12. The process of Claim 11, further comprising:

(a) leaching the material with a lixiviant to form a pregnant leach solution containing at least a portion of the metal,

(b) contacting the pregnant leach solution with a sorbent to form a loaded sorbent containing at least a portion of the metal,

(c) contacting the loaded sorbent with an eluant to form a loaded eluant containing at least a portion of the metal in the loaded sorbent and a spent sorbent, wherein the lixiviant includes at least one of cyanide, thiosulfate, and mixtures thereof, and the eluant includes at least one of a carbohydrate, ammonia, a hydroxide, a cyanide, an alcohol, a ketone, a nitrile, acetone, a cyanate, a hydrazine, a hydroxy acid, a carboxylic acid, a hydroxycarboxylic acid, a hydrocarbon, and mixtures thereof.

13. The process of Claim 11, wherein the metal is a member of at least one of Groups VIIIA, IB, OR IIB of the Periodic Table of the Elements.

14. The process of Claim 11, wherein the organic acid is one or more hydroxy acids.

15. The process of Claim 14, wherein the hydroxy acid is one or more hydroxycarboxylic acids.

16. The process of Claim 15, wherein the hydroxycarboxylic acid is selected from the group consisting essentially of glycolic acid, lactic acid, and mixtures thereof.

17. The process of Claim 12, wherein the regenerated sorbent is reused in step (c).

18. The regenerated sorbent made in the process of Claim 11.

19. The metal recovered in the process of Claim 11.

20. The process of Claim 11, further comprising:

contacting the spent carbon with a metal-containing solution to form a metal loaded carbon;

contacting the metal loaded carbon with at least one of an organic and inorganic acid to form a treated metal loaded carbon; and

contacting the treated metal loaded carbon with an eluant.

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21. Regenerated carbon for reuse in an elution process, comprising an organic acid adsorbed in a plurality of pores of the carbon.

22. The regenerated carbon of Claim 21, wherein the organic acid is a hydroxy acid.

23. The regenerated carbon of Claim 22 wherein the hydroxycarboxylic acid is selected from the group consisting of glycolic acid, lactic acid, and mixtures thereof.

24. The regenerated carbon of Claim 22, wherein regenerated carbon includes both the sulfuric acid and the organic acid.

25. The regenerated carbon of Claim 22, wherein the regenerated carbon includes a hydroxycarboxylic acid.

26. A process for eluting a metal from a sorbent, comprising:

contacting a metal-loaded sorbent with an organic acid or sulfuric acid to form a treated metal-loaded carbon; and

contacting the treated metal-loaded carbon with an eluant to form a barren sorbent and a metal-loaded eluant containing at least most of the metal loaded onto the metal-loaded sorbent.

27. The process of Claim 26, wherein the organic acid is a hydroxy acid.

28. The process of Claim 26, wherein the hydroxy acid is selected from the group consisting of glycolic acid, lactic acid, and mixtures thereof.

29. The process of Claim 26, wherein the sorbent is at least one of activated carbon, a resin, and mixtures thereof.

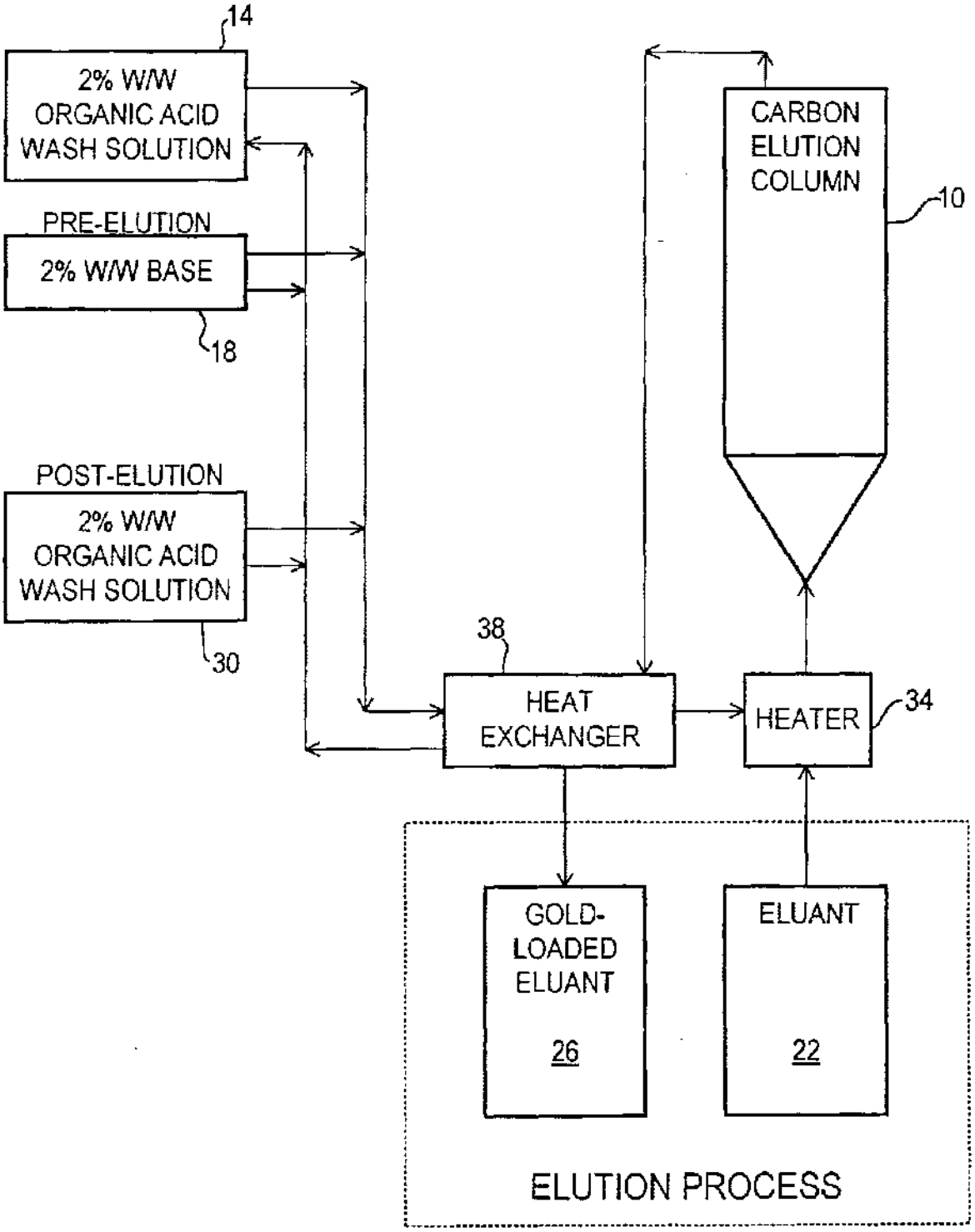

14
2% W/W
ORGANIC ACID
WASH SOLUTION
PRE-ELUTION
2% W/W BASE
18
POST-ELUTION
2% W/W
ORGANIC ACID
WASH SOLUTION
30
CARBON
ELUTION
COLUMN
10
38
HEAT
EXCHANGER
HEATER
34
GOLD-
LOADED
ELUANT
26
ELUANT
22
ELUTION PROCESS

FIG. 1

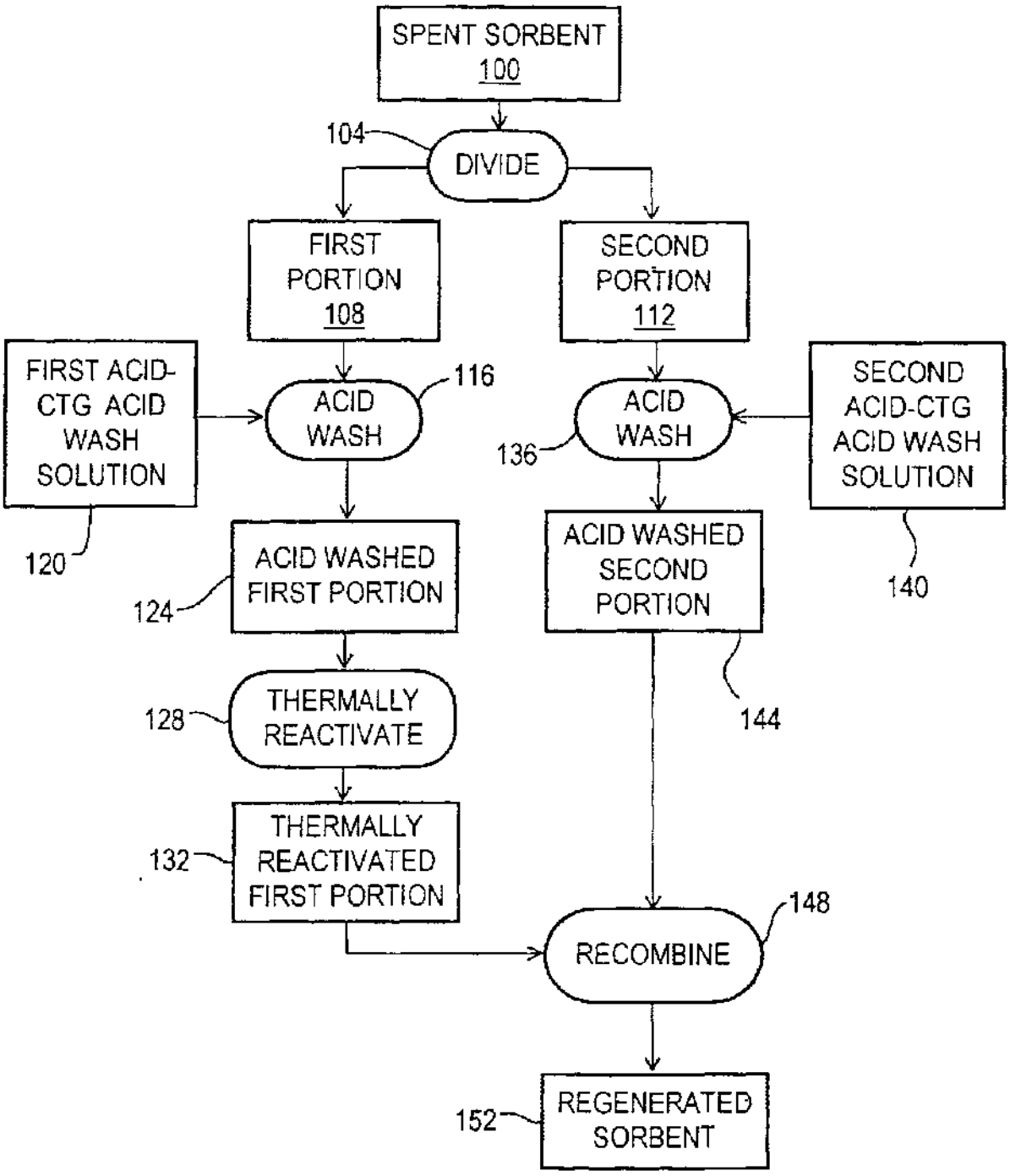

SPENT SORBENT
100
104
DIVIDE
FIRST PORTION
108
SECOND PORTION
112
FIRST ACID-CTG ACID WASH SOLUTION
120
ACID WASH
116
ACID WASH
136
SECOND ACID-CTG ACID WASH SOLUTION
140
ACID WASHED FIRST PORTION
124
ACID WASHED SECOND PORTION
144
THERMALLY REACTIVATE
128
THERMALLY REACTIVATED FIRST PORTION
132
RECOMBINE
148
REGENERATED SORBENT
152

