is made in regenerant solution make-up tank 114 coupled to regenerant solution line 110 as shown. In one design optimized regenerant solution 112 preferably includes a mixture of a salt or base, e.g., sodium chloride (NaCl) or sodium hydroxide (NaOH), a solvent and water. In one example, the solvent may include an alcohol or similar type solvent. In one example, optimized regenerant solution 112 includes about 50% to about 90% methanol by volume, about 10% to about 50% water by volume, and about 1% to about 5% salt or base by weight. In another example, optimized regenerant solution includes about 70% methanol by volume, about 28% water by volume, and about 2% salt or base by weight. As discussed above, preferably, selected anion exchange resin 104 and

regenerant solution 112 removes PFAS from water by a dual mechanism including desorption and ion exchange. For ion exchange removal of PFAS from selected anion exchange resin 104, the anion of the salt or base, e.g., chloride of the NaCl or the hydroxide group of NaOH of optimized regenerant solution 112 displaces the hydrophilic heads 24 or 26, Fig. 2, of PFAS 10 on exchange sites 18 of anion exchange resin 16 due to the high concentration of the anions in optimized regenerant solution 112. For desorption, the solvent, e.g., an alcohol, such as methanol, ethanol or similar type alcohol of the optimized regenerant solution 112 displaces hydrophobic carbon tails 12 of the PFAS 112 bonded to the backbone of anion exchange resin 16 due to the high concentration of the solvent in optimized regenerant solution 112. The result is system 100 and efficiently removes both large and small chain PFAS from water.

In one example, the PFAS removed by anion exchange resin 14 may include Perfluorobutyric acid (PFBA), Perfluoropentanoic acid (PFPeA), Perfluorobutane sulfonate (PFBS), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA),

Perfluorohexane sulfonate (PFHxS), 6:2 Fluorotelomer sulfonate (6:2 FTS), Perfluorooctanoic acid (PFOA), Perfluoroheptane sulfonate (PFHpS), Perfluorooctane sulfonate (PFOS), Perfluorononanoic acid (PFNA), 8:2 Fluorotelomer sulfonate (8:2 FTS).

System 100 also includes the separation and recovery system 124 coupled to line 122 which recovers optimized regenerant solution 120 for reuse as reclaimed regenerant solution 126 by line 128 coupled to line 110 and preferably to regenerant solution makeup tank 114. In one design, separation and recovery subsystem 124

provides reclaimed solvent 132 by line 128 as shown and solution 136 of concentrated PFAS, salt or base, and water by line 138 which is coupled to line 128 as shown. The PFAS in solution 138 is removed (discussed below) to provide solution 152 of concentrated salt or base and water output by line 138 coupled to line 128. Thus, reclaimed regenerant solution 126 preferably includes reclaimed solvent 132 and reclaimed salt or base and water.

In one design, separation and recovery subsystem 124 may include evaporation subsystem 130. In this example, spent regenerant solution 120 is subjected to evaporation by evaporation subsystem 130 to produce reclaimed solvent 132 output to line 128 and solution 136 of concentrated desorbed PFAS 36, salt or base and water. Condenser 140 may be utilized to condense reclaimed solvent 132. In another example, separation and recovery subsystem 124 may include one or more of a distillation subsystem 142 and/or a membrane separation subsystem 144 which similarly produce reclaimed solvent 132 for reuse by lines 128 and 110 and solution 136 of concentrated PFAS, salt or base, and water.

In one example, separation and recovery subsystem 124 may further include solvent purification subsystem 140 coupled to line 128 which removes carryover PFAS from separation and recovery subsystem 124 and provides purified reclaimed solvent 144 in line 128 for reuse as regenerant solution 112 via regenerant solution makeup tank 114 and regenerant solution line 110. In one example, solvent purification subsystem 140 is a small vessel, e.g., vessel 160 shown in caption 162 as shown having anion exchange resin 104 therein which removes carryover PFAS in line 134 to create concentrated PFAS in the vessel. When vessel 160 becomes saturated with PFAS, it can be removed and taken off-site for destruction.

Separation and recovery subsystem 122 may also include super-loading recovery subsystem 150 coupled to line 138 output by separation and recovery subsystem 124 having solution 136 of concentrated PFAS, salt or base, and water. Superloading recovery subsystem 130 creates ultra-concentrated PFAS waste product adsorbed to anion exchange resin 104 and concentrated salt or base or caustic water solution 152 purified for reuse. Super-loading recovery subsystem 150 preferably provides solution 152 of concentrated salt or base and water coupled to line 128 for reuse as regenerant solution 112 via regenerant solution makeup tank 114 and regenerant solution line 112. In one example, superloading and recovery subsystem 150 is a small vessel, e.g., vessel 170 in caption 172 as shown having anion exchange resin therein which provides ultra-concentrated PFAS on anion exchange resin 104 and outputs solution 152 of concentrated salt or base and water. When vessel 170 becomes saturated with PFAS, it can be removed and taken off-site for distribution. The small size and high concentration of PFAS reduces costs associated with removal of PFAS from water.

System 100 also preferably includes sample tap 156 or 158 as shown for testing the level of PFAS in treated water 116. When PFAS are detected in treated water 116, it means anion exchange resin 104 in vessel 102 has been saturated with PFAS attached to anion exchange resin 104 and anion exchange resin 104 need to be regenerated.

The sustainable method for removing concentrated per- and polyfluoroalkyl substances (PFAS) from one embodiment of this invention may include selecting an anion exchange resin configured to move PFAS and provide clean, treated water, step 200, Fig. 4. The selected anion exchange resin is then added to an anion exchange

vessel, step 202. A flow of water contaminated with PFAS is introduced to the anion exchange vessel such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water, step 204. An optimized regenerant solution is introduced to the anion exchange vessel to desorb PFAS from the anion exchange resin thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of desorbed PFCs and the optimized regenerant solution, step 206. The spent regenerant solution is then subjected to a separation and recovery process to recover the optimized regenerant solution for reuse and separate and concentrate the removed PFAS.

The result is that system 100, and the method thereof for removing and concentrating PFAS from water, efficiently and effectively removes PFAS from water, regenerates the anion exchange resin and then concentrates, or ultra concentrates, the desorbed PFAS with a solvent purification subsystem and/or on super-loading recovery subsystem in small vessels that can be inexpensively disposed of. Thus, system 100 and the method thereof provides a sustainable system and method for concentrating and removing PFAS from water and regenerating the selected anion exchange resin, which significantly reduces the cost to remove PFAS from water because it generates less toxic waste than conventional and known methods for removing PFAS. The separated and concentrated or ultra-concentrated PFAS is easier and less expensive to handle and transport. System 100 and the method thereof efficiently reclaims the solvent, salt or base, and water from the spent regenerant solution which further reduces cost.

Although specific features of the invention are shown in some drawings and not in others, this is for convenience only, as each feature may be combined with any

or all of the other features in accordance with the invention. The words "including", "comprising", "having", and "with" as used herein are to be interpreted broadly and comprehensively and are not limited to any physical interconnection. Moreover, any embodiments disclosed in the subject application are not to be taken as the only possible embodiments. Other embodiments will occur to those skilled in the art and are within the following claims.

In addition, any amendment presented during the prosecution of the patent application for this patent is not a disclaimer of any claim element presented in the application as filed: those skilled in the art cannot reasonably be expected to draft a claim that would literally encompass all possible equivalents, many equivalents will be unforeseeable at the time of the amendment and are beyond a fair interpretation of what is to be surrendered (if anything), the rationale underlying the amendment may bear no more than a tangential relation to many equivalents, and/or there are many other reasons the applicant cannot be expected to describe certain insubstantial substitutes for any claim element amended.

What is claimed is:

CLAIMS

1. A sustainable system for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water, the system comprising;

anion exchange vessel, including a selected anion exchange resin therein configured to remove PFAS from the water;

a line coupled to the vessel, configured to introduce a flow of water contaminated with PFAS such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water;

a regenerant solution line coupled to the anion exchange vessel configured to introduce an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin, thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of the removed PFAS and the optimized regenerant solution; and

a separation and recovery subsystem configured to recover the optimized regenerant solution for reuse and separate and concentrate the removed PFAS.

2. The system of claim 1 in which the PFAS is removed from the anion exchange resin by a dual mechanism including desorption and anion exchange.

3. The system of claim 2 in which the desorption includes providing the optimized regenerant solution having a predetermined concentration of a solvent configured to displace the adsorbed hydrophobic tails of PFAS from the backbone of

the anion exchange resin with the solvent, and providing a predetermined concentration of salt or base configured to displace hydrophilic heads of PFAS with inorganic anions.

4. The system of claim 3 in which optimized regenerant solution includes a mixture of a salt or a base, a solvent, and water.

5. The system of claim 4 in which the solvent includes an alcohol.

6. The system of claim 5 in which the optimized regenerant solution includes about 50% to about 90% methanol by volume, about 10% to about 50% water by volume, and about 1% to about 5% salt or base by weight.

7. The system of claim 6 in which the optimized regenerant solution includes about 70% methanol by volume, about 28% water by volume, and about 2% salt or base by weight.

8. The system of claim 1 in which the selected anion exchange resin includes a macroporous, strong base, anion exchange resin.

9. The system of claim 1 in which the separation and recovery subsystem includes one or more of: an evaporation subsystem, a distillation subsystem and/or a membrane separation subsystem.

10. The system of claim 9 further including a condenser coupled to the evaporation or distillation unit configured to condense the reclaimed regenerant solution.

11. The system of claim 1 in which the separation and recovery subsystem includes a solvent purification subsystem configured to remove carryover PFAS from the separation and recovery subsystem and to provide a purified, reclaimed solvent for reuse.

12. The system of claim 11 in which the solvent purification subsystem includes anionic exchange resin housed in a vessel.

13. The system of claim 1 in which the separation and recovery subsystem includes a super-loading recovery subsystem configured to create an ultra-concentrated PFAS waste product, and a solution of concentrated salt or base and water for reuse.

14. The system of claim 13 in which the super-loading recovery subsystem includes an anionic exchange resin housed in a vessel.

15. The system of claim 13 in which the super-loading recovery subsystem is configured to provide purified reclaimed water and purified reclaimed salt or base for reuse.

16. A sustainable method for removing and concentrating per- and polyfluoroalkyl substances (PFAS) from water, the method comprising:

selecting an anion exchange resin configured to remove PFAS and provide treated water;

adding the selected anion exchange resin to an anion exchange vessel;

introducing a flow of water contaminated with PFAS to a vessel such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water;

introducing an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of removed PFAS and the optimized regenerant solution; and

subjecting the spent regenerant solution to a separation and recovery process to recover the optimized regenerant solution for reuse and separate and concentrate the removed PFAS.

17. The method of claim 16 in which the PFAS is removed from the anion exchange resin by a dual mechanism including desorption and anion exchange.

18. The method of claim 17 in which the desorption includes providing a predetermined concentration of a solvent configured to displace hydrophobic tails of the PFAS on the backbone of the anion exchange resin with the solvent and providing a predetermined concentration of anions configured to displace hydrophilic heads of the PFAS with the anions.

19. The method of claim 18 in which the optimized regenerant solution

includes a mixture of a salt or a base, a solvent, and water.

20. The method of claim 19 in which the solvent includes an alcohol.

21. The method of claim 20 in which the optimized regenerant solution includes about 50% to about 70% methanol by volume, about 2% to about 28% water by volume, and about 1% to about 5% salt or base by weight.

22. The method of claim 21 in which the optimized regenerant solution includes about 70% methanol by volume, about 28% water by volume and about 2% salt or base by weight.

23. The method of claim 16 in which the selected anion exchange resin includes a macro-porous, strong base, anion exchange resin.

24. The method of claim 16 in which the separation and recovery process is configured to maximize recovery of optimized regenerant solution and minimize volume of concentrated desorbed PFAS.

25. The method of claim 16 in which the separation and recovery process includes one or more of evaporation, distillation and membrane separation.

26. The method of claim 25 in which the evaporation or vacuum distillation includes condensing the spent regenerant solution.

27. The method of claim 25 in which the separation and recovery process includes removing carryover PFAS to provide a purified reclaimed solvent for reuse.

28. The method of claim 16 in which the separation and recovery subsystem includes creating an ultra-concentrated PFAS waste product and a solution of concentrated salt or base and water for reuse.