FIG. 2

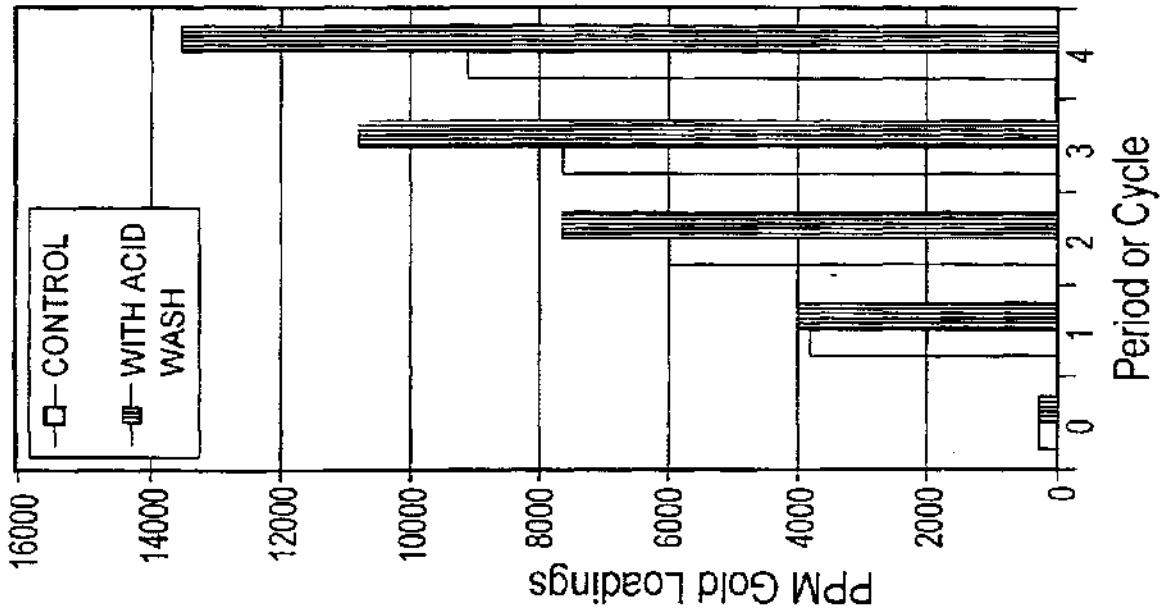

CONTROL
WITH ACID WASH
PPM Gold Loadings
Period or Cycle
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
3
4

FIG. 4

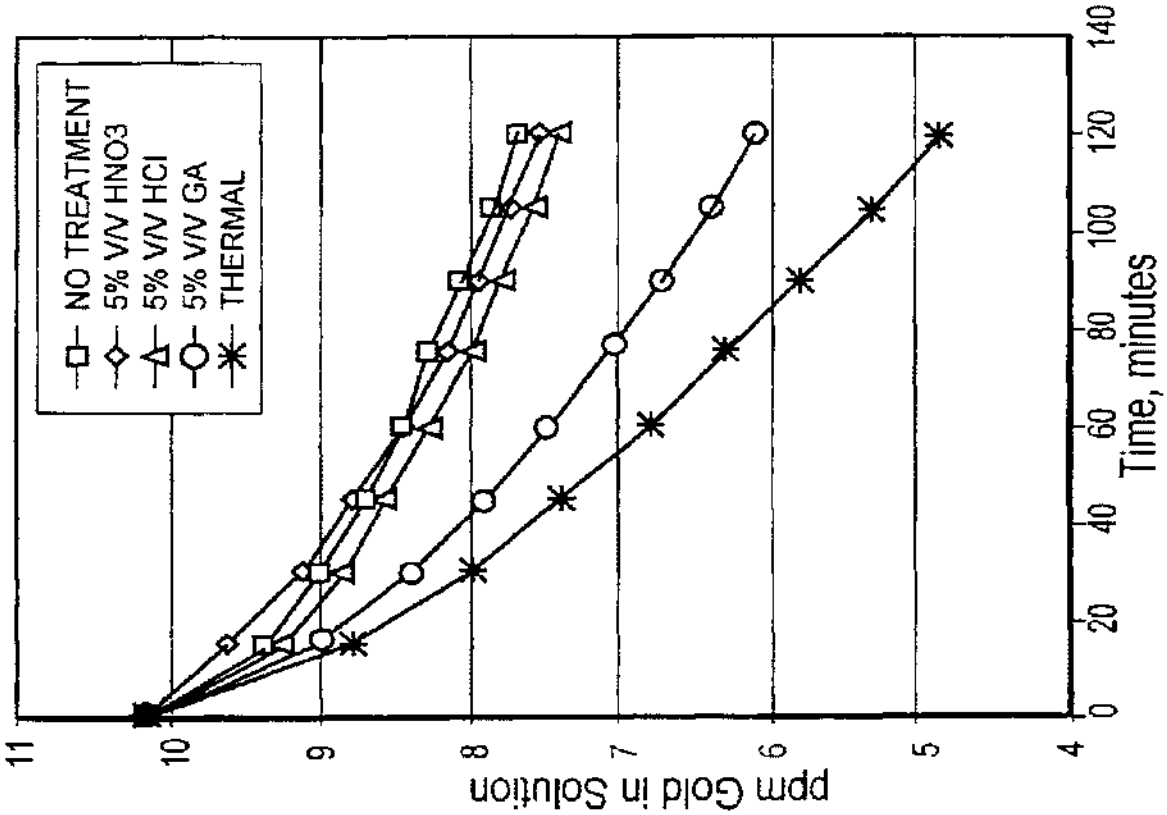

NO TREATMENT
5% V/V HNO3
5% V/V HCl
5% V/V GA
THERMAL
ppm Gold in Solution
Time, minutes
11
10
9
8
7
6
5
4
0
20
40
60
80
100
120
140

FIG. 3

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(54) POUDRE ADSORBANTE DESTINE A L'ELIMINATION DE MERCURE DANS DES COURANTS GAZEUX A TEMPERATURE ET HUMIDITE ELEVEES

(54) ADSORPTION POWDER FOR REMOVING MERCURY FROM HIGH TEMPERATURE, HIGH MOISTURE GAS STREAMS

(57)

There is disclosed an adsorption powder effective for capturing mercury from a high temperature, high moisture gas stream comprising: about 1-97% carbon; about 1-97% calcium hydroxide; about 1-97% cupric chloride impregnated carbon, and about 1-60% carbon impregnated with KI3. Additionally, a method of removing mercury from high temperature, high moisture gas streams is disclosed.

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(54) Titre : POUDRE ADSORBANTE DESTINE A L'ELIMINATION DE MERCURE DANS DES COURANTS GAZEUX A TEMPERATURE ET HUMIDITE ELEVEES

(54) Title: ADSORPTION POWDER FOR REMOVING MERCURY FROM HIGH TEMPERATURE, HIGH MOISTURE GAS STREAMS

(57) Abrégé/Abstract:
There is disclosed an adsorption powder effective for capturing mercury from a high temperature, high moisture gas stream comprising: about 1-97% carbon; about 1-97% calcium hydroxide; about 1-97% cupric chloride impregnated carbon, and about 1-60% carbon impregnated with KI3. Additionally, a method of removing mercury from high temperature, high moisture gas streams is disclosed.

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(54) Title: ADSORPTION POWDER FOR REMOVING MERCURY FROM HIGH TEMPERATURE, HIGH MOISTURE GAS STREAMS

(57) Abstract: There is disclosed an adsorption powder effective for capturing mercury from a high temperature, high moisture gas stream comprising: about 1-97% carbon; about 1-97% calcium hydroxide; about 1-97% cupric chloride impregnated carbon, and about 1-60% carbon impregnated with KI3. Additionally, a method of removing mercury from high temperature, high moisture gas streams is disclosed.

ADSORPTION POWDER FOR REMOVING MERCURY FROM HIGH TEMPERATURE, HIGH MOISTURE GAS STREAMS

BACKGROUND OF THE INVENTION

The present invention relates generally to removal of pollutants from high temperature, high moisture gas streams such as those found in devices designed to treat contaminated soil and in hazardous material incinerators. More particularly, the invention relates to the capture of mercury and other metals, dioxins, furans and other organic compounds from high temperature, high moisture gas streams using an adsorption powder containing cupric chloride.

Strict standards exist for particulate and total mercury emissions by coal-fired power plants, petroleum refineries, chemical refineries, coal fired furnaces, trash burning facilities, incinerators, metallurgical operations, thermal treatment units and other particulate and mercury emitting facilities. These same restrictions apply to mercury vapor, which can enter the atmosphere as a result of low temperature thermal desorption (LTTD) treatment of contaminated soils.

These stringent standards exist in order to protect the environment and the community. When mercury-containing gases are released, the gases disperse and mercury is deposited over a wide area. The dispersed mercury can accumulate in the soil or water supplies, where it may be incorporated into the food chain. Mercury is extremely harmful to aquatic life and ultimately to the humans who consume mercury-contaminated plants and animals. It is necessary, therefore, to have a safe and effective method of eliminating mercury from the environment.

The problem of the capture and treatment of mercury vapor, typically in the context of coal-fired power plants and waste incinerators, has been previously considered. For example, U.S. Patent No. 3,193, 987 discloses passing mercury-containing vapor over activated carbon impregnated with a metal which forms an amalgam with mercury. U.S. Patent No. 4,094,777 discloses passing a mercury-containing vapor over an adsorption mass consisting essentially of a support, sulfided

copper and sulfided silver. U.S. Patent No. 3,876,393 discloses passing mercury-containing vapors over activated carbon that has been impregnated with sulfuric acid. Selenium has also been used in the removal of mercury from a vapor. U.S. Patent No. 3,786,619 discloses passing a mercury-containing gas over a mass containing as an active component, selenium, selenium sulfide or other selenium compounds. Electrostatic precipitators and various filters have traditionally been used for mercury removal, although complex apparatus have also been disclosed. (See e.g., U.S. Patent Nos. 5,409,522 and 5,607,496.)

The problem of recapturing mercury from power plant gas streams is analogous to the need for recapturing mercury from incinerators that treat contaminated soils. A process currently in use at soil treatment facilities is known as low temperature thermal desorption (LTTD). LTTD is the main process by which contaminated soils are treated to remove mercury and other contaminants. In this process, contaminated soils are fed into a heating furnace, most commonly a rotary kiln/drum, where the soil is heated by conduction. The heating volatizes the soil components and when a thermal oxidizer is added, the components are oxidized to manageable gases, such as CO_2, Cl_2, NO_x and SO_x, where x is 1-3.

The hot gas stream is subsequently cooled. The stream may be quenched with water, which cools the stream and concurrently increases the moisture content. Although water quenching is a highly effective cooling method, this treatment increases the difficulty of removing mercury from the gas stream. The gas stream is further treated to reduce and remove metals, HCl, NO_x and SO_x using acid scrubbers, carbon beds, condensation units and through the addition of adsorption powders.

When adsorption powders are injected into the gas stream, mercury and other metals bind to moieties present in the powder, precipitating them from the gas stream. The powder-bound mercury is ultimately collected in a bag house for appropriate disposal, while the clean gas stream is exhausted to the outside atmosphere. The problem with standard LTTD methods is that some metals, such as mercury, are not removed from the stream at high efficiency and will move with

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the gas stream, ultimately into the environment. Other methods require the use of complex machinery and expensive adsorption beds. LTTD and other methods also suffer from the limitation that mercury removal from high moisture gas streams is much more difficult than mercury removal from dry streams.

Available adsorption powders remove organics, metals and other contaminants, but they do not effectively remove mercury. For example, one available powder (Sorbalite ™) consisting of carbon, calcium hydroxide and sulfur removes HCl from a gas stream, but removes only about 55-65% of the mercury. Another powder (WUELFRAsorb-C ™) consisting of alcohol saturated lime and activated carbon is also inefficient at removing mercury.

Some powders include sulfur or iodine impregnated carbon. At temperatures of 75°C or less, sulfur or iodine impregnated carbon based powders show a 95% mercury removal efficiency, however, powders formulated with sulfur impregnated carbon require a dry or low moisture gas stream to show this level of removal.

Finally, the mercury removal efficiency of the powders described and other available powders is known to be very temperature dependent, placing an additional limitation on powder formulations.

A pending application describing a process from the same inventors involved the use of solid fine cupric chloride that is not impregnated on carbon. This was found to be more difficult to handle because of the grinding process required to pulverize the cupric chloride which is generally provided in rock sizes. The grinding process requires a great amount of attention due to the dust production and associated heath hazards. Additionally, the powder is very corrosive and results in breakdown of the machinery used in the process.

Accordingly, there is a need in the industry for an adsorption powder that effectively removes metals and other organic compounds, in general, and mercury, in particular, from high temperature, high moisture gas streams generated by the incineration of contaminated soils, treatment of hazardous materials, combustion of coal and other mercury liberating sources. The powder must be inexpensive and

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easy to use. Ideally, such an adsorption powder can be employed at treatment facilities already in place and can take advantage of equipment already in position, without requiring retooling or reconfiguring existing equipment.

SUMMARY OF THE INVENTION

There is disclosed an adsorption powder and method for removing mercury and other metals and contaminants from a high temperature, high moisture gas stream comprising: about 1-97% carbon; about 1-97% calcium hydroxide; about 1-97% cupric chloride impregnated carbon and about 1-60% KI_3 impregnated carbon. A method for removing mercury and other metals, dioxins, furans and other organic compounds from high temperature, high moisture gas streams using the claimed powder is also disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

The instant invention will be more fully understood in the following detailed description, it being understood, however, that the invention is not confined to the precise disclosure. Changes and modifications may be made that do not affect the spirit of the invention, nor exceed the scope thereof, as expressed in the appended claims. Accordingly, the instant invention will now be described with particular reference to the accompanying drawings.

Figure 1 is a schematic diagram illustrating the design of an LTTD facility in which the claimed adsorption powder can be used to remove mercury from gas streams.

DETAILED DESCRIPTION OF THE INVENTION

There is disclosed an adsorption powder for removing mercury and other metals from a gas stream comprising:

a) about 1-97% carbon;

b) about 1-97% calcium hydroxide;

c) about 1-97% cupric chloride impregnated carbon; and

d) about 1-60% KI_3 impregnated carbon.

The powder more particularly comprises about 10-70% carbon, about 20-80% calcium hydroxide, about 1-50% cupric chloride impregnated carbon and about 1-50% KI_3 impregnated carbon. A preferred adsorption powder comprises about 20-60% carbon, about 30-70% calcium hydroxide, about 1-30% cupric chloride impregnated carbon and about -30% KI_3 impregnated carbon.

In a more preferred embodiment, the adsorption powder comprises about 25-45% carbon, about 40-60% calcium hydroxide, about 1-15% cupric chloride impregnated carbon and about 1-15% KI_3 impregnated carbon. The most preferred embodiment comprises about 40% carbon, about 40% calcium hydroxide, about 10% cupric chloride impregnated carbon and about 10% KI_3 impregnated carbon.

The use of the KI_3 impregnated carbon has been found to be optional as the powder lacking this component performed equally as well as one containing the KI_3 impregnated carbon.

Thus, in another embodiment of the invention, , the adsorption powder comprises about 10-70% carbon, about 20-80% calcium hydroxide and about 1-50% cupric chloride impregnated carbon.

There is also disclosed a process for removing mercury from a gas stream using the adsorption powder of the invention comprising the steps of:

a) placing a solid phase mercury-containing contaminated soil feed into a rotary kiln/drum;

b) heating said kiln/drum containing said soil feed to form gaseous and solid components of the sample;

c) transferring the gaseous component of said soil feed to an exhaust cleaning unit/afterburner and the solid component of clean soil to a soil cooling unit;

d) heating the gaseous component of said contaminated soil feed in said exhaust cleaning unit/afterburner;

e) cooling the gaseous component of said contaminated soil feed;

f) adding the adsorption powder of Claim 1 to the gaseous component;

g) transferring the powder-containing gaseous component to a baghouse; and

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h) releasing the substantially mercury-free gaseous component of said sample to the atmosphere.

An adsorption powder for the removal of mercury and other metals, dioxins, furans and other organic compounds must be efficient under a range of conditions. Currently available powders do not function well at high temperatures and in high moisture environments, conditions that are favorable to mercury removal.

High temperatures are necessary for effective removal of contaminants from soil. Temperatures of about 1800°F are necessary to volatize organics, metals and other impurities from the contaminated soil. Mercury that is trapped in contaminated soil, however, is most efficiently adsorbed on carbon at about 300-500°F. The most practical method of cooling a gas stream exiting an 1800°F oven is to inject water into the gas stream. Water injection cools the gas stream to a temperature favorable to mercury removal, but also increases the moisture content of the sample, which decreases the efficiency of available mercury adsorption powders. The mercury absorbing properties of available powders suffer dramatically in a high moisture environment. The adsorption powder of the invention, however, operates effectively even in a higher moisture environment.

Experiments with carbon sources showed that coal carbon was superior to wood carbon for mercury adsorption. Many available adsorption powders use wood carbon as a component, rather than coal carbon. Cupric chloride was observed to significantly enhance the adsorption of mercury from a gas stream and is the key to the instant invention. Cupric chloride supplies chlorine and activated copper to the elemental mercury in the exhaust stream. Elemental mercury reacts with the chlorine to form mercury chloride and the activated copper to form a stable mercury amalgam. Both forms of mercury are easily captured from the exhaust gas stream. KI_3 impregnated carbon was also found to increase mercury adsorption when it was included in the powder.

Figure 1 shows a schematic diagram of the actual process and equipment used to carry out the invention. Prescreened contaminated feed soil ready to be processed **2** is placed within soil cleaning unit **4**. The contaminated soil is heated to about 900°F or a temperature that will completely volatize the contaminates from the soil and generate a gas stream, as well as a clean/remediated solid soil component. Preferably, soil cleaning unit **4** is a rotary kiln. The gas stream is then passed out

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of soil cleaning unit **4** to dust remover **6**, while any solid fraction of the feed soil is transferred to clean soil cooling unit **8**, where the soil is cooled and prepared for reuse. Dust remover **6** is preferably a multi-tube dust collector.

After dust remover **6** removes any particulate matter from the gas stream sample, the gas stream is passed into the Exhaust Cleaning Unit **10.** The Exhaust Cleaning Unit heats the volatilized contaminates to a temperature of about 1800°F for a minimum of two seconds retention time, which assures complete destruction of any remaining organic or other contaminants. From the Exhaust Cleaning Unit **10,** the gas stream then passes through cooling chamber **12** wherein a water pump (not shown) injects water into the cooling chamber **12** to lower the temperature of the sample to about 360°F. This cooling process consequentially increases the moisture content of the sample.

The high temperature, high moisture gas stream is then contacted to the adsorption powder of the invention, which is stored in adsorbent storage silo **14** and injected into the gas stream. This powder formulation is effective in removing metals, particularly mercury, and other contaminants.

After the gas stream has been contacted to the adsorption powder, the powder/gas stream mixture continues on to baghouse **16.** The carbon component of the adsorption powder collects on the walls of bags and acts as a particulate filter for the gases leaving the baghouse. Baghouse **16** collects the particulate mercury-containing fraction of the adsorption powder mixture, which is transported to a suitable bulk storage facility **20** and subsequently removed. The gaseous fraction is released to the outside atmosphere through vent **18**, while the remaining dust particulate fraction is handled in a similar manner to the particulate mercury fraction of the adsorption powder mixture **20**.

EXAMPLE 1

A series of field tests were performed employing a preferred adsorption powder formulation. Three soil samples containing about 4.2 mg/kg of mercury were prepared by screening to 1 inch. The coarse material was discarded, and the remaining soil was fed into a soil cleaning unit and heated to about 900°F. The cleaned soil was transferred to a soil cooling unit and prepared for reuse. The exhaust stream was sent to a dust remover and the precipitated material was sent to the soil cooling unit. The exhaust stream was then fed into an exhaust cleaning unit, which was heated to

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about 1850°F. The exhaust gas was then cooled to about 360°F by quenching with water, and subsequently an adsorption powder comprising 40% coal carbon, 10% KI_3 impregnated carbon, 40% calcium hydroxide and 10% cupric chloride impregnated carbon was added. The exhaust stream/adsorption powder mixture was fed into a baghouse, where the mercury-bound particulate was separated from the mercury-free exhaust gas. The particulate material was removed from the baghouse for analysis and disposal, while gas analyzers on the exhaust stack recorded mercury emission levels. The results of the three, two hour runs are reported in the following table.

	Run 1	Run 2	Run 3	Average
LTTD Mercury Input (lbs/hr)	0.193	0.199	0.199	0.197
Clean Soil Mercury Output (lbs/hr)	0.0020	0.0020	0.0020	0.0020
Mercury Emission Rate (lbs/hr)	0.0012	0.0006	0.0007	0.0008
Mercury Removal Efficiency[1]	99.4%	99.7%	99.6%	99.6%

[1] *Removal Efficiency (%) = (Mass input - Stack Output- Clean Soil Output)/(Mass Input - Clean Soil Output)*

The average mercury removal efficiency of 99.6% exceeds the current mercury control efficiency specification of 96.5% efficiency, set by NJDEP air permit legislation. Mercury emissions were determined by EPA method 29-060.

Although the adsorption powder and method described and claimed are presented in the context of mercury removal from a gas stream, it should be appreciated that the powder and method are also useful for removing organics, metals and other contaminants from a gas stream.

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WHAT IS CLAIMED IS:

1. An adsorption powder for removing mercury and other metals, dioxins, furans and other organic compounds from a gas stream comprising:

a) about 1-97% carbon;

b) about 1-97% calcium hydroxide;

c) about 1-97% cupric chloride; and

d) about 1-60% KI_3 impregnated carbon.

2. The adsorption powder of claim 1 wherein the adsorption powder comprises about 10-70% carbon, about 20-80% calcium hydroxide, about 1-50% cupric chloride impregnated carbon and about 1-50% KI_3 impregnated carbon.

3. The adsorption powder of claim 1 wherein the adsorption powder comprises about 20-60% carbon, about 30-70% calcium hydroxide, about 1-30% cupric chloride impregnated carbon and about -30% KI_3 impregnated carbon.

4. The adsorption powder of claim 1 wherein the adsorption powder comprises about 25-45% carbon, about 40-60% calcium hydroxide, about 1-15% cupric chloride impregnated carbon and about 1-15% KI_3 impregnated carbon.

5. The adsorption powder of claim 1 wherein the adsorption powder comprises about 30% carbon, about 50% calcium hydroxide, about 10% cupric chloride impregnated carbon and about 10% KI_3 impregnated carbon.

6. The adsorption powder of claim 1 wherein the adsorption powder comprises about 10-70% carbon, about 20-80% calcium hydroxide, about 1-50% cupric chloride impregnated carbon.

7. The adsorption powder of claim 1 wherein the carbon is coal carbon.

8. A method for removing mercury and other metals, dioxins, furans and other organic compounds from a gas stream using the adsorption powder of claim 1 comprising the steps of:

a) placing a solid phase mercury-containing contaminated soil feed into a rotary kiln/drum;

b) heating said kiln/drum containing said soil feed to form gaseous and solid components of the sample;

c) transferring the gaseous component of said soil feed to an exhaust cleaning unit/afterburner and the solid component of clean soil to a soil cooling unit;

d) heating the gaseous component of said contaminated soil feed in said exhaust cleaning unit/afterburner;

e) cooling the gaseous component of said contaminated soil feed;

f) adding the adsorption powder of Claim 1 to the gaseous component;

g) transferring the powder-containing gaseous component to a baghouse; and

h) releasing the substantially mercury-free gaseous component of said sample to the atmosphere.

9. The method of Claim 8 wherein the adsorption powder used in step f) comprises about 40% carbon, about 40% calcium hydroxide, about 10% cupric chloride impregnated carbon and about 10% KI_3 impregnated carbon.