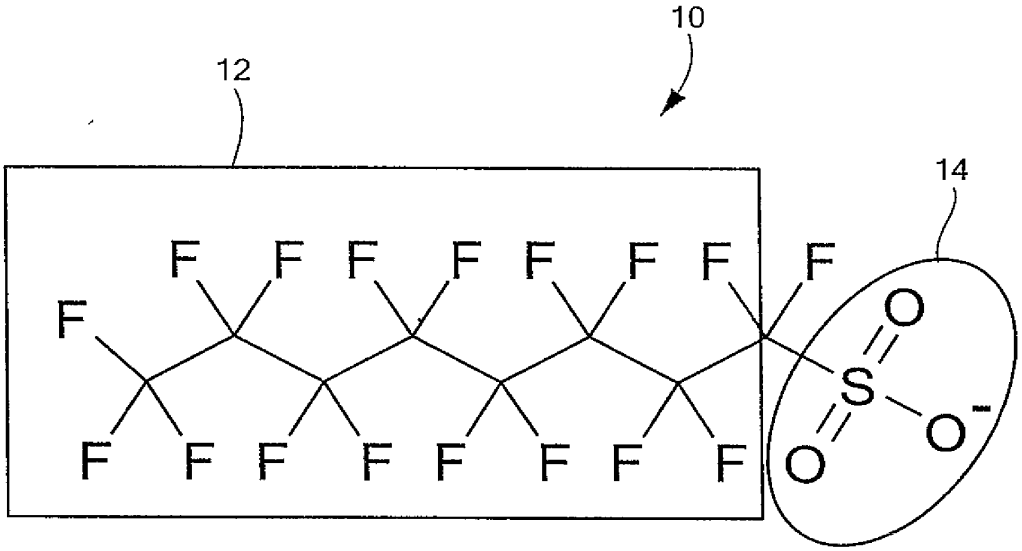


FIG. 1

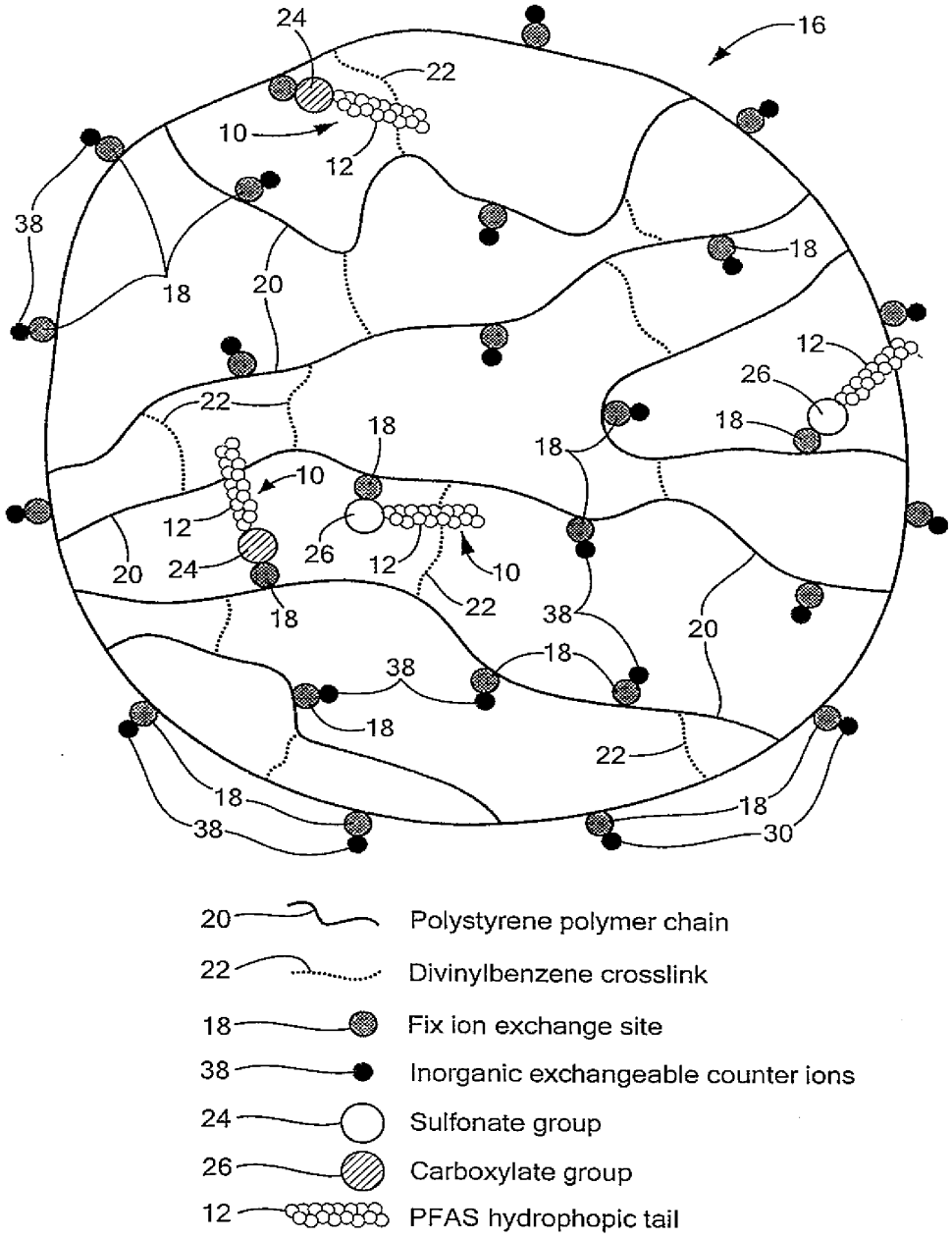

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18
30
20 Polystyrene polymer chain
22 Divinylbenzene crosslink
18 Fix ion exchange site
38 Inorganic exchangeable counter ions
24 Sulfonate group
26 Carboxylate group
12 PFAS hydrophopic tail

FIG. 2

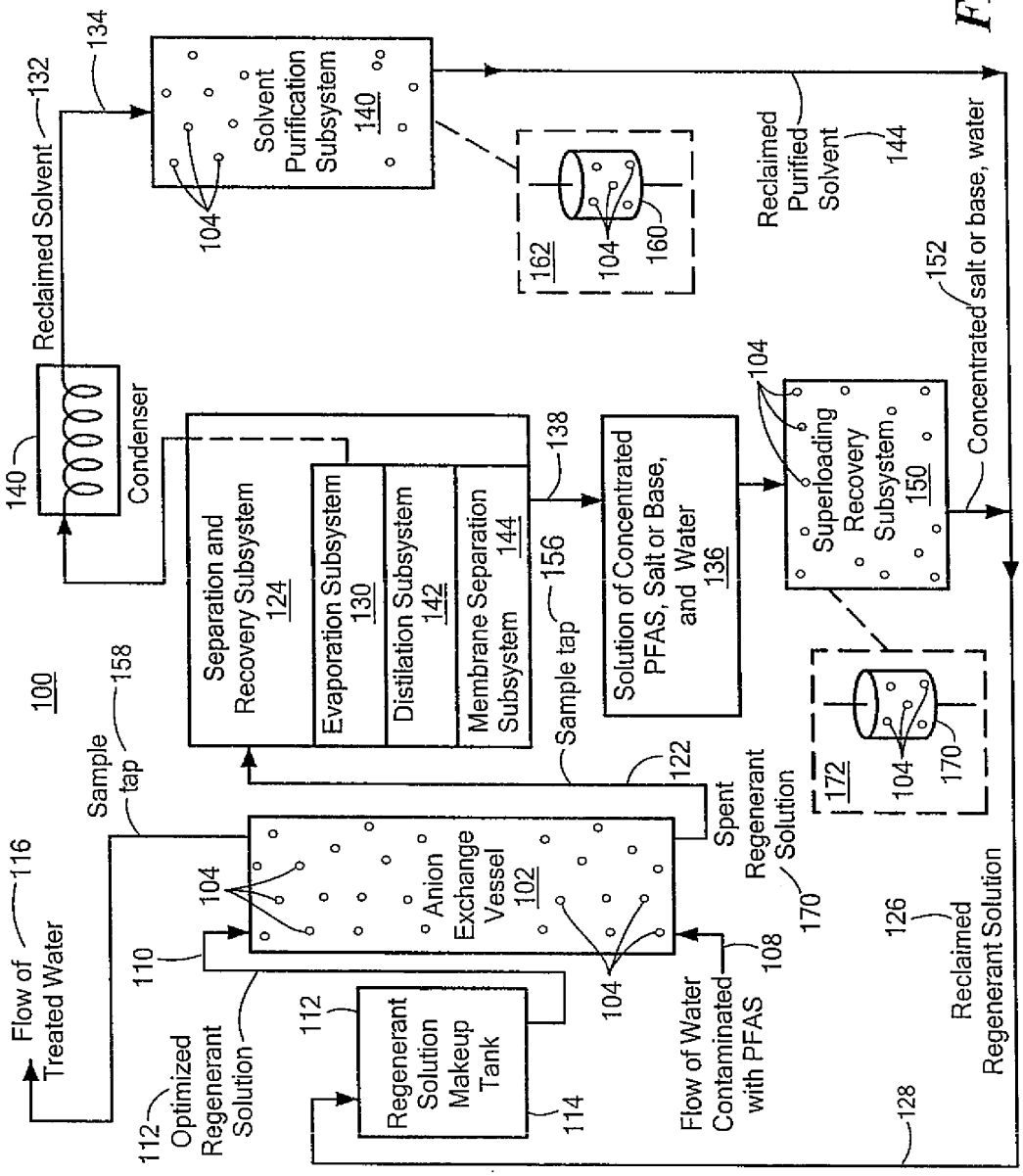

100
Flow of Treated Water
116
Sample tap
158
Anion Exchange Vessel 102
104
110
Optimized Regenerant Solution
112
Regenerant Solution Makeup Tank
114
Flow of Water Contaminated with PFAS
108
Spent Regenerant Solution
170
122
Sample tap
156
Separation and Recovery Subsystem 124
Evaporation Subsystem 130
Distillation Subsystem 142
Membrane Separation Subsystem 144
138
Solution of Concentrated PFAS, Salt or Base, and Water 136
Superloading Recovery Subsystem 150
Concentrated salt or base, water
152
Reclaimed Purified Solvent
144
Solvent Purification Subsystem 140
Reclaimed Solvent
132
134
Condenser
140
162
160
172
170
126
Reclaimed Regenerant Solution
128

FIG. 3

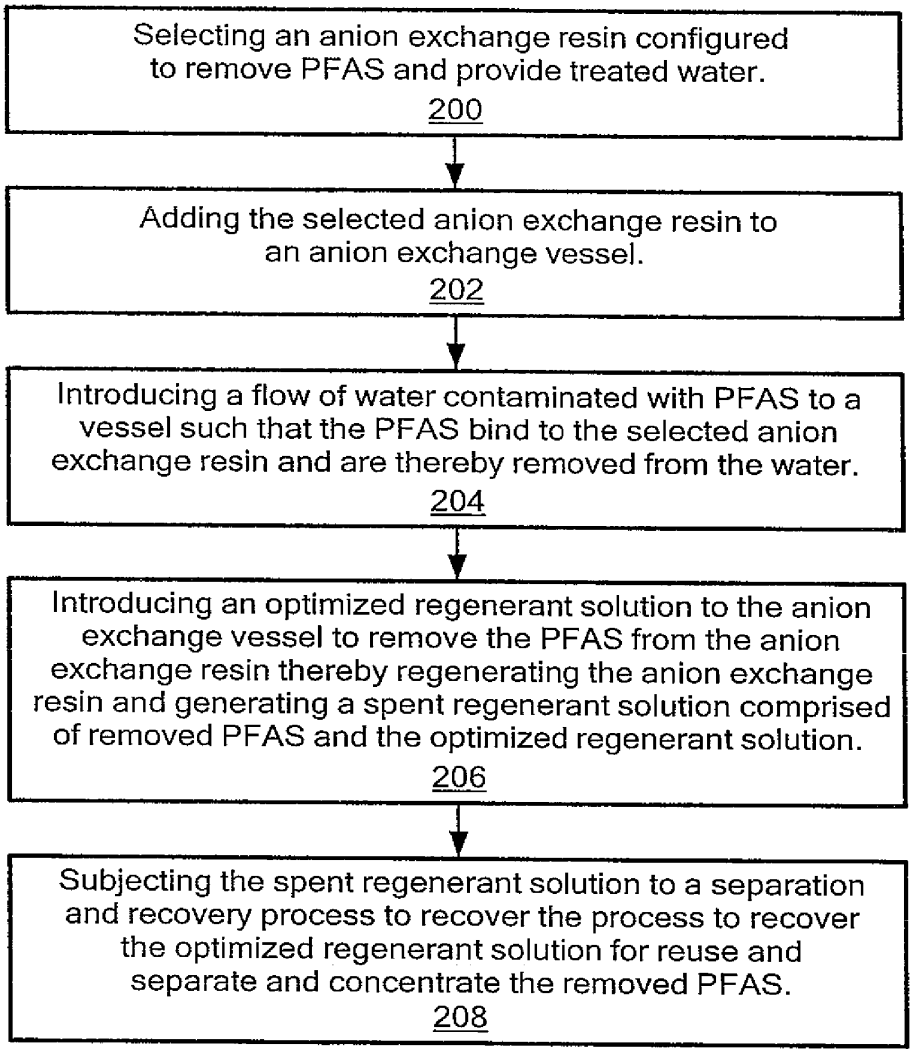

Selecting an anion exchange resin configured to remove PFAS and provide treated water.
200
Adding the selected anion exchange resin to an anion exchange vessel.
202
Introducing a flow of water contaminated with PFAS to a vessel such that the PFAS bind to the selected anion exchange resin and are thereby removed from the water.
204
Introducing an optimized regenerant solution to the anion exchange vessel to remove the PFAS from the anion exchange resin thereby regenerating the anion exchange resin and generating a spent regenerant solution comprised of removed PFAS and the optimized regenerant solution.
206
Subjecting the spent regenerant solution to a separation and recovery process to recover the process to recover the optimized regenerant solution for reuse and separate and concentrate the removed PFAS.
208

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/25754

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C02F 1/42; C02F 1/58 (2017.01)
CPC - Y02W10/00; C02F2001/422

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2008/0182913 A1 (Higuchi et al.) 31 July 2008 (31.07.2008) para [0001], [0013], [0014], [0015], [0019], [0021], [0025], [0030], [0042], [0042], [0048], [0051]	1-2, 8-9, 16-17, 23, 25 --- 3-7, 10-15, 18-22, 24 and 26-28
Y	US 2005/0177000 A1 (Fuhrer et al.) 11 August 2005 (11.08.2005) para [0014], [0016], [0023], [0024], [0025], [0036], [0043], [0047]	3-7, 10-15, 18-22, 24 and 26-28
A	US 2013/0334140 A1 (Podesta et al.) 19 December 2013 (19.12.2013) para [0001], [0019], [0037], [0049], [0056]	1-28
A	US 2005/0145571 A1 (Strauss et al.) 07 July 2005 (07.07.2005) entire document	1-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 June 2017	06 JUL 2017
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)

Electronic Acknowledgement Receipt

EFS ID:	40115565
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
Filer Authorized By:	Nicholas Charalambos Kokkinos
Attorney Docket Number:	123450.013001
Receipt Date:	27-JUL-2020
Filing Date:	03-APR-2020
Time Stamp:	17:16:23
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	123450_013001_IDS_Transmittal_Letter_07_27_2020.pdf	20640 1ecfe1eeda2fa39b3b34df5bd9e721173d79ea72	no	2

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	123450_013001_Information_Disclosure_Statement_SB08_07_27_2020.pdf	1034641 c4c5ca4250b671f6881d9fba2b4bb87b74a4db90	no	4
Warnings:					
Information:					
3	Foreign Reference	FR3077069A1.pdf	1102841 05e72774d30e1336dcd50d51419683f9f53efde8	no	29
Warnings:					
Information:					
4	Foreign Reference	WO2017180346A1.pdf	1185320 177b970887427c7f243bbc66db9ea323c4f8ec17	no	31
Warnings:					
Information:					
5	Foreign Reference	Johnson_8001.pdf	256545 701404c2ab9e199f049ca780774dc91cada0bf23	no	6
Warnings:					
Information:					
			Total Files Size (in bytes):	3599987	

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Docket No.: 123450.013001
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Rebecca L. DISTEFANO et al.