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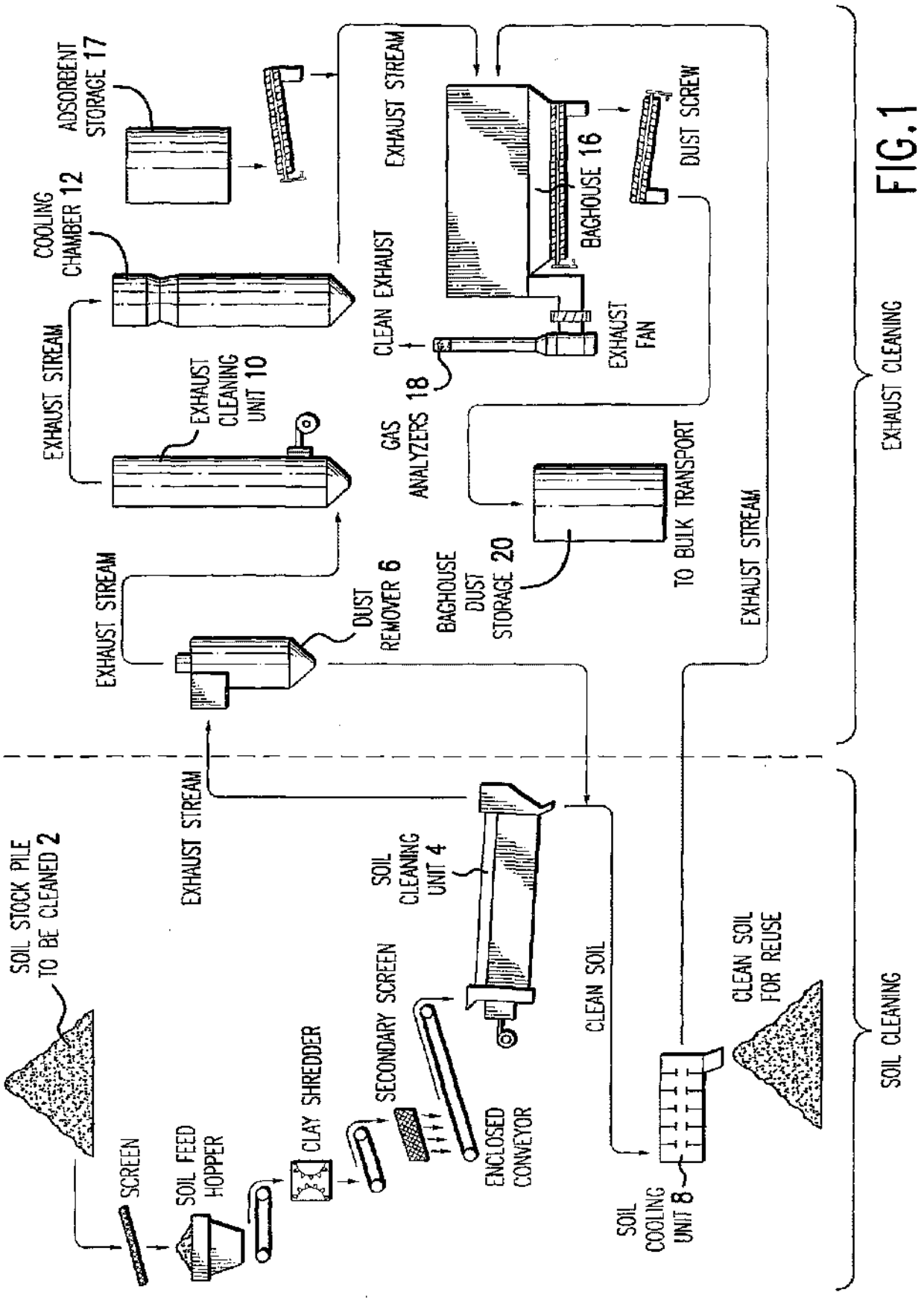

ADSORBENT STORAGE 17
COOLING CHAMBER 12
EXHAUST STREAM
EXHAUST CLEANING UNIT 10
CLEAN EXHAUST
GAS ANALYZERS 18
EXHAUST FAN
BAGHOUSE 16
DUST SCREW
EXHAUST STREAM
DUST REMOVER 6
BAGHOUSE DUST STORAGE 20
TO BULK TRANSPORT
EXHAUST STREAM
EXHAUST CLEANING
EXHAUST STREAM
SOIL CLEANING UNIT 4
SOIL STOCK PILE TO BE CLEANED 2
SCREEN
SOIL FEED HOPPER
CLAY SHREDDER
SECONDARY SCREEN
ENCLOSED CONVEYOR
CLEAN SOIL
SOIL COOLING UNIT 8
CLEAN SOIL FOR REUSE
SOIL CLEANING

FIG. 1

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(54) Titre : SORBANTS POUR L'OXYDATION ET L'ELIMINATION DU MERCURE
(54) Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

(57) Abrégé/Abstract:
A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non-carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can be regenerated and reused. Base sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

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(54) **Title**: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

(57) **Abstract**: A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non-carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can be regenerated and reused. Base sorbent treatment and preparation methods are also described. New methods for in flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is being filed on 02 February 2010, as a PCT International Patent application in the name of Energy & Environmental Research Center Foundation, a U.S. national corporation, applicant for the designation of all countries except the U.S., and Edwin S. Olson, a citizen of the U.S., Michael J. Holmes, a citizen of the U.S., and John H. Pavlish, a citizen of the U.S., applicants for the designation of the U.S. only, and claims priority to U.S. Continuation-in-Part Patent Application Serial No. 12/429,058 filed on 23 April 2009.

BACKGROUND OF THE INVENTION

Technical Field of the Invention

[0002] The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

[0003] The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, a day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

[0004] Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a particulate control device such as a baghouse or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when an ESP is used to collect the carbon because the contact time of the carbon with the gas is very short.

[0005] A major problem with existing carbon injection systems is that the sorbent is relatively unreactive toward mercury. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

[0006] One solution has been to add an oxidative sorbent comprising an aluminosilicate material impregnated with a very heavy dosage of one or more oxidative metal halides plus activated carbon. For example, refer to Varma et al. (20070140940). However, the amounts of metal salts required for Hg oxidation are generally relatively large and expensive. Also, several of the salts that can be used in such a process are highly toxic. Although the metal salts are present for oxidation in this process, activated carbon is essential for getting adsorption of the Hg. As such, there is no synergistic role for the aluminosilicates as they appear to be only a support for the oxidizing salts.

[0007] Another approach has been the injection of aluminosilicate particulate such as bentonite, which contains neither oxidizing salts nor halogen complexes with a Lewis base site, and thus lacks the more powerful oxidizing capability of the said complexes as described in this application. For example, see U.S. Patent No. 7,413,719. Additionally, the injection of an aluminosilicate (kaolin or metakaolin) containing

calcium hypochlorite which thermally decomposes to form halogen is also known. For example, see U.S. Patent Application No. 20030103882. Thus these and similar impregnated aluminosilicate technologies require time in flight at appropriate high temperatures to heat the impregnated salt(s) to generate an oxidation site. This clearly represents a kinetic barrier to activation in contrast to the extremely fast complexing reaction of the Lewis acid on the surface of the appropriate Lewis base sorbent described in the present patent. The kinetic barrier is only for heating up the calcium hypochlorite to decompose it to Cl atoms or molecules. Halogen (bimolecular or atomic) would complex with carbon or noncarbon at any lower temperature to form reactive oxidation sites. Also, halide would require a very high temp or strong acid to form reactive halogen or halogen complex.

[0008] Yet another approach is the injection of bentonite plus a metal sulfide and a metal salt, none of which is oxidizing to elemental mercury and would require a slow thermal activation step. For example, see U.S. Patent Application No. 20070119300.

[0009] The injection of halogen or halogen precursors in a hot zone, followed by contact with an alkaline material in a wet or dry scrubber is another approach known in the art. With such an approach, elemental mercury is claimed to be oxidized by the halogen to Hg(II) which is collected by the alkaline material in the scrubber. For example, see U.S. Patent No 6,808,692 (Oehr), U.S. Patent No. 3,849,267 (Hilgen), U.S. Patent No. 5,435,980 (Felsvang), U.S. Patent No. 6,375,909 (Dangtran), U.S. Patent Application No. 20020114749 (Cole), U.S. Patent No. 6,638,485 (Iida), U.S. Patent Application No. 20030185718 (Sellakumar), U.S. Patent Application No. 20030147793 (Breen), and U.S. Patent No. 6,878,358 (Vosteen). However, even though it is known to inject halogen forms at some stage of the combustion process, such a process does not utilize a complexing method on a sorbent surface for conducting the oxidation and capture. Further, the alkaline material is rapidly surface-coated by the large concentrations of acid gases, lowering its capacity for adsorption of Hg(II). It is also recognized that the halogen forms initially introduced or generated are far more reactive to the large concentrations of SO_2 and moisture in the flue gas, and so gas-phase reactions of the halogens with Hg are hindered. In contrast, the present invention takes advantage of the Lewis acid complexes that rapidly form on the sorbent surface to effect the Hg oxidation, rather than rely on gas phase reactions for oxidation. Thus HCl, HBr, SO_2Br, and other gas-phase products all festoon the surface and promote the activity of the sorbent by forming complexes with the sorbent to form a promoted sorbent.

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[0010] Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants, including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY

[0011] The various embodiments of the present invention overcome the various aspects of the deficiencies of the prior art and provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

[0012] A halogen/halide-promoted sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises any activated carbon and/or non-carbon compound, such as porous or vesicular felsic or basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the promoted sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. Methods for in-flight preparation, introduction, and control of the sorbent, promoter and promoted sorbent into the mercury contaminated gas stream are described.

[0013] When a promoted or a non-promoted base sorbent reacts with elemental or oxidized mercury, a mercury/sorbent chemical composition is formed and, in the case of elemental mercury reacting with the promoted base sorbent, the mercury is oxidized. As discussed in further detail in other portions of the specification, the base sorbent may be either a carbon or a non-carbon material or a combination thereof. Additionally, the mercury/sorbent chemical composition may be comprised of covalent bonds, ionic bonds and/or chemical complexes between the promoted or non-promoted base sorbent and the oxidized mercury. The Lewis basic groups on the non-promoted base sorbent, or the non-promoted portions of a promoted base sorbent, are available for reaction with the Lewis acid groups of already existing oxidized mercury in the mercury containing gas. Thus, mercury may be removed from the mercury containing gas stream through the formation of multiple and various mercury/sorbent chemical compositions even within the same process. For example, multiple sites on a sorbent particulate can form

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multiple and various mercury/sorbent chemical compositions in the case where only a portion of the sites on the base sorbent particulate are promoted.

[0014] In some embodiments, a carbon and/or non-carbon promoted sorbent and/or a combination thereof is provided comprising a sorbent structure that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream. The carbon sorbent comprises reactive Lewis acid groups/sites; the non-carbon sorbent comprises reactive Lewis basic groups/sites.

[0015] In an embodiment, a promoted carbon and/or non-carbon sorbent is provided wherein the base sorbent is selected from the group consisting of carbon, activated carbon, porous or vesicular felsic and basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof, with an average particle size similar to that of fly ash produced from a thermal process (combustion or gasification) or greater than that of fly ash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the promoted sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter greater than about 40 micrometers.

[0016] In another embodiment, the promoted sorbent comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced.

[0017] In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt% of the concentration of the promoter on the finished sorbent.

[0018] In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the base sorbent.

[0019] In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor

form when combined with the base sorbent. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base sorbent. In another embodiment, the promoter and optional secondary component are combined with the base sorbentsubstantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

[0020] In an embodiment, a method is provided comprising providing a granular base sorbent and reacting the base sorbent with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. In another embodiment the reaction product has an average particle-size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment, the reaction product has a mass mean particle diameter greater than about 40 micrometers.

[0021] In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the promoter is in the gas phase when contacting the base sorbent (carbon, non-carbon, or their combination). In another embodiment, the promoter is in an organic solvent when contacting the base sorbent (carbon, non-carbon, or their combination).

[0022] In another embodiment, the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

[0023] In another embodiment, the method further comprises reacting the granular non-carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the non-carbon base sorbent. In another embodiment, the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity,

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mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

[0024] In an embodiment, the promoted sorbent is introduced by direct injection into the flue gas stream. In another embodiment, the base sorbent is promoted within the flue gas stream

[0025] In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a base sorbent, either by injection or in situ creation, into a mercury-containing flue gas stream, collecting greater than 70 wt% of the mercury in the flue gas on the promoted sorbent to produce a cleaned flue gas, and substantially recovering the promoted sorbent from the cleaned flue gas. In embodiments where less than 70 wt% mercury removal is desired, the required removal is attained using less base sorbent as would be required with standard base sorbent. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered promoted sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of base sorbent and promoter. In another embodiment the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

[0026] In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination).

[0027] In another embodiment, the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination), a promoter, and an optional secondary component to enhance the reactivity and capacity of the promoted sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

[0028] In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt% of the promoter content. In another embodiment, the method further comprises adding to the promoted sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2,

CS_2, P_2S_5, and combinations thereof.

[0029] In an embodiment, the method further comprises coinjecting an optional alkaline material, including without limitation alkaline and alkaline-earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce promoted sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

[0030] In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the promoted sorbent. In another embodiment, the promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within the flue gas stream or in a transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination), wherein the rate at which the promoter is added and the rate of promoted sorbent injection are determined by a digital computer based, at least in part, on the monitored mercury content of the cleaned flue gas.

[0031] In an embodiment, a method for reducing the mercury content of a mercury and ash-containing gas stream is provided wherein particulate carbon and/or non-carbon promoted sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the promoted sorbent particles, the promoted sorbent particles are separated from the ash particles on the basis of size, and the promoted sorbent particles are reinjected to the gas stream. In another embodiment, the mercury-containing promoted sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is coinjected into the gas stream. In another embodiment, the promoted sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

[0032] In an embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is disclosed. The method comprises reacting a carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted carbon sorbent; allowing said promoted carbon sorbent to interact with a mercury-containing gas to capture mercury

in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0033] In a further emobodiment, the method comprises reacting a non-carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted non-carbon sorbent; allowing said promoted non-carbon sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the non-carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the non-carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the non-carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0034] In a further embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is presented. The method comprises reacting a base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted sorbent, wherein said base sorbent is selected from the group consisting of a non-carbon material, a carbon material, and combination thereof; allowing said promoted sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas.

[0035] In some embodiments, the base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some

embodiments, the base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In some embodiments, introducing the base sorbent and the promoter comprises injecting the base sorbent and the promoter into the mercury-containing gas. In some embodiments, the promoter is introduced into the mercury-containing gas upstream of the introduction of the base sorbent. In some embodiments, the promoter is introduced upstream of a boiler or a combustion chamber. In an embodiment, the rate at which the base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0036] In an embodiment, the base sorbent for the promoted sorbent is selected from the group consisting of carbon, activated carbon, porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof. In embodiments, the non-carbon material comprises Lewis basic groups and the carbon material comprises Lewis acid groups. In some cases, the non-carbon material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals. The alkaline-earth metals comprise Group I and Group II alkaline-earth metals. In some other cases, the non-carbon material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

[0037] In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and inorganic species on the non-carbon base sorbent. In some embodiments, the inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof. In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and metal-oxygen-metal structures on the non-carbon base sorbent. In some embodiments, the promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof. In an embodiment, the promoted sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof. In some embodiments, the interaction between promoted sorbent and said mercury-containing

gas stream comprises mercury diffusing from the gas phase onto said promoted sorbent surface; and reacting with the activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on the promoted sorbent surface.

[0038] In an embodiment, the method for reducing mercury in a mercury-containing gas to a desired level further comprises pretreating the base sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof. In some cases, the pretreating methods comprise chemical treatment, thermal treatment, vacuum treatment, and combinations thereof. In some embodiments, chemical treatment comprises acid treatment and alkaline treatment. In an embodiment, [[,]] the method for reducing mercury in a mercury-containing gas to a desired level further comprises introducing an alkali component into the mercury-containing gas.

[0039] As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from combustion and gasification systems.

[0040] The foregoing has outlined rather broadly the features and technical advantages 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 that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also 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

[0041] For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

[0042] Figure 1 schematically illustrates methods for preparation of promoted carbon and/or non-carbon sorbents in accordance with the present invention.

[0043] Figure 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

[0044] Figure 3 schematically illustrates preparation of promoted carbon and/or non-carbon sorbents and processes for flue gas mercury reduction in flue gases and/or

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product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon and/or non-carbon sorbent.

[0045] Figure 4 illustrates a mechanism for promotion of metal oxide base sorbent via formation of a reactive halogen complex sorbent and subsequent capture of elemental mercury on the promoted sorbent.

[0046] Figure 5A schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

[0047] Figure 5B schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

DETAILED DESCRIPTION

[0048] Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

[0049] The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide-promoted sorbents using a bromide (or other halogen/halide) treatment of the promoted sorbent, that capture mercury via mercury–sorbent surface reactions, at very short contact times of seconds or less. The reactivity of the promoted sorbent toward the pollutants (i.e., mercury) is greatly enhanced, and the sorption capacity can be regenerated; i.e., the promoted sorbent may be regenerated, recycled and/or reused.

[0050] The treated base sorbents (carbon, non-carbon, or their combination), treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

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[0051] Hereinafter the disclosure may at times discuss the use of carbon base sorbents in further details; however the use of non-carbon base sorbents and a combination of carbon and non-carbon base sorbents is also contemplated to at least the same degree as carbon base sorbents.

[0052] Referring now to Figure 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture in a mercury containing gas, such as a flue gas and/or product gas from gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base sorbent while block 20 illustrates adding a halogen or halide promoter that reacts with the base sorbent to produce a product-promoted sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A to produce a product-promoted sorbent suitable for injection.

[0053] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base sorbent as shown by block 10, adding a halogen or halide promoter that reacts with the base sorbent, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product-promoted sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A to produce a product-promoted sorbent suitable for injection.

[0054] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base sorbent as illustrated at block 10 and adding a halogen or halide promoter and a secondary component to the base sorbent together, with which they react to produce a product-promoted sorbent as illustrated by block 40. As above, in embodiments where vapor additions are made to the base sorbent, no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A to produce a product-promoted sorbent suitable for injection.

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[0055] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-50 in combination with path 20-50. In this embodiment, a base sorbent as illustrated by block 10 is introduced to the mercury containing gas as illustrated by block 50 while a halogen or halide promoter as illustrated by block 20 is introduced to the mercury containing gas stream. Thus the base sorbent and promoter react at block 50 to produce a product-promoted sorbent. In a similar manner, a secondary component as illustrated by block 30 may be added to the halogen or halide promoter as illustrated by block 20 and introduced into the mercury containing gas as illustrated by block 50. In embodiments where both the halogen or halide promoter and secondary component are added, for example, by vapor, no further steps may be taken. In embodiments where the halogen or halide and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A and/or block 30A.

[0056] Referring still to Figure 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a mercury containing gas stream is treated with product-promoted carbon sorbent prepared as described above.

[0057] In some preferred embodiments, the carbon base sorbent provided may preferably be any of several types, as understood by those skilled in the art. For example, the carbon base sorbent may include powdered activated carbon, granular activated carbon, carbon black, unburned carbon, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product-promoted carbon sorbent, or other types as known in the art.

[0058] In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle size greater than the fly ash in a mercury containing gas, such as a flue gas stream, to be treated.

[0059] In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle-size distribution greater than that of the fly ash or entrained ash in a flue gas stream, or other mercury containing gas, to be treated, such that the activated carbon and ash can be separated by physical means.

[0060] In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the carbon base sorbent may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

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[0061] Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

[0062] Referring now to Figure 4, a theory is illustrated developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure 4, a molecular bromine molecule forms a complex with the surface of the base sorbent comprising a high surface area form of a metal oxide. Complexing with bromine can occur at surface and defect sites on the surface of the glassy amorphous tectosilicates by association with the Lewis basic oxygen lining the interstitial cavities and the alkali actions on the surface. Molecular hydrogen bromide or an electrophilic or Lewis acid bromine compound react to form a similar structure. The precedence for this promotion of a metal oxide surface complex with an acidic species is described in a paper by Stark and Klabunde (Klabunde, K.J. Chem. Mater. 1996, 8, 1913-1918) who showed addition of acids, HCl, SO_3, and NO, to a MgO surface to form a surface complex. In US Patent 6,517,423 to Koper et al. the described surface complexes were active for destroying biological agents and toxins. As shown in Figure 4, addition of halogens to a metal oxide surface (A) can form a complex that could be described as a bromide-oxybromide species (B), in which electrophilic reactivity is maintained, owing to the formation of positive charges on the surface. The electrophilic complex formed on the metal oxide base sorbent comprises an active site for oxidation of elemental mercury. Addition of mercury to the complex results in formation of a mercury oxygen bond and, simultaneously, a mercury bromine bond as shown in complex C in Figure 4. Thus the final structure is a stable oxidized Hg form (D) described as a metaloxymercuric bromide.

[0063] In summary, it has now been found that the formation of the new bromide complex with the metal oxide surface increases the surface reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus as the mercury electrons are drawn toward the positive surface oxygen, the halide anion electrons are pushing in from the other side, stabilizing the

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positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus adding HBr or Br_2 to the appropriate metal oxide forms a similar surface bromide complex, in which the positive oxygen oxidizes the mercury with the assistance of the bromide ion.

[0064] In embodiments, a non-carbon base sorbent with Lewis basic sites/groups comprising metal-oxygen-metal structures is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the metal-oxygen-metal structures of the non-carbon base sorbent form metastable complexes, which are responsible for mercury capture via chemisorption. For example, metastable complexes may form between a halogen promoter and inorganic species on a non-carbon base sorbent, wherein inorganic species include sodium (Na), calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe) compounds, and combinations thereof. In some embodiments, the metastable complexes comprise a dihalogen group, such as Br-Cl, Br-Br, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a halogen atom, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a hydrohalogen group, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a Group V or Group VI halide, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metal-oxygen-metal structures of the base sorbent are complexed with combinations of the functional groups disclosed herein. Without wishing to be limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these metastable complexes.

[0065] In embodiments, a carbon base sorbent with Lewis acid sites/groups comprising graphene sheets is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the grapheme sheets of the carbon base sorbent form stable compounds, which are responsible for mercury capture via chemisorption. Without being limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these stable compounds. As one skilled in the art would appreciate, the versatility of chemistry associated with the base sorbent (carbon, non-carbon, or combination thereof) and the promoter of this disclosure enables versatile applications of the promoted sorbent system for mercury

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capture. This is especially advantageous because mercury content in flue gases varies from facility to facility, from operation to operation, and from day to day.

[0066] Examples of non-carbon base sorbents are amorphous forms of tectosilicates that comprise nanoscale cavities lined with Lewis basic oxygen associated with Group I alkali metals and Group II alkaline-earth metals. Such tectosilicates can be found in naturally occurring minerals, including, but not limited to, perlite and pumacite. Examples of non-carbon base sorbents also include amorphous forms of phyllosilicates. It is appreciated that other minerals may be used and also treated chemically and thermally to increase the activity of the base sorbent materials, such as phyllosilicates in the amorphous forms.

[0067] In some embodiments, bentonites are used as non-carbon base sorbents, including sodium bentonite and calcium bentonite. The use of other types of bentonites is contemplated as is known to one skilled in the art. The application of bentonite base sorbents is by introducing them into the flue gas at a location of the mercury capture system wherein the temperature of that location is below 800°C.

[0068] In some embodiments, the base sorbents are treated chemically and/or thermally to increase their activity. For example, perlite as a base sorbent may go through vacuum treatment and then thermal treatment so as to reduce the moisture contained therein, increase its activity, and potentially alter its morphology. Other treatment processes include chemical treatment, such acid treatment and alkaline treatment. These treatment methods may be combined to achieve desired effects as known to one skilled in the art. One of the desired effects is to increase the number of available Lewis acid sites/groups in the carbon base sorbent and/or the number of available Lewis basic sites/groups in the non-carbon base sorbent for subsequent activation via reaction with a promoter disclosed herein.

[0069] Referring now to Figure 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted base sorbents and flue gas mercury reduction in accordance with preferred embodiments of the present invention. In the exemplary embodiment shown, there is provided a base sorbent reservoir 110, a halogen/halide promoter reservoir 120, a secondary component reservoir 130, and an alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the alkali component reservoir 180, flow control devices 208 and 209 can be used independently, together, or not at all. Further, reservoirs 110, 120, 130 and 180 are optional and can be used in any combination, or not at all, whereby the otherwise stored components can be

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introduced into the system by other means either together or independently. Further, the alkali and secondary components may not be used at all within the system, if so desired.

[0070] As shown, reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in Figure 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

[0071] For clarity, single injection points 116 or 119 are shown in Figure 3, although one skilled in the art will understand that multiple injection points and/or locations are within the scope of the present invention. In the embodiment shown, transport line 15 comprises multiple lines allowing for multiple injections and separate and/or combined injections of base sorbent 110 and promoter 120 and/or 130. One mode of operation, by example, comprises providing base sorbent 110 in a common line which is promoted inline "in-flight" using promoter 120 and/or 130 and injected at point 116. Another mode of operation, by example, comprises transport and injection of a base sorbent 110 in a separate line to a point downstream of the injection of promoter 120 and/or 130 in a line at point 116 which is upstream of injection of base sorbent 110, resulting in in-flight preparation at a promoted sorbent within stream 15.

[0072] In the exemplary embodiment shown, an optional optical density measuring device(s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

[0073] Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more ESPs, or other particulate removal devices as are

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known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at multiple locations upstream and/or downstream of 140 when parallel, sequential, or combinations thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142 and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152 and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

[0074] An optional continuous emission monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35 to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

[0075] In operation, as example, promoted sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25 by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury clean flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, and 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, and 209 can also be adjusted manually or by some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

[0076] Referring still to Figure 3, several embodiments are illustrated for preparation and injection of promoted sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base sorbent from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206.