Application No.: 16/839,862 Confirmation No.: 5111

Filed: April 3, 2020 Art Unit: 1736

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Examiner: Not Yet Assigned

SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT (IDS)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with 37 C.F.R. § 1.97, Applicant(s) hereby make of record the following additional documents. A PTO Form SB/08 and a full copy of each of the documents required under 37 C.F.R. § 1.98(a)(2) accompany this statement.

Applicant(s) have become aware of the following documents, cited in an International Search Report issued June 30, 2020, during the prosecution of International Application No. PCT/US2020/026661, which corresponds to the above referenced application, and in accordance with 37 C.F.R. § 1.97(c) and (e)(1) or (b)(3), hereby submit(s) these documents for the Examiner's consideration. These documents are cited on the enclosed PTO Form SB/08, and a copy of each document required under 37 C.F.R. § 1.98(a)(2) cited thereon are enclosed as well.

This statement is not to be interpreted as a representation that the cited documents are material, that an exhaustive search has been conducted, or that no other relevant information exists. Nor shall the citation of any document herein be construed *per se* as a representation that such

document is prior art. Moreover, Applicant(s) understand(s) the Examiner will make an independent evaluation of the cited documents.

This Information Disclosure Statement is filed before the mailing date of a first Office Action on the merits (37 C.F.R. § 1.97(b)(3)).

In accordance with 37 C.F.R. § 1.704(d)(1), each item of information contained in this Information Disclosure Statement (i) was first cited in any communication from a patent office in a counterpart foreign or international application or from the United States Patent and Trademark Office and this communication was not received by any individual designated in 37 C.F.R. § 1.56(c) more than thirty days prior to the filing of this Information Disclosure Statement; or (ii) is a communication that was issued by a patent office in a counterpart foreign or international application or by the United States Patent and Trademark Office, and this communication was not received by any individual designated in 37 C.F.R. § 1.56(c) more than thirty days prior to the filing of this Information Disclosure Statement.

Applicant believes no fee is due with this response. However, if a fee is due, please charge our Deposit Account No. 50-0436, under Order No. 123450.13001 from which the undersigned is authorized to draw.

Dated: July 27, 2020

Respectfully submitted,

Electronic signature: /Nicholas Kokkinos/
Nicholas C. Kokkinos
Registration No.: 76,979
Troutman Pepper Hamilton Sanders LLP
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412.454.5060 (Fax)
Nicholas.Kokkinos@troutman.com (E-Mail)

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01160

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Not for submission under 37 CFR 1.99)

Application Number	16839862
Filing Date	2020-04-03
First Named Inventor	Rebecca L. Distefano
Art Unit	1736
Examiner Name	Not Yet Assigned
Attorney Docket Number	123450.13001

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	9199862	B2	2015-12-01	Kuramitsu et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

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Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01161

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1736
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.13001

	1	McNamara et al., "Comparison of Activated Carbons for Removal of Perfluorinated Compounds from Drinking Water", American Water Works Association, January 2018 (13 pages)	
	2	Wang et al., "Influence of cations on the partition behavior of perfluoroheptanoate (PFHpA) and perfluorohexanesulfonate (PFHxS) on waste water sludge", Chemosphere, Vol. 131, July 2015, pp. 178-183	
	3	Westreich et al., "The removal of short-chain and long-chain perfluoroalkyl acids and sulfonates via granular activated carbons: A comparative column study", Remediation Journal, December 4, 2018; Vol. 29(1) pp. 19-26	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01162

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	16839862
	Filing Date	2020-04-03
	First Named Inventor	Rebecca L. Distefano
	Art Unit	1736
	Examiner Name	Not Yet Assigned
	Attorney Docket Number	123450.13001

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

☒ See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Nicholas Kokkinos/	Date (YYYY-MM-DD)	2020-06-26
Name/Print	Nicholas C. Kokkinos	Registration Number	76979

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01163

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01164

Electronic Acknowledgement Receipt

EFS ID:	39835154
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Michael Vertullo
Filer Authorized By:	Nicholas Charalambos Kokkinos
Attorney Docket Number:	123450.13001
Receipt Date:	26-JUN-2020
Filing Date:	03-APR-2020
Time Stamp:	10:10:11
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal Letter	123450_13001_IDS_Transmittal_Letter_06_26_2020.pdf	18412 5bb1983b0404b47b83e5fdb9e26905f654f0a663	no	2

Warnings:

Information:					
2	Information Disclosure Statement (IDS) Form (SB08)	123450_13001_Information_Disclosure_Statement_SB08_06_26_2020.pdf	1034607 dd9a9a0047e689d46fc3c14286ad293aa361ac4	no	4
Warnings:					
Information:					
3	Non Patent Literature	jaw201801mcnamara_pr-3_clear.pdf	7062665 bc66744db8b3d40b0e7b59c19e203037d14e9ed5	no	13
Warnings:					
Information:					
4	Non Patent Literature	Wang_178.pdf	677451 1625d0f4acae6fe784b0d8255b8657672ea26ea5	no	6
Warnings:					
Information:					
5	Non Patent Literature	Westreich_19-26Remediation-Journal.pdf	584324 b1865b49b82b468571171abae805872f01e3fa62	no	8
Warnings:					
Information:					
			Total Files Size (in bytes):	9377459	

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New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Docket No.: 123450.13001
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Rebecca L. Distefano et al.

Application No.: 16/839,862 | Confirmation No.: 5111

Filed: April 3, 2020 | Art Unit: 1736

For: PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE | Examiner: Not Yet Assigned

INFORMATION DISCLOSURE STATEMENT (IDS)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

Pursuant to 37 C.F.R. §§ 1.56, 1.97, and 1.98, the attention of the United States Patent and Trademark Office is hereby directed to the references listed on the attached PTO/SB/08. It is respectfully requested that the information be expressly considered during the prosecution of the above-identified application, and that the references be made of record therein and appear among the "References Cited" on any patent to issue therefrom.

This Information Disclosure Statement is filed within three months of the filing date of a national application other than a continued prosecution application under 37 C.F.R. § 1.53(d) (37 C.F.R. § 1.97(b)(1)).

In accordance with 37 C.F.R. § 1.98(a)(2)(ii), copies of U.S. patents and U.S. patent application publications are not submitted. Submitted herewith are copies of non-patent literature in accordance with 37 C.F.R. § 1.98(a)(2).

In accordance with 37 C.F.R. § 1.97(g), the filing of this Information Disclosure Statement shall not be construed as a representation that a search has been made. In accordance with 37 C.F.R. § 1.97(h), the filing of this Information Disclosure Statement shall not be construed to be an admission that the information cited in this Information Disclosure Statement is, or is considered to be, material to patentability as defined in 37 C.F.R. § 1.56(b).

It is submitted that the Information Disclosure Statement is in compliance with 37 C.F.R. § 1.98, and the Examiner is respectfully requested to consider the listed references.

Applicant believes no fee is due with this response. However, if a fee is due, please charge our Deposit Account No. 50-0436, under Order No. 123450.13001 from which the undersigned is authorized to draw.

Dated: June 26, 2020

Respectfully submitted,

Electronic signature: /Nicholas Kokkinos/
Nicholas C. Kokkinos
Registration No.: 76,979
PEPPER HAMILTON LLP
501 Grant Street
Suite 300
Union Trust Building
Pittsburgh, Pennsylvania 15219-4429
412.454.5000
412.454.5060 (Fax)
kokkinon@pepperlaw.com (E-Mail)

Exhibit 1042
Norit Americas, Inc. v. Calgon Carbon Corporation
01168

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
16/839,862	04/03/2020	Rebecca L. DISTEFANO	123450.13001

CONFIRMATION NO. 5111

93724
Pepper/Calgon Carbon Corporation
Suite 300, Union Trust Building
501 Grant Street
Pittsburgh, PA 15219-4429

INFORMAL NOTICE

OC000000116187143

Date Mailed: 04/14/2020

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- A properly executed inventor's oath or declaration has not been received for the following inventor(s):
  Rebecca L. DISTEFANO
  Richard A. MIMNA

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/smberhe/

Exhibit 1042
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01169

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 16/839,862

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	660
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	13 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	1 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1720

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)	OR	RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
16/839,862	04/03/2020	1736	1880	123450.13001	13	1

CONFIRMATION NO. 5111

93724
Pepper/Calgon Carbon Corporation
Suite 300, Union Trust Building
501 Grant Street
Pittsburgh, PA 15219-4429

FILING RECEIPT

OC000000118187142

Date Mailed: 04/14/2020

Receipt is acknowledged of this non-provisional utility patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF FIRST INVENTOR, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection.

Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please submit a written request for a corrected Filing Receipt, including a properly marked-up ADS showing the changes with strike-through for deletions and underlining for additions. If you received a "Notice to File Missing Parts" or other Notice requiring a response for this application, please submit any request for correction to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections provided that the request is grantable.

Inventor(s)

Rebecca L. DISTEFANO, Oakdale, PA;
Richard A. MIMNA, Oakdale, PA;

Applicant(s)

CALGON CARBON CORPORATION, Moon Township, PA;

Assignment For Published Patent Application

CALGON CARBON CORPORATION, Moon Township, PA

Power of Attorney: None

Domestic Priority data as claimed by applicant

This appln claims benefit of 62/828,790 04/03/2019

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

If Required, Foreign Filing License Granted: 04/13/2020

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 16/839,862**

Projected Publication Date: 10/08/2020

Non-Publication Request: No

Early Publication Request: No

Title

PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

Preliminary Class

423

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific

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countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop

technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

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Norit Americas, Inc. v. Calgon Carbon Corporation
01174

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Rebecca	L.	DISTEFANO	

Residence Information (Select One) ● US Residency Non US Residency Active US Military Service

City	Oakdale	State/Province	PA	Country of Residence	US

Mailing Address of Inventor:

Address 1	203 Heritage Drive		
Address 2			
City	Oakdale	State/Province	PA
Postal Code	15071	Country	US

Inventor 2 Remove

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Richard	A.	MIMNA	

Residence Information (Select One) ◉ US Residency Non US Residency Active US Military Service

City	Oakdale	State/Province	PA	Country of Residence	US

Mailing Address of Inventor:

Address 1	201 Heritage Drive		
Address 2			
City	Oakdale	State/Province	PA
Postal Code	15071	Country	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button. Add

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE	

☐ **An Address is being provided for the correspondence Information of this application.**

Customer Number	93724		
Email Address	docketingpgh@pepperlaw.com	Add Email	Remove Email

Application Information:

Title of the Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE		
Attorney Docket Number	123450.13001	**Small Entity Status Claimed**	☐
Application Type	Nonprovisional		
Subject Matter	Utility		
Total Number of Drawing Sheets (if any)	7	**Suggested Figure for Publication (if any)**	3

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	93724		

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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE	

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, 365(c), or 386(c) or indicate National Stage entry from a PCT application. Providing benefit claim information in the Application Data Sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the "Application Number" field blank.

Prior Application Status	Pending		Remove
Application Number	Continuity Type	Prior Application Number	Filing or 371(c) Date (YYYY-MM-DD)
	Claims benefit of provisional	62/828790	2019-04-03

Additional Domestic Benefit/National Stage Data may be generated within this form by selecting the **Add** button. Add

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55. When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)[i] the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(i)(1) and (2). Under the PDX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Remove

Application Number	Country[i]	Filing Date (YYYY-MM-DD)	Access Code[i] (if applicable)

Additional Foreign Priority Data may be generated within this form by selecting the **Add** button. Add

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

☐ This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA.

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Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE	

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant **must opt-out** of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is **ONLY** reviewed and processed with the **INITIAL** filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby **grants the USPTO authority** to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ A. Applicant **DOES NOT** authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.

☐ B. Applicant **DOES NOT** authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE	

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant 1 Remove

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

Clear

● Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

Name of the Deceased or Legally Incapacitated Inventor:

If the Applicant is an Organization check here. ☒

Organization Name	CALGON CARBON CORPORATION		
Mailing Address Information For Applicant:			
Address 1	3000 GSK Drive		
Address 2			
City	Moon Township	**State/Province**	PA
Country	US	Postal Code	15108
Phone Number		Fax Number	
Email Address			

Additional Applicant Data may be generated within this form by selecting the Add button. Add

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

PTO/AIA/14 (02-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
Title of Invention	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE	

Assignee 1

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	123450.13001
	Application Number	
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This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

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ABSTRACT:

Sorbent materials that are treated with ions, salts, oxides, hydroxides, or carbonates of calcium, magnesium, strontium, or barium are useful in removing perfluoroalkyl and polyfluoroalkyl substances (PFAS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), 2,3,3,3,-tetrafluoro-2-(heptafluoropropoxy)propanoate and heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether, and similar compounds from liquids and gases are disclosed. The sorbent materials with the disclosed treatments offer improved performance as measured against untreated sorbent materials.

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Claims:

1. A method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising:

   providing a first sorbent material including about 0.5 wt.% to about 25 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and

   contacting the first sorbent material with a liquid or gas containing the PFAS.

2. The method of claim 1, wherein the first sorbent material includes one or more of carbonaceous char, activated carbon, reactivated carbon, and carbon black.
3. The method of claim 2, wherein the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.
4. The method of claim 2, wherein the first sorbent material is reactivated carbon.
5. The method of claim 2, wherein the first sorbent material is a reagglomerated activated carbon.
6. The method of claim 1, further comprising:

   providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and

   contacting the second sorbent material with the liquid or gas containing the PFAS.

7. The method of claim 1, wherein the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium, an oxide of strontium, or an oxide of barium.
8. The method of claim 7, wherein the first sorbent material includes one or more of MgO or CaO.

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9. The method of claim 1, wherein the ion, salt, oxide, hydroxide, or carbonate of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation, chemical vapor deposition, or physical vapor deposition.
10. The method of claim 1, wherein the first sorbent material includes about 1 wt.% to about 20 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
11. The method of claim 10, wherein the first sorbent material includes about 2 wt.% to about 8 wt.% of an ion, salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.
12. The method of claim 1, wherein the first sorbent material is a reactivated carbon comprising ions, oxides or carbonates of calcium, magnesium, sodium, potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, potassium and zinc.
13. The method of claim 12, wherein the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, and zinc.

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PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE

RELATED APPLICATIONS:

[001] This application claims priority to U.S. Provisional Application Serial No. 62/828,790 filed on April 3, 2019, the content of which is hereby incorporated by reference in its entirety.

BACKGROUND:

[002] Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a group of compounds that include perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), and compounds produced by the GENX process such as 2,3,3,3,-tetrafluoro-2-(heptafluoropropoxy)propanoate and heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether. Such highly fluorinated compounds enjoyed widespread industrial use for many years, owing to their chemical durability, excellent surfactant properties, and key role as precursors to fluoropolymers including polytetrafluoroethylene.

[003] Unfortunately, these same properties render PFAS resistant to degradation in the environment, while simultaneously leading to bioaccumulation when ingested over time. Some recent studies have linked PFAS to various detrimental health effects, most notably elevated levels of cholesterol, but also kidney cancer, testicular cancer, thyroid disease, and pregnancy-induced hypertension.

[004] To date, several technologies have been employed to remove PFAS compounds from the environment and from drinking water. Such technologies include granular activated carbon (GAC), ion exchange resins, and reverse osmosis. GAC has emerged as a leading solution, but there is continued need for performance improvements so that the GAC is even more effective at removing PFAS compounds from the environment and from drinking water.

SUMMARY:

[005] The disclosure describes sorbent materials that have improved performance in removing PFAS, including but not limited to PFOA, PFOS, and similar compounds from liquids and gases. The disclosed embodiments include:

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[006] In one embodiment, there is a method of removing perfluoroalkyl and polyfluoroalkyl substances (PFAS) from liquid or gas, the method comprising providing a first sorbent material including about 0.5 wt.% to about 25 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium or combination or compound thereof to thereby increase the sorbent capacity of the sorbent material to perfluoroalkyl and polyfluoroalkyl substances (PFAS) relative to sorbent material that does not include the ion, salt, oxide, hydroxide, or carbonate; and contacting the first sorbent material with a liquid or gas containing the PFAS.

[007] In another embodiment, the first sorbent material includes one or more of carbonaceous char, activated carbon, reactivated carbon, and carbon black.

[008] In another embodiment, the carbonaceous char, activated carbon, reactivated carbon, or carbon black are formed from at least one of bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, or polymer fibers.

[009] In another embodiment, wherein the first sorbent material is reactivated carbon.

[0010] In another embodiment, the first sorbent material is a reagglomerated activated carbon.

[0011] In another embodiment, there is a further step of providing a second sorbent material that includes one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural zeolite, synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, and metal oxides, and contacting the second sorbent material with the liquid or gas containing the PFAS.

[0012] In another embodiment, the first sorbent material includes one or more of an oxide of magnesium, an oxide of calcium, an oxide of strontium, or an oxide of barium.

[0013] In another embodiment, the first sorbent material includes one or more of MgO or CaO.

[0014] In another embodiment, the ion, salt, oxide, hydroxide, or carbonate of the first sorbent material is included in the first sorbent material by one or more of dry mixing, wet impregnation, chemical vapor deposition, or physical vapor deposition.

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[0015] In another embodiment, the first sorbent material includes about 1 wt.% to about 20 wt.% of an ion, salt, oxide, hydroxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.

[0016] In another embodiment, the first sorbent material includes about 2 wt.% to about 8 wt.% of an ion, salt, oxide, or carbonate of magnesium, calcium, strontium, barium, or combinations or compounds thereof.

[0017] In another embodiment, the first sorbent material is a reactivated carbon comprising ions, oxides or carbonates of calcium, magnesium, sodium, potassium, and zinc, and the reactivated carbon has not undergone any process to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, potassium and zinc.

[0018] In another embodiment, the reactivated carbon has not undergone any acid washing to remove or reduce the amount of the ions, oxides, or carbonates of calcium, magnesium, sodium, and zinc.

BRIEF DESCRIPTION OF THE DRAWINGS:

[0019] Aspects, features, benefits and advantages of the embodiments described herein will be apparent with regard to the following description, appended claims, and accompanying drawings where:

[0020] FIG. 1 is a graphical representation of the results of rapid small scale column testing activated carbon and reactivated carbon having elevated calcium content.

[0021] FIG. 2 is a graphical representation of further results of rapid small scale column testing of activated carbon and reactivated carbon having elevated calcium content.

[0022] FIG. 3 is a graphical representation comparing the results of testing activated carbon, reactivated carbon having elevated calcium content, and activated carbon having elevated magnesium content.

[0023] FIG. 4 is a graphical representation of the results of testing activated carbons and reactivated carbons having elevated calcium content.

[0024] FIG. 5 is a graphical representation of further results of testing activated carbons and reactivated carbons having elevated calcium content.

[0025] FIG. 6 is a graphical representation of further results of testing activated carbons and reactivated carbons having elevated calcium content.

[0026] FIG. 7 is a graphical representation of the results of testing virgin coal-based activate carbons, acid washed reactivated carbon having elevated calcium content,

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reactivated carbon having high calcium content, activated carbon with high magnesium content, and activated carbon with pulverize magnesium oxide content.

DETAILED DESCRIPTION:

[0027] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0028] As used in this document, the singular forms "a," "an," and "the" include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term "comprising" means "including, but not limited to."

[0029] As used herein, the term "about" means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

[0030] As used herein, the term "sorbent material" is meant to encompass all known materials from any source that are capable of absorbing or adsorbing liquids and/or gases. For example, sorbent materials include, but are not limited to, activated carbon, reactivated carbon, natural and synthetic zeolite, silica, silica gel, alumina, zirconia, and diatomaceous earths.

[0031] As used herein, the term "perfluoroalkyl and polyfluoroalkyl substances (PFAS)" means any perfluoroalkyl or polyfluoroalkyl substance, mixture of such substances, or derivative of one or more such substances. Examples of PFAS include perfluoroalkyl sulfonate, perfluoroalkane sulfonic acid (PFSA), N-Butyl perfluoroalkane sulfonamide (BuFASA), N-Butyl perfluoroalkane sulfonamido ethanols (BuFASE), N-Butyl perfluoroalkane sulfonamido acetic acid (BuFASAA), N-Ethyl perfluoroalkane sulfonamide (EtFASA), N-Ethyl perfluoroalkane sulfonamido ethanol (EtFASE), N-Ethyl perfluoroalkane sulfonamido acetic acid (EtFASAA), perfluoroalkane sulfonamide (FASA), Perfluoroalkane sulfonamido ethanol (FASE), Perfluoroalkane sulfonamido acetic acid (FASAA), N-Methyl perfluoroalkane sulfonamide (MeFASA), N-Methyl perfluoroalkane sulfonamido acetic acid

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(MeFASAA), N-Methyl perfluoroalkane sulfonamido ethanol (MeFASE), N-Methyl perfluorooctane sulfonamide (MeFOSA), perfluoroalkane sulfonyl fluoride (PASF), 4,8-dioxa-3H-perfluorononanoate, ammonium perfluorooctanoate (APFO), fluoroprotein (FP), fluorotelomer carboxylic acid (FTCA), fluorotelomer alcohol (FTOH), fluorotelomer sulfonate (FTS), fluorotelomer sulfonic acid (FTSA), perfluoroalkyl acid (PFAA), perfluoroalkylsulfonamidoethanol (PFOSE), and any derivatives thereof. These include, for example and without limitation, perfluorooctanoic acid (PFOA), perfluorooctane sulfonate, perfluorooctanesulfonic acid (PFOS), 2,3,3,3,-tetrafluoro-2-(heptafluoropropoxy)propanoate, ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate, 1,2,2,2-tetrafluoroethyl ether, 4:2-Fluorotelomersulfonic acid (4:2 FtS), 6:2-Fluorotelomersulfonic acid (6:2 FtS), 8:2-fluorotelomersulfonic acid (8:2 FtS), perfluorobutanoic acid (PFBA), perfluorobutane sulfonate, perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonate, perfluorohexane sulfonic acid (PFHxS), perfluorohexanoate, perfluorohexanoic acid (PFHxA), 4,8-dioxa-3H-perfluorononanoate, ammonium perfluorooctanoate (APFO), N-Ethyl perfluorooctane sulfonamide (EtFOSA),N-Ethyl perfluorooctane sulfonamido ethanol (EtFOSE), perfluorooctane sulfonamide (PFOSA), perfluorooctane sulfonamido acetic acid (FOSAA), perfluorooctane sulfonamido ethanol (FOSE), perfluorobutanoate, perfluorobutanoic acid, perfluorobutyrate, perfluorobutyric acid, perfluoroalkyl carboxylate, perfluoroalkyl carboxylic acid (PFCA), perfluorodecanoate, perfluorodecanoic acid (PFDA), perfluorododecanoate, perfluorododecanoic acid (PFDoA), perfluorododecane sulfonate (PFDoS), perfluorododecane sulfonic acid (PFDoSA), perfluorodecane sulfonate, perfluorodecane sulfonic acid (PFDS), perfluoroheptanoate, perfluoroheptanoic acid (PFHpA), perfluoroheptane sulfonate, perfluoroheptane sulfonic acid (PFHpS), perfluorononanoate, perfluorononanoic acid (PFNA), perfluorononane sulfonate, perfluorononane sulfonic acid (PFNS), perfluorooctanoate, perfluorophosphonic acid (PFPA), perfluoropentanoate, perfluoropentanoic acid (PFPeA), perfluoropentane sulfonate, perfluoropentane sulfonic acid (PFPeS), perfluorophosphinic acid (PFPiA), Perfluorotetradecanoic acid (PFTeDA), Perfluorotridecanoic acid (PFTrDA), perfluoroundecanoate, perfluoroundecanoic acid (PFUnA), perfluoroundecane sulfonate (PFUnS), perfluoroundecane sulfonic acid (PFUnSA), or polytetrafluoroethylene (PTFE).

SORBENT MATERIALS

[0032] The disclosure provides a variety of sorbent materials including, but not limited to, carbonaceous char, activated carbon, reactivated carbon, carbon black, natural and

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synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, or metal oxides. The sorbent materials may be used alone or in combination. In some embodiments where sorbent materials are used in combination, multiple treated sorbents are mixed together; such treated sorbents can be the same or different. In other embodiments, a sorbent material that is treated as described herein is combined with a sorbent material that is not treated. For example, in an embodiment, a first sorbent material that is treated according to the disclosure and is one or more of carbonaceous char, activated carbon, reactivated carbon, or carbon black and is mixed with a second sorbent that is not treated according to the disclosure and is one or more of carbonaceous char, activated carbon, reactivated carbon, carbon black, natural and synthetic zeolite, silica, silica gel, alumina, alumina clay, zirconia, diatomaceous earths, or metal oxides.

[0033] In some embodiments, the sorbent material is activated carbon or reactivated carbon. In such embodiments, the activated or reactivated carbon is prepared from any precursor carbonaceous material known in the art including, but not limited to bituminous coal, sub-bituminous coal, lignite coal, anthracite coal, wood, wood chips, sawdust, peat, nut shells, pits, coconut shell, babassu nut, macadamia nut, dende nut, peach pit, cherry pit, olive pit, walnut shell, wood, lignin, polymers, nitrogen-containing polymers, resins, petroleum pitches, bagasse, rice hulls, corn husks, wheat hulls and chaff, graphenes, carbon nanotubes, polymer fibers, and any other carbonaceous material or combinations thereof. In some embodiments, the carbonaceous material may be derived from activated carbons produced from various precursors that have been in-use and subsequently reactivated and/or regenerated. In some embodiments, the sorbent material feedstock is provided in a preoxidized state. In other embodiments, the sorbent material feedstock is provided in an unoxidized state.