The halogen/halide may be combined and react with the base sorbent according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base sorbent prior to injection point 116 or downstream at point 116. This results in in-flight preparation of a promoted sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with the base sorbent prior to entering transport line 115. Still further, the halogen/halide may be contacted and react with the base sorbent by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebulliated or flueidized bed of base sorbent, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base sorbent in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in Figure 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to Figure 1.

[0077] Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131b and 131c.

[0078] Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with the base sorbent, promoted sorbent, or optional secondary components. Being able to vary on-site the amount of the optional alkali component relative to base sorbent, promoted sorbent, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

[0079] In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base sorbent. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

[0080] In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebulliated or flueidized

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bed of granular or fibrous base sorbent, with the promoted sorbent so produced removed from the top of the bed via gas entrainment for injection.

[0081] In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted sorbent may comprise from about 1 to about 30 g of halogen/halide per 100 g of base sorbent. In some preferred embodiments, the promoted sorbent may comprise a secondary component in concentration of from about 1 to about 15 wt% of the concentration of the halogen/halide component.

[0082] In still other embodiments, the product-promoted sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

[0083] In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

[0084] Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with hot flue gas components leaves little to react with elemental mercury. The atomic elemental halogen form, which includes the flueorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury, but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

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[0085] The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view, therefore, a halide salt-treated sorbent will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen-Promoted Sorbent Characteristics

[0086] The promoted sorbent described here has a very high initial reactivity for oxidizing mercury and therefore, can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the promoted sorbents produced using the inventive technology. The time interval required for the mercury and the promoted sorbents of the present invention to successfully interact in a flue gas duct, with subsequent collection of the mercury on the promoted sorbent and ash, is very short – less than seconds. Clearly, such collection times require the promoted sorbent to have both high capacity and high reactivity toward mercury. The promoted sorbent can be utilized in a very finely powdered form to minimize mass-transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the promoted sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a promoted sorbent containing a halide component formed on and/or within the base sorbent structure that provides a sorbent that is highly active on initial contact with the mercury-contaminated gas stream, which allows for very effective capture of the mercury.

[0087] The inventive sorbents chemically combine bromine species with Lewis acid/basic sites on the base sorbent. For example, x-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus the promoted sorbent produced from halogen and base sorbent does not represent a molecular halogen form, but rather a new chemically modified structure. This phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of

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mercury. Thus an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury shown in Figure 2. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

[0088] It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the promoted sorbent, typically exceeding that of both the untreated base sorbent and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

[0089] It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio on-site in order to overcome and optimize for a given set of site conditions.

[0090] The synergy that can be gained when coinjecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e., sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants, thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully

consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury-binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than AC; thus more of it can be used, still resulting in overall lower costs.

In-Flight Sorbent Preparation

[0091] As stated previously, the halogen promoted sorbent can be readily produced in-flight. This is accomplished by, for example, contacting the vapors of any combination of halogens and, optionally, a second component, in-flight, with base sorbent particles. The particles may be dispersed in a stream of transport air (or other gas, such as the flue gas itself), which also conveys the halogen/halide-promoted sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

[0092] Referring to Figures 5A and 5B, process flow diagrams are shown as examples of the process for mercury removal from a mercury containing gas, such as a flue gas. In an embodiment shown at Figure 5A, gas inlet stream 501 passes through chamber 301 and enters air heater 302 as stream 502; then it exits air heater 302 as stream 503 and passes through particulate control device 303 and enters scrubber 304 as stream 504; finally it exits scrubber 304 as stream 505. As shown, chamber 301 is a boiler, however, one skilled in the art will appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection streams 401, 402, 403 and 404, in addition to stream 501, are multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

[0093] Figure 5B shows an embodiment similar to that of FIG. A, but with the position of the scrubber and particulate control device switched. Specifically, gas inlet stream 501' passes through chamber 301' and enters air heater 302' as stream 502'; then it exits air heater 302' as stream 503' and passes through scrubber 304' and enters particulate control device 303' as stream 504'; finally it exits particulate control device 303' as stream 505'. As shown, chamber 301 is a boiler, however, one skilled in the art will

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appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection stream locations 401', 402', 403' and 404', in addition to stream 501', represent multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

[0094] At each of the aforementioned injection stream locations 401, 401', 402, 402', 403, 403', 404 and 404', 501, 501' multiple injection points are contemplated so that promoter and base sorbent may be injected as a single injection stream or as separate injection streams, as further illustrated in the following exemplary embodiments.

[0095] In an embodiment, a promoter is introduced to chamber 301 at location 401. A base sorbent (carbon, non-carbon, or their combination) is introduced at location 402 upstream of air heater 302. In a further embodiment, a promoter is introduced to at location 402 upstream of air heater 302. A base sorbent (carbon, non-carbon, or their combination) is also introduced at location 402 either as a separate stream or as a mixed single stream with the promoter. In another embodiment, a promoter is introduced at locations 401 and 402. A base sorbent (carbon, non-carbon, or their combination) is introduced at location 402 either as a separate stream or as a mixed single stream with the promoter.

[0096] With the aid of this disclosure, one of ordinary skill in the art will be able to configure the process in many different fashions for mercury removal using the promoted sorbent. All these configurations are considered equivalents of the disclosed process and therefore are within the scope of the claimed invention.

Advantages of On-Site Preparation

[0097] In-flight preparation of the halogen/halide-promoted sorbent on location produces certain advantages. For example, the treatment system can be combined with the base sorbent injection system at the end-use site. With this technique, the halogen/halide is introduced to the base sorbent air (or other gas, including to the flue gas or other mercury containing gas) mixture in a transport line (or flue gas duct part of the base sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.

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- The inventive process uses existing hardware and operation procedures.
- The inventive technology ensures that the sorbent is always fresh and, thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- The inventive process allows rapid on-site tailoring of additive–sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when fuels are changed or loads are reduced, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

[0098] With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide-promoted sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g., bromine) to the base sorbent structure.

Sorbent Injection Location

[0099] Some of the preferred embodiments contemplate the use of a halogen-promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen-promoted sorbent comprise a powdered modified AC prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base AC and/or with the use of a halogen-based sorbent and any other combinations of the sorbent technologies provided in this patent. Other embodiments allow for in-flight preparation of promoted sorbents by using and combining the promoters and base sorbents. Alternatively, embodiments include methods wherein the base sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

[00100] Any of the above embodiments of the halogen/halide-promoted carbon and/or non-carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed, and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon and/or non-carbon itself contrasts with the earlier, more expensive, conventional methods of

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adding a reagent (such as peroxide, gold, triiodide, etc.) to a base sorbent. The halogen/halide-promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in copending, commonly owned PCT Patent Application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT," which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

[00101] Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

EXAMPLES

[00102] To more clearly illustrate the present invention, an example is presented below. This example is intended to be illustrative, and no limitations to the present invention should be drawn or inferred from the example presented herein.

Example 1 – Non-carbon-Promoted Sorbent Tests at Full-Scale Plants

[00103] Full-scale commercial tests were conducted at several coal-burning facilities equipped with ESPs wherein three types of pre-cursers were injected upstream of an ESP at 325°F. In all, more than thirty tests were performed with variations in base sorbent material, base sorbent material injection rates and promoter injection rates. Promoters were halogen-based materials. Base sorbents were clay-based materials such as perlite and pumacite, which are vesicular forms of tectosilicates comprising silicates and aluminate tetrahedra with alkali metals in the interstitual spaces. Each base sorbent was injected upstream from the ESP.

[00104] The flue gas flow rate for the test was approximately 23 million $dsft^3/hr$ with a corresponding mercury flow rate of 0.0097 lbs Hg/hr. Initial mercury concentration in

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the flue gas prior to the introduction of the base sorbent or promoted sorbent was approximately 0.000417 lbs Hg/million dsft^3.

[00105] As shown in Table 1, each base sorbent was injected at three different test rates: about 100 lb/hr ("Low"), about 150 lb/hr ("Ave.") and about 200 lb/hr ("High"). At each test rate, the mercury removal rate was measured both with and without the use of a promoter to show the relative benefit of introducing the promoter into the flue gas stream. For the tests where promoter was injected into the flue gas stream, promoter was injected at about 20 lb/hr for the "Low" tests, at about 25 lb/hr for the "Ave." tests and from about 30 to about 50 lb/hr for the "High" tests. The percent mercury removal for each test was calculated based on measurements taken from the inlet flue gas and the outlet flue gas. The results as shown in Table 1 clearly show a significant improvement in mercury capture when a promoter and base sorbent are injected, as compared to the injection of a base sorbent alone.

Table 1. Test Data for Non Carbon-Promoted Sorbents

Base Sorbent Material	Base Sorbent Injection Rate (lb/hr)			Promoter Injection Rate (lb/hr)			Percent Removal of Mercury (%)		
	Low	Ave.	High	Low	Ave.	High	Low	Ave.	High
Perlite	100	150	200	0	0	0	37	40	43
	100	150	200	20	25	35	55	72	74
Pumacite	100	150	200	0	0	0	25	25	25
	100	150	200	20	25	50	52	60	65
Clay-Based Mix of Silica and Alumina	100	150	200	0	0	0	50	52	54
	100	150	200	20	25	30	58	65	74

[00106] While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

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Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

[00107] The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

[00108] The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

[00109] Although the invention is described herein as a promoted sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

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1. A method for separating mercury from a mercury containing gas comprising:

(a) providing a non-carbon sorbent material;

(b) providing a halogen or halide promoter;

(c) promoting at least a portion of the non-carbon sorbent material by chemically reacting the non-carbon sorbent material with the halogen or halide promoter to form a promoted halogenated sorbent;

(d) chemically reacting elemental mercury in the mercury containing gas with the promoted halogenated sorbent to form a mercury/sorbent chemical composition; and

(e) separating particulates from the mercury containing gas to form a cleaned gas, the particulates including ash and the first mercury/sorbent chemical composition.

2. The method of claim 1, further comprising the step of injecting the non-carbon sorbent material and the halogen or halide promoter into the mercury containing gas.

3. The method of claim 2, wherein said halogen or halide promoter and the non-carbon sorbent material are injected into the mercury containing gas at the same location.

4. The method of claim 2, wherein said halogen or halide promoter and the non-carbon sorbent material are injected into the mercury containing gas at separate locations.

5. The method of claim 4, wherein said halogen or halide promoter is injected into the mercury-containing gas upstream of the injection of said non-carbon sorbent material.

6. The method of claim 5, wherein said halogen or halide promoter is injected into a combustion chamber that produces a mercury-containing gas, and the non-carbon sorbent material is injected downstream of the combustion chamber.

7. The method of claim 6, wherein said halogen or halide promoter is additionally injected downstream of the combustion chamber.

8. The method of claim 6, wherein said combustion chamber is a boiler and the mercury-containing gas is a flue gas.

9. The method of claim 3, wherein said halogen or halide promoter and non-carbon sorbent material are injected downstream of a chamber that produces a mercury-containing gas.

10. The method of claim 9, wherein said chamber is a boiler and the mercury-containing gas is a flue gas.

11. The method of claim 2, wherein the rate at which said non-carbon sorbent material is injected or the rate at which said promoter is injected or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially a desired level.

12. The method of claim 1, wherein said non-carbon sorbent material is selected from the group consisting of porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof.

13. The method of claim 12, wherein said non-carbon sorbent material is a material that reacts with oxidized mercury in the mercury-containing gas to form a second mercury/sorbent chemical composition.

14. The method of claim 1, wherein said non-carbon sorbent material comprises Lewis basic groups.

15. The method of claim 1, wherein said non-carbon sorbent material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals.

16. The method of claim 15, wherein said alkaline-earth metals comprise Group I and Group II alkaline-earth metals.

17. The method of claim 1 wherein said non-carbon sorbent material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

18. The method of claim 1, wherein said promoted sorbent comprises metastable complexes formed between said promoter and inorganic species on the non-carbon sorbent.

19. The method of claim 18 wherein said inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof.

20. The method of claim 1, wherein said promoted sorbent comprises metastable complexes formed between said promoter and metal-oxygen-metal structures on the non-carbon sorbent.