[0034] When the sorbent material is an activated carbon or a reactivated carbon, it is of various grades and types selected based on performance requirements, cost, and other considerations. In some embodiments, the sorbent material is activated carbon or reactivated carbon that is in powdered form. In other embodiments, the sorbent material is activated carbon or reactivated carbon that is granular form, where such granular activated carbon or reactivated carbon is formed by pulverizing a precursor carbonaceous material, forming the resultant pulverized material into briquettes, and subsequently pulverizing the briquettes into the desired size. The resultant granular material is then heated to perform various operations including removal of volatile compounds and activating the precursor carbonaceous material that is included therein. In still further embodiments, the sorbent material is activated carbon

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or reactivated carbon that is in pelletized form. In such embodiments, the sorbent material is formed by pulverizing a precursor carbonaceous material, extruding the pulverized material along with binder material into pellets. The pellets are then heated to perform various operations including removal of volatile compounds and activating the precursor carbonaceous material that is included therein.

[0035] The sorbent material made from activated carbon and/or reactivated carbon is formed by any useful process. In some embodiments, the activated carbon and/or reactivated carbon is formed by carbonization, activation, and/or reactivation. In some embodiments, the activated carbon and/or reactivated carbon is formed by oxidizing and devolatizing the carbonaceous material, with steam and/or carbon dioxide gasified to form the pore structure in the activated carbon or reactivated carbon that gives the activated carbon or reactivated carbon sorbent material properties. The initial oxidation and devolatilization process may include a chemical treatment with a dehydrating chemical, such as phosphoric acid, sulfuric acid, sodium hydroxide, potassium hydroxide, and combinations of those.

[0036] In some embodiments, the activated carbon is granular activated carbon (GAC), which is defined as activated carbon particles sized to be retained on a 50-mesh sieve (holes of about 0.300 mm). In other embodiments, the activated carbon is powdered activated carbon (PAC), which is defined as particles that pass through an 80-mesh sieve (holes of about 0.180 mm). While these particle size ranges are mentioned for activated carbon sorbent materials, it is also contemplated that any of the discloses sorbent materials may be measured by the above 50-mesh and 80-mesh sieve sizes.

[0037] In some embodiments, the sorbent material is a reactivated sorbent material that has previously had its sorbent capacity exhausted and that has been reactivated to restore at least some of the original sorbent capacity Any of the above listed sorbent materials can be reactivated following service, and the reactivation can be performed by heat, pressure, chemical exposure, or combinations of the above. In some embodiments, the reactivated sorbent material is reactivated carbon. Reactivated carbon is manufactured by heating spent, exhausted activated carbon in furnaces that are devoid of oxygen and using steam as a selective oxidant. During reactivation, absorbed and adsorbed organic compounds are either volatilized from the activated carbon or pyrolized to form carbon char. In some embodiments, heating takes place above about 700°C, and the resulting reactivated carbon may thereafter be reused for various purposes including water treatment. In some embodiments, the temperature of heating is about 500°C, about 550°C, about 600°C, about 650°C, about 700°C, about 750°C, about 800°C, about 850°C, about 900°C, about 950°C,

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about 1000°C, about 1050°, about 1100°C, or any range that is made of any two or more points in the above list.

[0038] In some embodiments, the sorbent material is deployed in applications that expose it to waters that include mineral content. In some embodiments, the mineral content includes calcium carbonate which accumulates on the sorbent material during its use in filtering water. In such embodiments, reactivation of the spent sorbent material results in the following reaction: $CaCO_3$ (s) → CaO (s) + CO_2 (g). As will be seen in the Examples, this regeneration technique results in reactivated sorbent material having improved sorbent performance for PFAS compounds, which includes PFOA and PFOS compounds. It is contemplated that the same performance improvements apply not only to PFAS compounds, but also to other chemically similar or chemically related compounds.

[0039] In some embodiments, the sorbent material is treated with an ion, salt, oxide, hydroxide, or carbonate of International Union of Pure and Applied Chemistry (IUPAC) Group 2, the alkaline earth metals. Of those compounds, Mg, Ca, Sr, Ba, and combinations thereof are contemplated as useful. Exemplary oxides include MgO, CaO, SrO, BaO, and combinations thereof. The combination may be by mixture of the above listed ions, salts, oxides, hydroxides, or carbonates, or by chemical combination of the above listed ions, oxide, hydroxides, or carbonates, in any stoichiometry. Each of the above mentioned compounds may be used alone or in combination, and they may further be used in any possible stoichiometry. Combinations of one or more ions, oxides, hydroxides, and carbonates of IUPAC Group 2 are also contemplated. The combination may be by mixture, or by stoichiometry or doping the metals in the oxides that the activated carbon is treated with. The treatment of the sorbent material with one or more treatment materials may be by any suitable method, including dry mixing, wet impregnation, chemical vapor deposition, physical vapor deposition, or combinations of the above. Furthermore, the same or different treatments may be used to deposit more than one material on the sorbent material. The treatment may also be achieved as a byproduct of sorbent material use without a separate treatment step. For example, in some embodiments, sorbent materials that are used in active service and which become laden with minerals that are naturally present in water including ions, oxides and carbonates of calcium, magnesium, sodium, potassium, magnesium, and zinc. Examples of such minerals include but are not limited to calcium ions, calcium oxides and hydroxides, calcium carbonate ($CaCO_3$), magnesium ions, magnesium oxides and hydroxides, magnesium carbonate ($MgCO_3$), sodium ions, sodium oxides and hydroxides, sodium carbonate (Na_2CO_3), potassium ions, potassium oxides and hydroxides, potassium

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carbonate (K_2CO_3), zinc ions, zinc oxides and hydroxides, zinc carbonate ($ZnCO_3$), and combinations of the above. The treatment is contemplated to improve the sorbent performance of the sorbent materials. It is contemplated that the same performance improvements apply to PFAS compounds including PFOA and PFOS, as well as other chemically similar or chemically related compounds.

[0040] The amount of the above ion, oxide, hydroxide, carbonate, or combination of those materials is measured by weight with respect to the total weight of the treated sorbent material and the ion, oxide, hydroxide, carbonate, or combination of those materials. The amount of the ion, salt, oxide, hydroxide, or carbonate is not limited and in some embodiments is less than about 25% wt.%, less than about 20 wt.%, less than about 15 wt.%, less than about 10 wt.%, less than about 8 wt.%, less than about 6 wt.%, less than about 4 wt.%, less than about 2 wt.%, less than about 1 wt.%, less than about 0.9 wt.%, less than about 0.8 wt.%, less than about 0.7 wt.%, less than about 0.6 wt.%, less than about 0.5 wt.%, less than about 0.4 wt.%, less than about 0.3 wt.%, less than about 0.2 wt.%, or less than about 0.1 wt.%. In some embodiments the amount of the ion, salt, oxide, hydroxide, or carbonate is about 25% wt.%, about 20 wt.%, about 15 wt.%, about 10 wt.%, about 9 wt.%, about 8 wt.%, about 7 wt.%, about 6 wt.%, about 5 wt.%, about 4 wt.%, about 3 wt.%, about 2 wt.%, about 1 wt.%, about 0.9 wt.%, about 0.8 wt.%, about 0.7 wt.%, about 0.6 wt.%, about 0.5 wt.%, about 0.4 wt.%, about 0.3 wt.%, about 0.2 wt.%, about 0.1 wt.%, or any range formed of any of the above two endpoints. In some embodiments, the amount of the ion, salt, oxide, hydroxide, or carbonate is about 1 wt.% to about 10 wt.%, about 2 wt.% to about 10 wt.%, about 4 wt.% to about 10 wt.%, about 6 wt.% to about 10 wt.%, about 1 wt.% to about 8 wt.%, about 2 wt.% to about 8 wt.%, about 4 wt.% to about 8 wt.%, about 4 wt.% to about 6 wt.%, or about 6 wt.% to about 8 wt.%.

[0041] The sorbent material can be formed by various techniques. In one embodiment, the sorbent material includes activated carbon that is a reagglomerated activated carbon. In reagglomerated activated carbon, the precursor carbonaceous material which is usually coal is pulverized to a powder. The powder is next mixed with a binder. The mixture of powder and binder is then reagglomerated into briquettes. The briquettes are then crushed and sized. The now crushed and sized briquettes are carbonized to harden the binder, and finally the crushed, sized, and carbonized briquette materials are thermally activated. This process forms a granulated activated carbon. During this process, the one or more ions, salts, oxides, hydroxides, or carbonates of IUPAC Group 2 elements, including Mg, Ca, Sr, Ba, and combinations can be added. In one embodiment, powders of the ions, salts, oxides,

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hydroxides, or carbonates are mixed with the pulverized coal before mixing with a binder. In another embodiment, a liquid solution of the ions, salts, oxides, hydroxides, or carbonates is applied to the crushed and sized briquettes before the carbonization step. In another embodiment, a liquid solution of the ions, salts, oxides, hydroxides, or carbonates is mixed after the carbonization step but before the activation step.

[0042] In some embodiments, the sorbent material is formed from a precursor that is a spent activated carbon that was previously used for water filtration and which is reactivated. In particular, spent activated carbon that has been used in point of use filters, point of entry filters, portable filters, and municipal drinking water filtration frequently contain significant amounts of inorganic minerals that reside on the surface of the activated carbon materials. In other embodiments, the precursor carbonaceous material is a spent activated carbon that was not previously used for water filtration, but was used for other applications. The other applications include food processing, beverage processing, sugar refining, wastewater treatment, waste gas treatment, tank cleaning, tank degassing, and combinations of the above. In some embodiments, the spent activated carbon that was previously used for water filtration contains one or more inorganic materials that are present in ground water including ions, oxides and carbonates of calcium, magnesium, sodium, potassium, and zinc.

[0043] In some embodiments, the sorbent material formed from a precursor that is a spent activated carbon is not treated to remove any of the inorganic materials that are present in ground water. This means that the sorbent material will include ions, oxides, and carbonates of calcium, magnesium, sodium, potassium, and zinc. In still further embodiments, the sorbent material formed from a precursor that is a spent activated carbon is not treated by acid washing to remove any of the inorganic materials that are present in ground water. In such embodiments, the one or more ions, salts, oxides, hydroxides, or carbonates that are present in ground water have been slowly impregnated onto the surface of the spent activated carbon, and are retained during reactivation to thereby form a sorbent material.

USES

[0044] The sorbent materials of the disclosure are useful whenever it is necessary to remove PFAS, PFOA, PFOS or chemically similar or chemically related compounds from liquids and/or gases, including water. The removal may be for the purposes of human or animal consumption, or for environmental remediation. Specific applications include point

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of use filters, point of entry filters, portable filters, municipal drinking water filtration, municipal waste filtration, and industrial waste filtration. In some embodiments, the sorbent materials of the disclosure are used alone, without any other sorbent materials. In some embodiments, the sorbent materials of the disclosure are used in combination with other sorbent materials.

[0045] Although the sorbent materials of the disclosure are primarily disclosed as removing PFAS, PFOA, PFOS, or chemically similar or chemically related compounds, the use of the sorbent materials is not so limited. In still further embodiments, the sorbent materials are suitable for removing any compounds and/or byproducts that cause taste and odor problems in water. Such compounds are referred to as "taste and odor compounds" throughout the application. Examples of such taste and odor compounds include one or more of trans-1, 10-dimethyl-trans-9-decalol ("Geosmin"), 2-methylisoborneol (MIB), isopropylmethoxypyrazine (IPMP), isobutylmethoxypyrazine (IBMP), methyl tertiary butyl ether (MTBE), 2,4-heptadienal, decandienal, octanal, chlorine, chloramine, chlorophenols, iodoform, hydrocarbons, volatile organic compounds (VOCs), iron, iron oxides, copper, copper oxides, zinc, zinc oxides, manganese, and manganese oxides.

[0046] In some embodiments, the sorbent materials are provided within a container. The container holds the sorbent materials and allows the liquid or gas to flow on or through the container, thus bringing the liquid or gas in contact with the sorbent materials. In some embodiments, the container is a permanent container that is installed within a device or process facility and which is connected by piping or other fluid conduits so that the liquid or gas flows through the container. From time to time, the spent sorbent materials are emptied from the container and replaced by virgin sorbent materials or reactivated sorbent materials, or both, in order to ensure that the sorbent materials remain effective in removing PFAS, PFOA, PFOS, or chemically similar or chemically related compounds from liquid or gas that flows through the container. The physical form of the sorbent materials within the container is not limited, and the sorbent materials can be provided loose (alone) or formed as a cartridge with other structural materials that hold it in place or which are mixed as a binder.

[0047] In some embodiments, the container itself is designed to be replaced rapidly and with minimal change to outside components such as pumps and conduits that convey the liquids or gases to the container. In such embodiments, the container is referred to as a "cartridge," and it can be connected and disconnected from surrounding components. In some embodiments, the cartridge is disposable, such as in consumer drinking water applications. In other embodiments, the cartridge is intended to be refurbished, with the

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cartridge containing spent sorbent returned for cleaning or reactivation of the sorbent material, refilled with fresh virgin or reactivated sorbent material, and returned to service following completion of the refurbishing operation.

[0048] The above sorbent materials may be used alone or in combination with other materials. In some embodiments, a composition is formed where a sorbent material is combined with a binder and molded, extruded, or otherwise formed into shapes or pellets. The binder is not limited and includes inorganic binder and organic binder. As examples of inorganic binder, metals, ceramics, clays, glasses, or combinations of one or more of the above are commonly used. As examples of organic binders, petroleum resins and/or pitches, natural resins and/or pitches, polymers, or combinations of one or more of the above are used.

EXAMPLES:

[0049] While several experimental Examples are contemplated, these Examples are intended to be non-limiting.

EXAMPLE 1

[0050] A column of granulated activated carbon (GAC) was constructed to test for the adsorption of PFAS compounds. First, an exhausted stock of FILTRASORB 400 (F400) that was previously used to filter municipal drinking water is provided. Such materials are available from Calgon Carbon Corp. of Moon Township, PA. FILTRASORB F400 is a coal-based granular activated carbon having 2 wt.% maximum moisture, effective size of about 0.55 mm to about 0.75 mm, and an apparent density of about 0.54 g/cm^3. The exhausted F400 is reactivated under elevated temperatures with steam in a rotating kiln to restore its surface activity and break down any organic compounds.

[0051] The now-reactivated F400 is designated as F400 CMR (Custom Municipal React). The reactivated F400 CMR is similar to virgin F400 material, but because the reactivated F400 CMR was previously used to treat groundwater with elevated calcium levels, the reactivated F400 CMR has a higher calcium content than virgin F400 activated carbon. In Example 1, the F400 CMR had a calcium content of about 0.36 wt.% versus 0.05 wt.% for virgin F400.

[0052] Referring now to FIG. 1, the results of a PFAS rapid small scale column test (RSSCT) using a PFOA breakthrough curve is shown. The testing was conducted according to ASTM D6586-03(2014) but scaled down to a column diameter of 0.62 cm. The inlet concentrations were about 0.9 μg/L PFOA and about 1.7 μg/L total PFAS and data was

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logged to yield a breakthrough curve. Breakthrough was measured as the concentration in µg/L that broke through a column of virgin F400 or F400 CMR. Also shown in FIG. 1 is the EPA Health Advisory Limit of 70 parts per trillion, which is equivalent to 0.07 µg/L breakthrough concentration. The amounts plotted are amounts of PFOA in the water.

[0053] As shown in FIG. 1, the virgin F400 carbon began to show elevated concentrations at about 10,000 bed volumes of water passing through the carbon in the bed, indicating that there was initial breakthrough of PFOA. In contrast, FIG. 1 shows that the F400 CMR resisted breakthrough of PFOA until at least about 20,000 bed volumes of water passing through the carbon in the bed. The greater breakthrough bed volume equivalents of water indicate that a filter that is constructed using a bed of F400 CMR activated carbon can absorb and adsorb greater amounts of harmful PFAS compounds than the same filter constructed with virgin F400 activated carbon.

EXAMPLE 2

[0054] Using the same procedures as above in Example 1, a column of GAC was constructed and tested using the same virgin F400 activated carbon and the F400 CMR reactivated carbon that has elevated levels of calcium as in Example 1. The resulting columns were tested with an inlet concentration of about 230 ng/L PFOA concentration in water, which is about 230 nanograms per liter of PFOA. The total concentration of perfluorinated chemicals (PFC) in the inlet water was about 1.2 µg/L, which includes the above concentration of PFOA.

[0055] The results of Example 2 are shown in FIG. 2. In FIG. 2, the endurance of the GAC column is again shown by the breakthrough in bed volume equivalents. The virgin F400 began to show signs of breakthrough at about 70,000 bed volumes, while the reactivated F400 CMR only showed signs of breakthrough at about 95,000 bed volumes.

EXAMPLE 3

[0056] A MgO agglomerated carbon was prepared. The MgO agglomerated carbon is manufactured from reagglomerated metallurgical grade bituminous coal. During the reagglomeration process, the pulverized coal was impregnated with magnesium oxides which were added in a dry state.

[0057] An additional CMR reactivated carbon was also prepared and is referred to as "CMR High Ca." The CMR High Ca reactivated carbon is similar to virgin F400 carbon and previously described CMR reactivated carbon, except CMR High Ca has an increased

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calcium content. The CMR High Ca reactivated carbon as tested had a calcium content of about 2 wt.% versus about 0.36 wt.% for CMR and 0.05 wt.% for virgin F400 carbon.

[0058] The above described F400, MgO Agglomerated, and F400 High Ca were tested to determine the simulated days of operation. In these tests, the inlet concentration of PFOA + PFOS was 345 ng/L, the inlet concentration of PFOA was 185 ng/L, and the inlet concentration of PFOS was 160 ng/L. The bed volumes were tested until they exhibited a breakthrough concentration of 70 ppt of PFOA, PFOS, or both PFOA and PFOS (shown as PFOA + PFOS). The results of these tests are described in Table 1 below:

TABLE 1

Sample	PFOA + PFOS		PFOA		PFOS	
	Days	**Bed Volumes**	**Days**	**Bed Volumes**	**Days**	**Bed Volumes**
F400	90	12851	140	19990	251	35839
MgO Agglomerated	174	25282	230	33419	549	79770
CMR High Ca (about 2 wt.% Ca)	133	19066	172	24657	402	57628

[0059] The specification characteristics of the same three activated carbons in Table 1 was also tested. This testing includes results for the apparent density of the carbon when measured using ASTM 2854-09(2014). The results of this testing are provided below in Table 2:

TABLE 2

	Apparent Density (g/cm^3)	**Days to 70 parts per trillion (ppt) PFOA + PFOS**
F400	0.54	90
MgO Agglomerated	0.51	174
CMR High Ca (about 2 wt.% Ca)	0.59	133

[0060] The results of the testing demonstrate that the treatment of activated carbon with various components has a significant effect on the performance of the activated

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carbon that is used as the sorbent for PFOA, PFOS, and/or combinations of these two classes of compounds found in drinking water applications.

EXAMPLE 4

[0061] Using the same procedures as above in Example 1, a column of GAC was constructed and tested using the same F400 and CMR F400 discussed above. The results of Example 4 are shown in FIGS. 4-6. FIG. 4 shows the results for the adsorption of different PFOA compounds. The endurance of the GAC columns is shown by the PFOA effluent concentration breakthrough in bed volume equivalents. The columns were tested with an inlet concentration of about 153 ng/L PFOA concentration in water, which is about 153 nanograms per liter of PFOA.

[0062] FIG. 5 shows the results for the adsorption of 4:2 FtS (6:2-fluorotelomersulfonic acid) compounds. The endurance of the GAC columns is shown by the 4:2 FtS effluent concentration breakthrough in bed volume equivalents. The columns were tested with an inlet concentration of about 130 ng/L 4:2 FtS concentration in water, which is about 130 nanograms per liter of 4:2 FtS.

[0063] FIG. 6 shows the results for the adsorption of PFOS compounds. The endurance of the GAC columns is shown by the PFOS effluent concentration breakthrough in bed volume equivalents. The columns were tested with an inlet concentration of about 177 ng/L PFOS concentration in water, which is about 177 nanograms per liter of PFOS.

EXAMPLE 5

[0064] A CMR reactivated carbon was prepared and is referred to as "Acid Washed CMR 0.65% Ca." The Acid Washed CMR 0.65% Ca reactivated carbon is the same as the CMR High Ca described above, except it is acid washed and has decreased Ca content. The CMR High Ca, also referred to as "CMR 2 wt.% Ca," as tested had a Ca content of about 2 wt.%. The Acid Washed CMR 0.65% Ca as tested had a Ca content of about 0.65 wt.%.

[0065] Two other samples of GAC were prepared and are referred to as "AdMix MgO 4.8% as Mg" and "AdMix MgO 12% as Mg." These samples were obtained by adding pulverized MgO to activated CAL 12X40 GAC (Calgon Carbon Corporation), activated carbon from coal-based reagglomerated bituminous virgin carbon. Specifically, AdMix MgO 4.8% as Mg was prepared by adding 8% of pulverized MgO to CAL 12X40 and AdMix MgO 12% as Mg was prepared by adding 20% of pulverized MgO to CAL 12X40. The resulting AdMix MgO 4.8% as Mg and AdMix MgO 12% as Mg samples as tested had a divalent cation content of about 4.8% and about 12% respectively.

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[0066] The MgO Agglomerated sorbent discussed above was tested and had a divalent cation content of about 4%. The MgO Agglomerated is different than the AdMix MgO 4.8% as Mg and AdMix MgO 12% as Mg because the MgO in the MgO Agglomerated is added prior to the carbonizing and activating of the carbon.

[0067] Using the same procedures as above in Example 1, a column of GAC was constructed and tested using CAL –Virgin Carbon (CAL 12X40), Acid Washed CMR 0.65% Ca, CMR High Ca (about 2 wt.% Ca), Agglomerated MgO, AdMix MgO 4.8% as Mg, and AdMix MgO 12% as Mg.

[0068] The specification characteristics of the GAC were also tested. This testing includes results for the percent of divalent cation measured using Proton Induced X-ray Emission (PIXE). This testing also includes results for the apparent density of the carbon when measured using ASTM 2854-09(2014). The results of this testing are provided below in Table 3:

TABLE 3

Sample	**Divalent Cation (%)**	**Apparent Density (g/cm^3)**	**Bed Volume Equivalent at 25% Breakthrough**
CAL –Virgin Carbon	0.05	0.49	21740
Acid Washed CMR 0.65% Ca	0.65	0.55	15757
CMR 2 wt.% Ca	2.0	0.59	18162
Agglomerated MgO	4.0	0.51	27930
AdMix MgO 4.8% as Mg	4.8	0.49	22837
AdMix MgO 12% as Mg	12.0	0.49	18614

[0069] The results of Example 5 are shown in FIG. 7. FIG. 7 shows the results for the adsorption of PFOA compounds. The endurance of the GAC columns is shown by the PFOA effluent concentration breakthrough in bed volume equivalents. The columns were tested with an inlet concentration of about 61 ng/L PFOA concentration in water, which is about 61 nanograms per liter of PFOA. The Acid Washed CMR 0.65% Ca began to show signs of breakthrough first followed by the CAL –Virgin Carbon, CMR 2 wt.% Ca, Agglomerated MgO, AdMix MgO 4.8% as Mg, and AdMix MgO 12% as Mg.

[0070] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is also understood that this disclosure is not limited to particular compositions, methods, apparatus, and articles, as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0071] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0072] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (for example, bodies of the appended claims) are generally intended as "open" terms (for example, the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," et cetera). While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups. It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present.

[0073] For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at

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least one" and indefinite articles such as "a" or "an" (for example, “a” and/or “an” should be interpreted to mean “at least one” or “one or more”); the same holds true for the use of definite articles used to introduce claim recitations.

[0074] In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (for example, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to “at least one of A, B, and C, et cetera” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, “a system having at least one of A, B, and C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, et cetera). In those instances where a convention analogous to “at least one of A, B, or C, et cetera” is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (for example, “a system having at least one of A, B, or C” would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, et cetera). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase “A or B” will be understood to include the possibilities of “A” or “B” or “A and B.”

[0075] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0076] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, et cetera. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, et cetera. As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to

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ranges that can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0077] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

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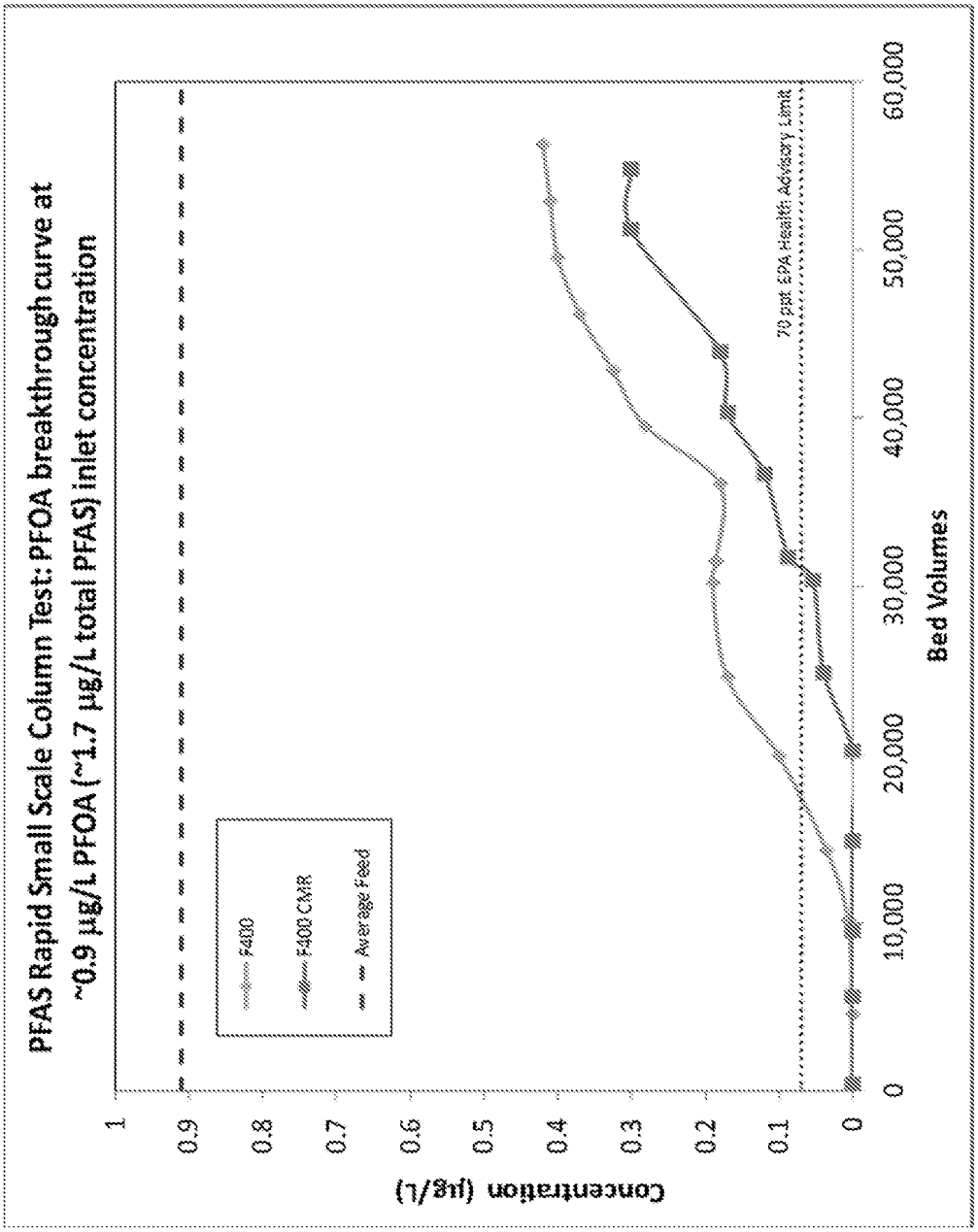