21. The method of claim 20, wherein said promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof.

22. The method of claim 1, wherein said promoted sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof.

23. The method of claim 1, wherein said interaction between promoted sorbent and said mercury-containing gas stream comprises:

mercury diffusing from the gas phase onto said promoted sorbent surface; and

reacting with activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on the sorbent surface.

24. The method of claim 1 further comprising pretreating said sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof on said sorbent.

25. The method of claim 24, wherein pretreating said sorbent comprises chemical treatment, thermal treatment, vacuum treatment, and combinations thereof.

26. The method of claim 25, wherein said chemical treatment comprises acid treatment and alkaline treatment.

27. The method of claim 1 further comprising introducing an alkali component into the mercury-containing gas.

28. The method of claim 1, wherein a carbon sorbent is reacted with said promoter to produce a promoted carbon sorbent.

29. The method of claim 28, wherein said carbon sorbent or said promoter or combination thereof are introduced into the mercury-containing gas at one or more locations.

30. The method of claim 29, wherein the rate at which said carbon sorbent is introduced or the rate at which said promoter is introduced or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially a desired level.

31. The method of claim 28, wherein said carbon sorbent comprises activated carbon.

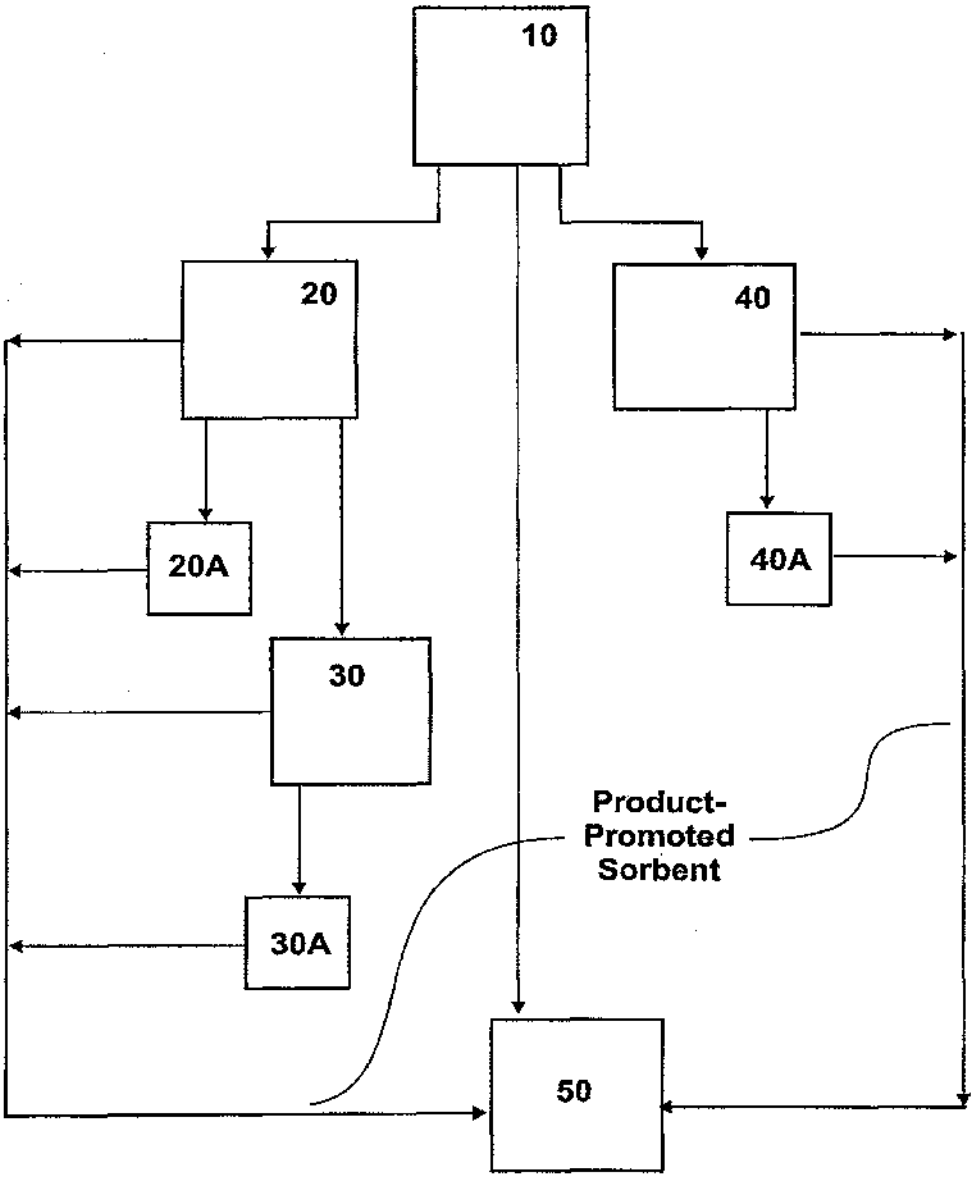


FIG. 1

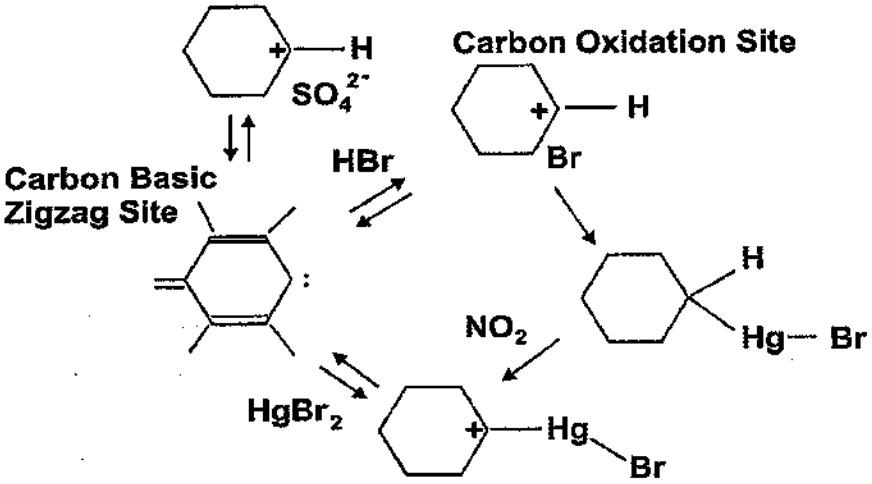

Carbon Oxidation Site
H
SO_4^{2-}
HBr
Carbon Basic
Zigzag Site
H
Br
H
Hg— Br
NO_2
$HgBr_2$
Hg
Br

FIG. 2

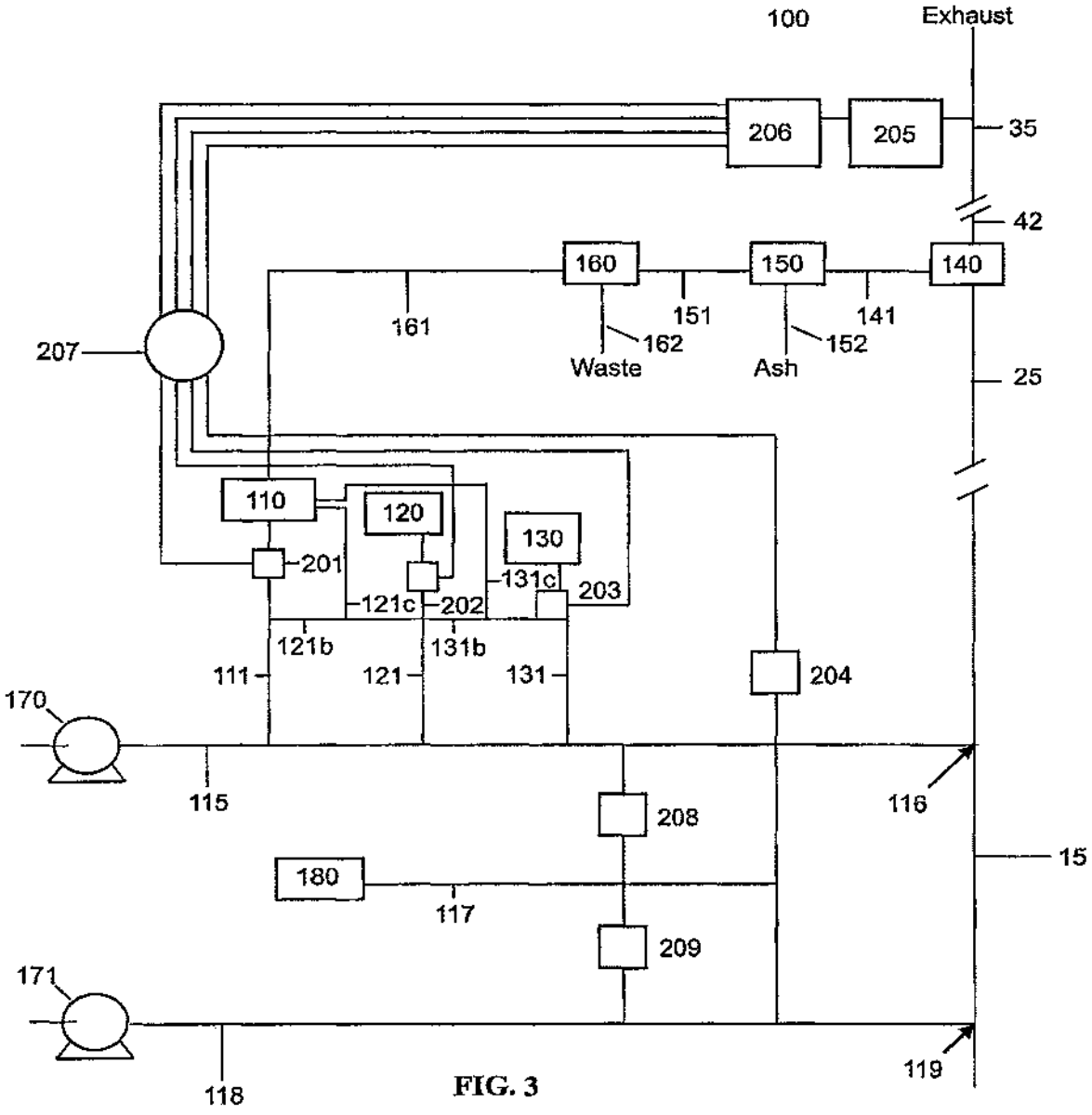

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Exhaust
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205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
25
110
120
130
201
131c
121c
202
203
121b
131b
111
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115
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180
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171
118
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FIG. 3

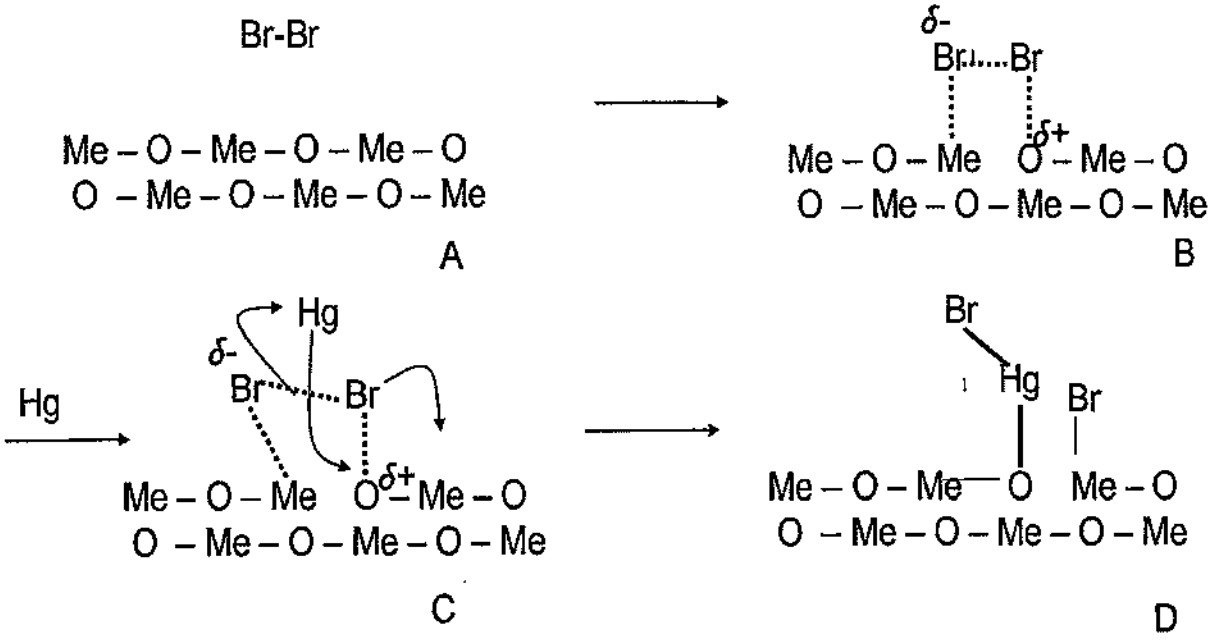

Br-Br
Me – O – Me – O – Me – O
O – Me – O – Me – O – Me
A
δ-
Br
Br
δ+
Me – O – Me
O – Me – O
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O
B
Hg
Hg
δ-
Br
Br
δ+
Me – O – Me
O – Me – O
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FIG. 4