PFAS Rapid Small Scale Column Test: PFOA breakthrough curve at
~0.9 µg/L PFOA (~1.7 µg/L total PFAS) inlet concentration
F400
F400 C&R
Average Feed
70 ppt EPA Health Advisory Limit
Concentration (µg/L)
Bed Volumes
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
10,000
20,000
30,000
40,000
50,000
60,000

FIG. 1

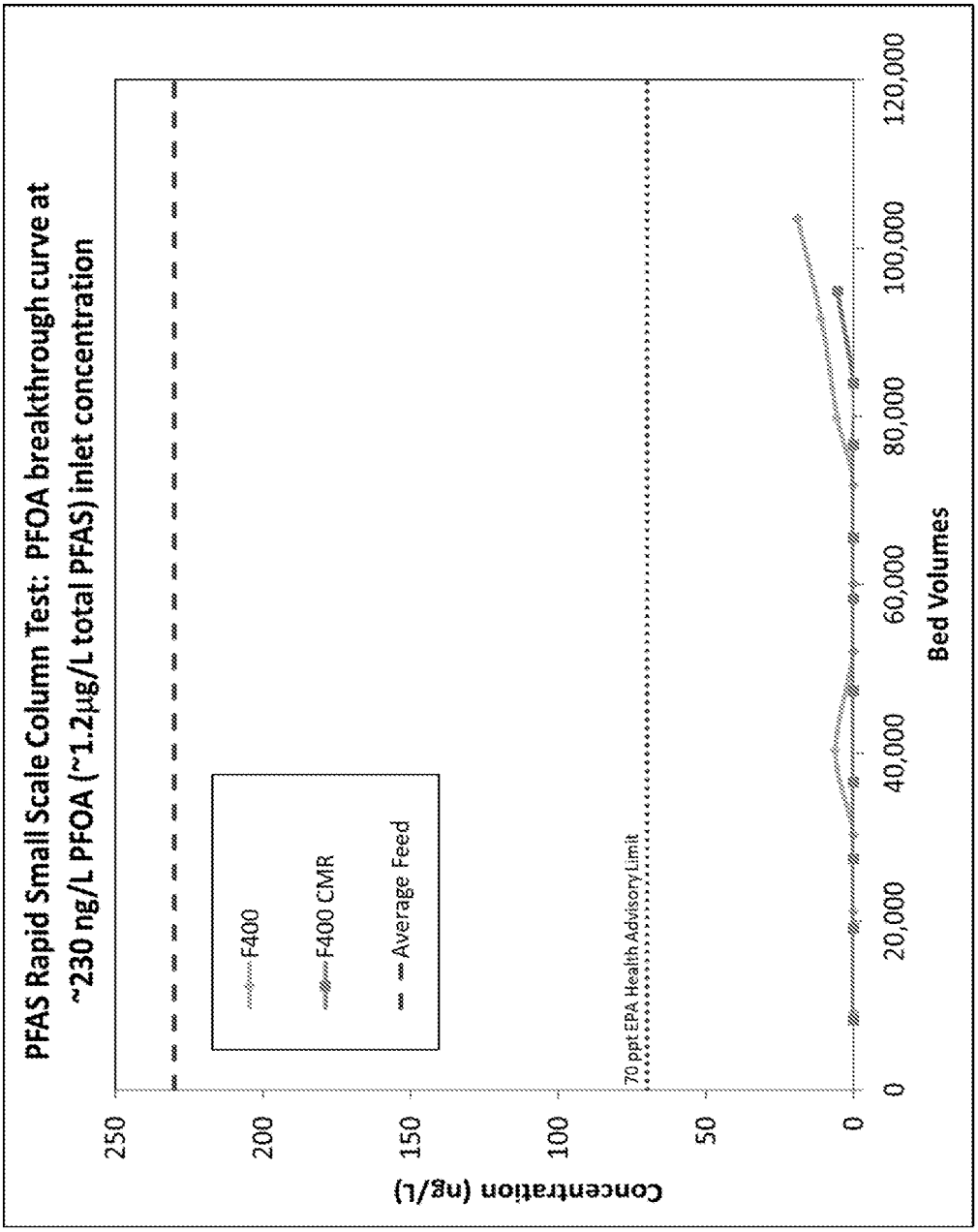

PFAS Rapid Small Scale Column Test: PFOA breakthrough curve at
~230 ng/L PFOA (~1.2µg/L total PFAS) inlet concentration
Concentration (ng/L)
250
200
150
100
50
0
0
20,000
40,000
60,000
80,000
100,000
120,000
Bed Volumes
F400
F400 CMR
Average Feed
70 ppt EPA Health Advisory Limit

FIG. 2

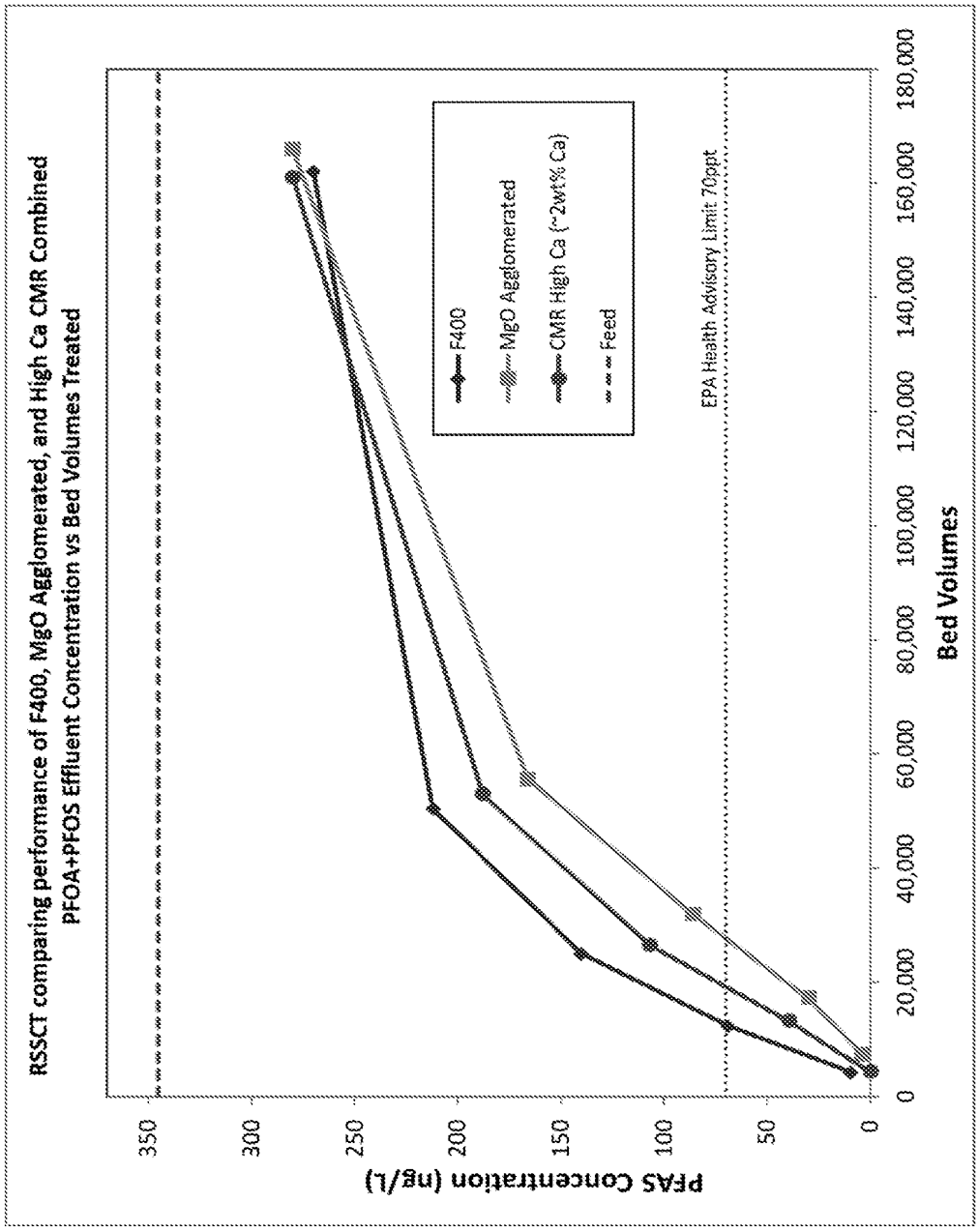

RSSCT comparing performance of F400, MgO Agglomerated, and High Ca CMR Combined
PFOA+PFOS Effluent Concentration vs Bed Volumes Treated
PFAS Concentration (ng/L)
350
300
250
200
150
100
50
0
0
20,000
40,000
60,000
80,000
100,000
120,000
140,000
160,000
180,000
Bed Volumes
F400
MgO Agglomerated
CMR High Ca (~2wt% Ca)
Feed
EPA Health Advisory Limit 70ppt

FIG. 3

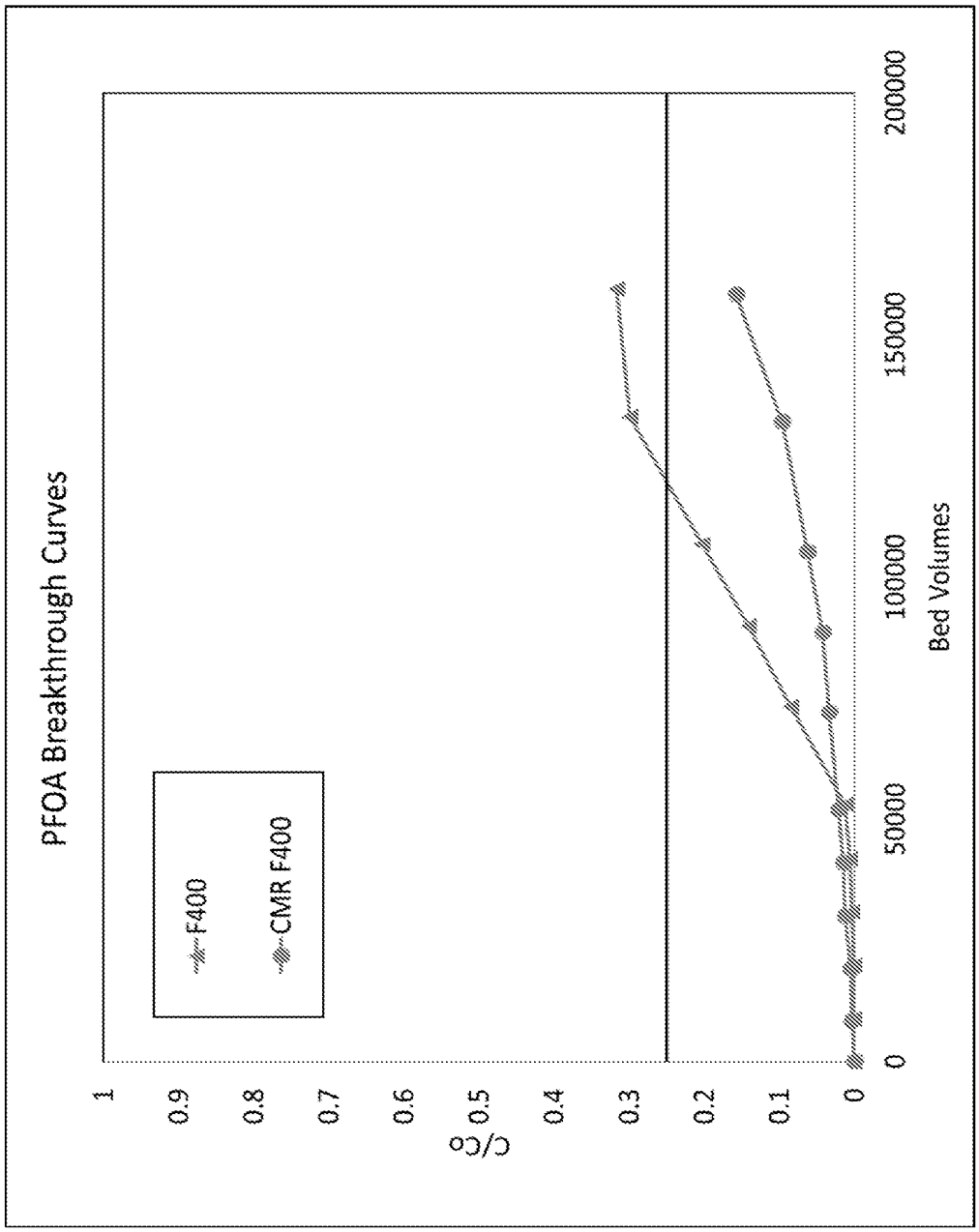

PFOA Breakthrough Curves
F400
CMR F400
C/C0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50000
100000
150000
200000
Bed Volumes

FIG. 4

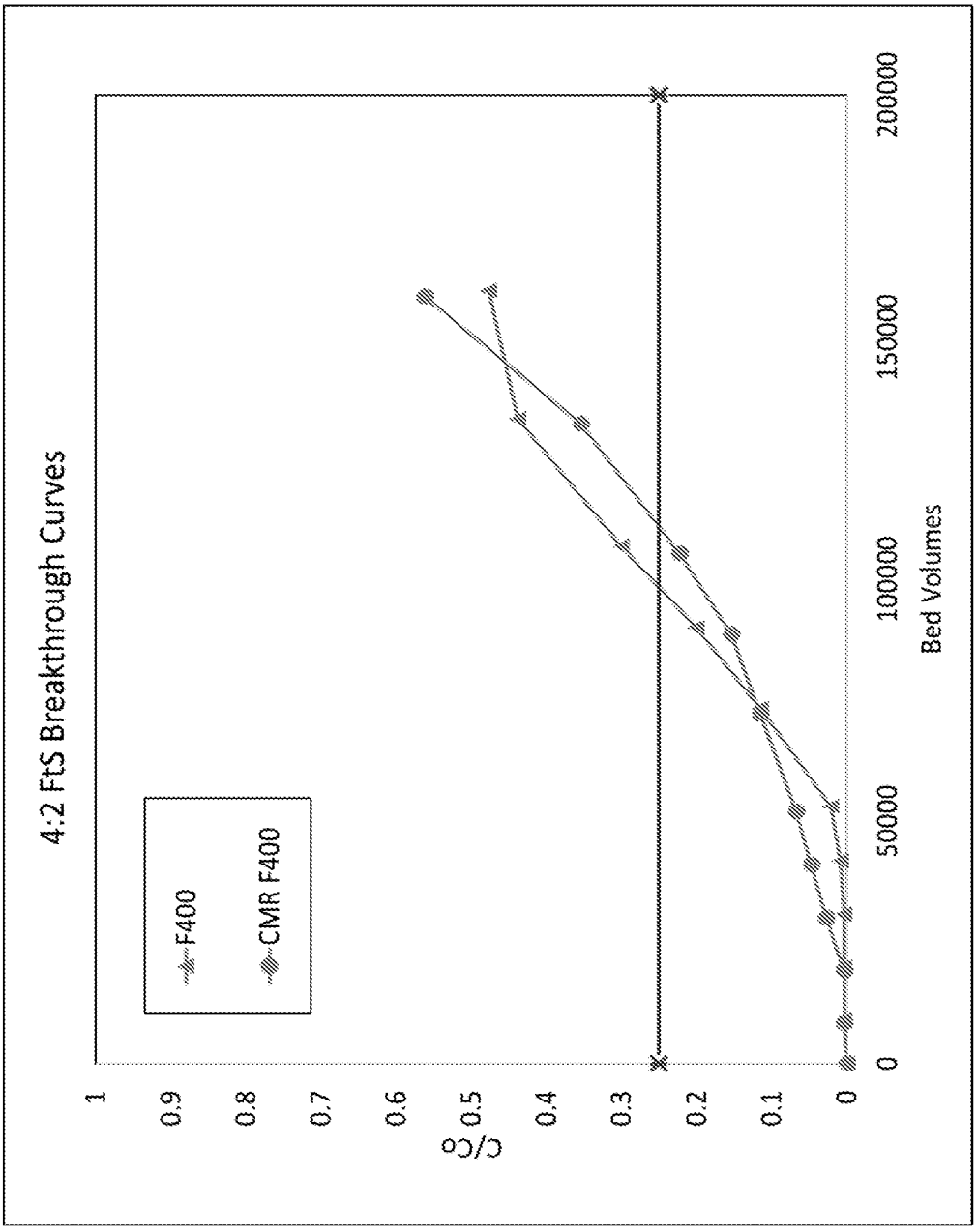

4:2 FtS Breakthrough Curves
F400
CMR F400
C/Co
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50000
100000
150000
200000
Bed Volumes

FIG. 5

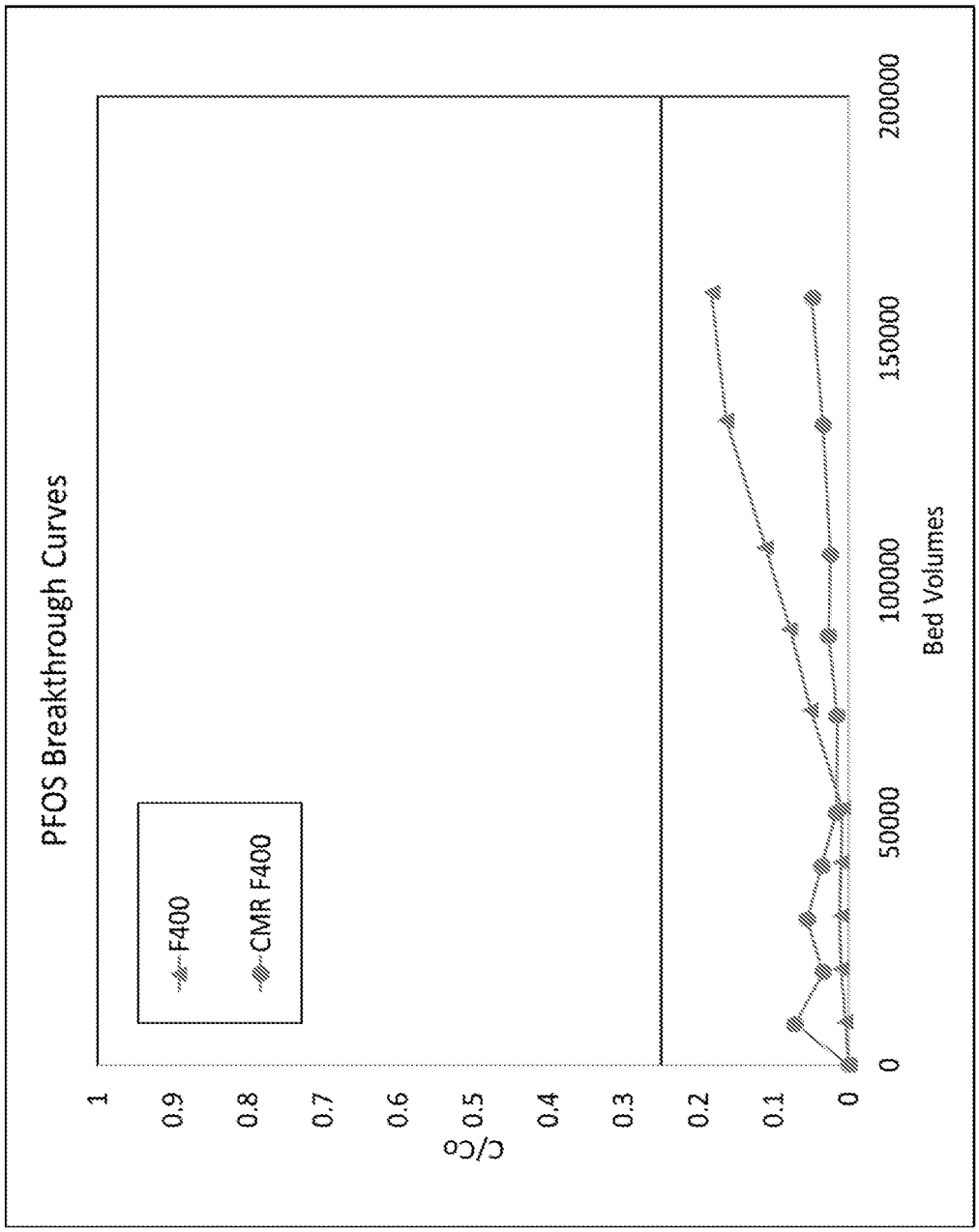

PFOS Breakthrough Curves
F400
CMR F400
C/Co
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
50000
100000
150000
200000
Bed Volumes

FIG. 6

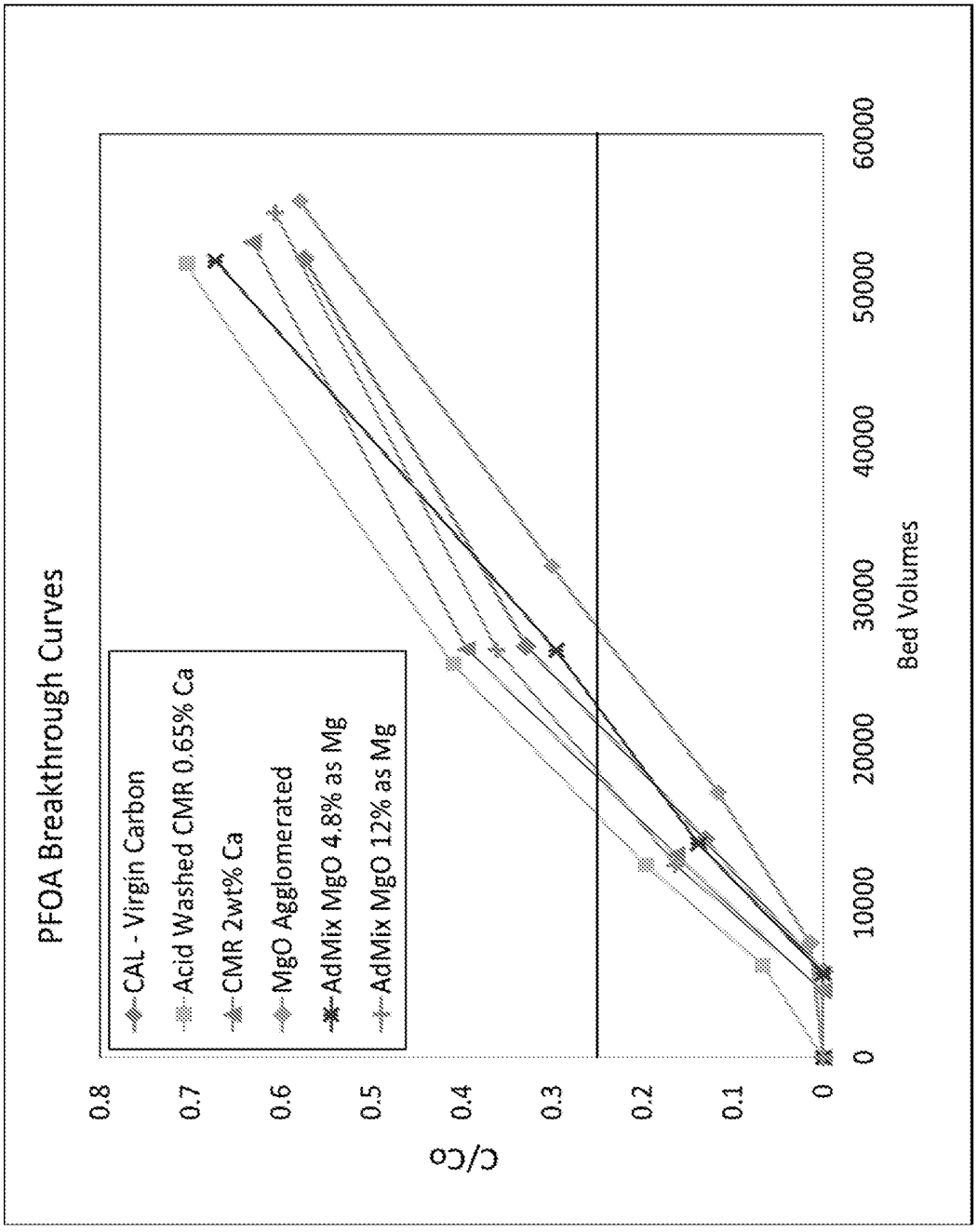

PFOA Breakthrough Curves
CAL - Virgin Carbon
Acid Washed CMR 0.65% Ca
CMR 2wt% Ca
MgO Agglomerated
AdMix MgO 4.8% as Mg
AdMix MgO 12% as Mg
C/Co
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10000
20000
30000
40000
50000
60000
Bed Volumes

FIG. 7

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
Attorney Docket Number:	123450.13001

Filed as Large Entity

Filing Fees for Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	300	300
UTILITY SEARCH FEE	1111	1	660	660
UTILITY EXAMINATION FEE	1311	1	760	760
Pages:				
Claims:				
Miscellaneous-Filing:				
LATE FILING FEE FOR OATH OR DECLARATION	1051	1	160	160
Petition:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**1880**

Electronic Acknowledgement Receipt

EFS ID:	39058847
Application Number:	16839862
International Application Number:	
Confirmation Number:	5111
Title of Invention:	PERFLUOROALKYL AND POLYFLUOROALKYL SORBENT MATERIALS AND METHODS OF USE
First Named Inventor/Applicant Name:	Rebecca L. DISTEFANO
Customer Number:	93724
Filer:	Nicholas Charalambos Kokkinos/Paula Watson
Filer Authorized By:	Nicholas Charalambos Kokkinos
Attorney Docket Number:	123450.13001
Receipt Date:	03-APR-2020
Filing Date:	
Time Stamp:	16:39:35
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$1880
RAM confirmation Number	E202043G40228149
Deposit Account	500436
Authorized User	Paula Watson
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows: 37 CFR 1.16 (National application filing, search, and examination fees) 37 CFR 1.17 (Patent application and reexamination processing fees)	

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Application Data Sheet	123450-13001_ADS.pdf	1796605 c6e525bb3b30d66cd8977f553680f8c955beea13	no	8
Warnings:					
Information:					
2		123450-13001_Application.pdf	208801 cc96af7479b5e33d122a29d90754599d0e37beae	yes	22

Multipart Description/PDF files in .zip description		
Document Description	**Start**	**End**
Abstract	22	22
Claims	20	21
Specification	1	19

Warnings:					
Information:					
3	Drawings-only black and white line drawings	123450-13001_Figures.pdf	744328 55ede320cf0a965538b1d31ebe3c37d7946900f6	no	7
Warnings:					
Information:					
4	Fee Worksheet (SB06)	fee-info.pdf	36900 bfcfc821b08e07bd83a40628822edd85ee6c354e	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	2786634		

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

DocCode – SCORE

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