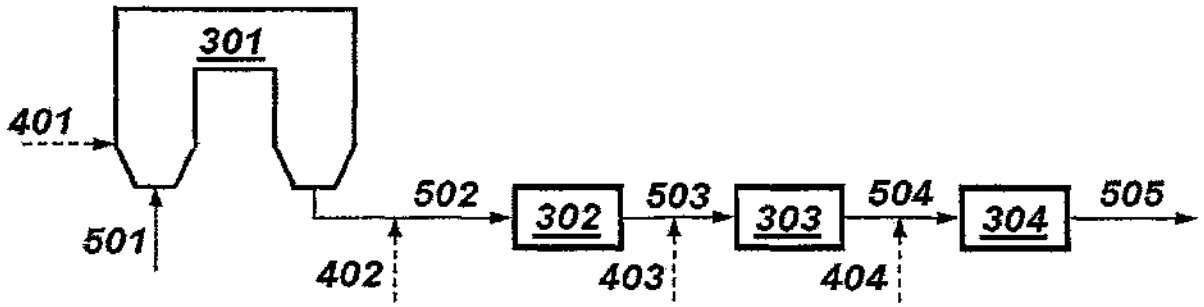

301
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FIG. 5A

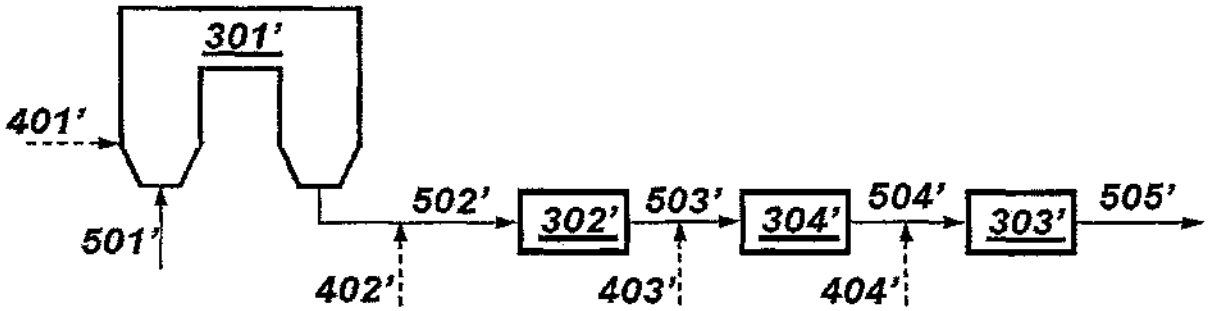

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303'
505'

FIG. 5B

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(54) **Titre : SORBANTS POUR L'OXYDATION ET L'ELIMINATION DU MERCURE**
(54) **Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY**

(57) **Abrégé/Abstract:**
A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non- carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can be regenerated and reused. Base sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

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(54) **Title**: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

(57) **Abstract**: A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non-carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can be regenerated and reused. Base sorbent treatment and preparation methods are also described. New methods for in flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

BACKGROUND OF THE INVENTION

Technical Field of the Invention

[0002] The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

[0003] The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, a day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

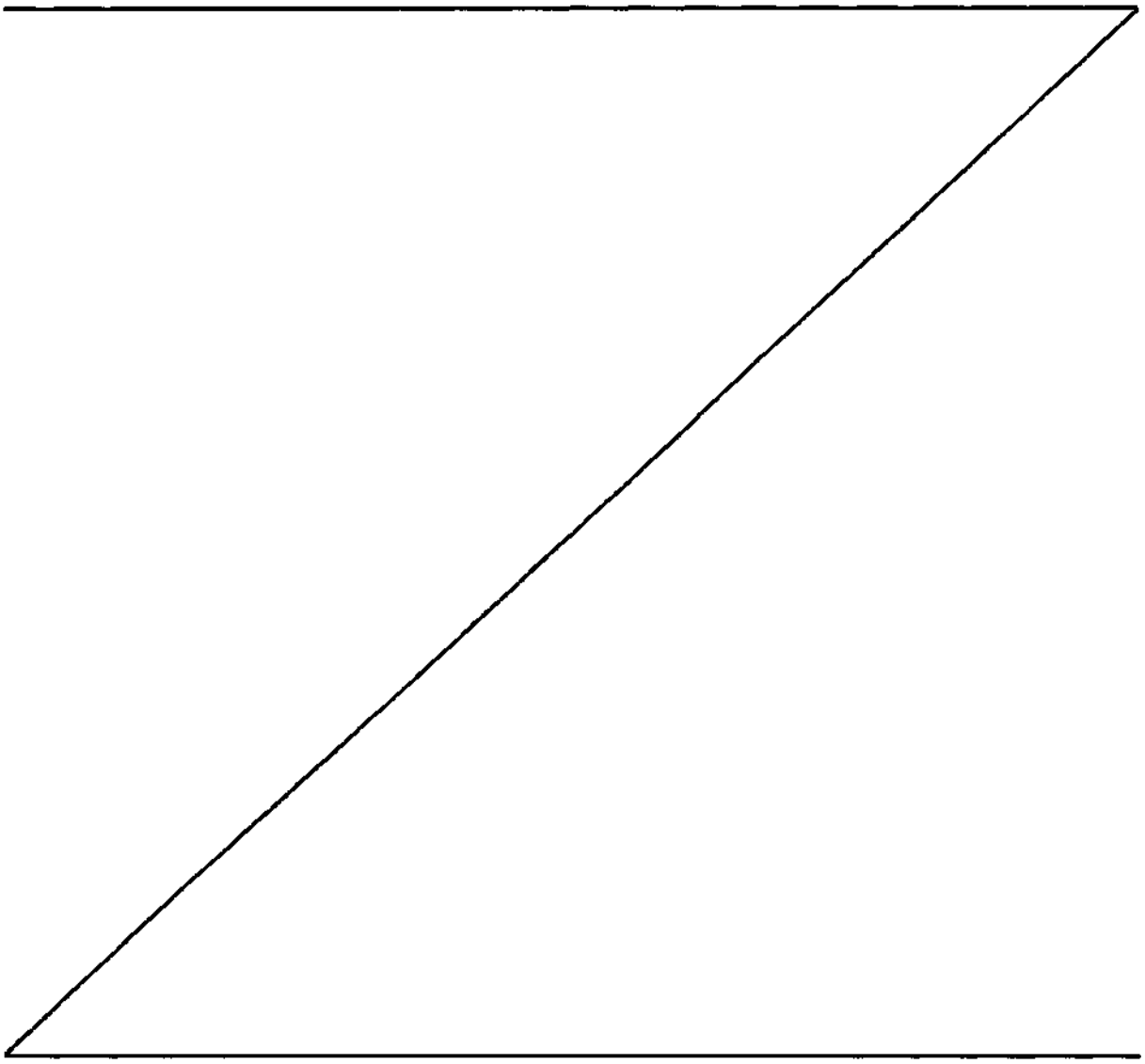
[0004] Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a particulate control device such as a baghouse or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when an ESP is used to collect the carbon because the contact time of the carbon with the gas is very short.

[0005] A major problem with existing carbon injection systems is that the sorbent is relatively unreactive toward mercury. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

[0006] One solution has been to add an oxidative sorbent comprising an aluminosilicate material impregnated with a very heavy dosage of one or more oxidative metal halides plus activated carbon. For example, refer to Varma et al. (published US application no. 2007/0140940). However, the amounts of metal salts required for Hg oxidation are generally relatively large and expensive. Also, several of the salts that can be used in such a process are highly toxic. Although the metal salts are present for oxidation in this process, activated carbon is essential for getting adsorption of the Hg.

As such, there is no synergistic role for the aluminosilicates as they appear to be only a support for the oxidizing salts.

[0007] Another approach has been the injection of aluminosilicate particulate such as bentonite, which contains neither oxidizing salts nor halogen complexes with a Lewis base site, and thus lacks the more powerful oxidizing capability of the said complexes as described in this application. For example, see U.S. Patent No. 7,413,719. Additionally, the injection of an aluminosilicate (kaolin or metakaolin) containing



calcium hypochlorite which thermally decomposes to form halogen is also known. For example, see U.S. Patent Application No. 20030103882. Thus these and similar impregnated aluminosilicate technologies require time in flight at appropriate high temperatures to heat the impregnated salt(s) to generate an oxidation site. This clearly represents a kinetic barrier to activation in contrast to the extremely fast complexing reaction of the Lewis acid on the surface of the appropriate Lewis base sorbent described in the present patent. The kinetic barrier is only for heating up the calcium hypochlorite to decompose it to Cl atoms or molecules. Halogen (bimolecular or atomic) would complex with carbon or noncarbon at any lower temperature to form reactive oxidation sites. Also, halide would require a very high temp or strong acid to form reactive halogen or halogen complex.

[0008] Yet another approach is the injection of bentonite plus a metal sulfide and a metal salt, none of which is oxidizing to elemental mercury and would require a slow thermal activation step. For example, see U.S. Patent Application No. 20070119300.

[0009] The injection of halogen or halogen precursors in a hot zone, followed by contact with an alkaline material in a wet or dry scrubber is another approach known in the art. With such an approach, elemental mercury is claimed to be oxidized by the halogen to Hg(II) which is collected by the alkaline material in the scrubber. For example, see U.S. Patent No 6,808,692 (Oehr), U.S. Patent No. 3,849,267 (Hilgen), U.S. Patent No. 5,435,980 (Felsvang), U.S. Patent No. 6,375,909 (Dangtran), U.S. Patent Application No. 20020114749 (Cole), U.S. Patent No. 6,638,485 (Iida), U.S. Patent Application No. 20030185718 (Sellakumar), U.S. Patent Application No. 20030147793 (Breen), and U.S. Patent No. 6,878,358 (Vosteen). However, even though it is known to inject halogen forms at some stage of the combustion process, such a process does not utilize a complexing method on a sorbent surface for conducting the oxidation and capture. Further, the alkaline material is rapidly surface-coated by the large concentrations of acid gases, lowering its capacity for adsorption of Hg(II). It is also recognized that the halogen forms initially introduced or generated are far more reactive to the large concentrations of SO_2 and moisture in the flue gas, and so gas-phase reactions of the halogens with Hg are hindered. In contrast, the present invention takes advantage of the Lewis acid complexes that rapidly form on the sorbent surface to effect the Hg oxidation, rather than rely on gas phase reactions for oxidation. Thus HCl, HBr, SO_2Br, and other gas-phase products all festoon the surface and promote the activity of the sorbent by forming complexes with the sorbent to form a promoted sorbent.

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[0010] Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants, including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY

[0011] The various embodiments of the present invention overcome the various aspects of the deficiencies of the prior art and provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

[0011-a] An embodiment of the invention relates to a method for separating mercury from a mercury containing gas comprising:

(a) providing a carbon sorbent material and a non-carbon sorbent material, wherein the carbon sorbent material comprises activated carbon;

(b) providing a halogen or halide promoter;

(c) promoting at least a portion of the carbon sorbent material and the non-carbon sorbent material by chemically reacting the carbon sorbent material and the non-carbon sorbent material with the halogen or halide promoter to form a promoted halogenated carbon sorbent and a promoted halogenated non-carbon sorbent;

(d) chemically reacting elemental mercury in the mercury containing gas with the promoted halogenated carbon sorbent and the promoted halogenated non-carbon sorbent to form a mercury/sorbent chemical composition; and

(e) separating particulates from the mercury containing gas to form a cleaned gas, the particulates including ash and the mercury/sorbent chemical composition.

[0011-b] Another embodiment of the invention relates to the method defined hereinabove, further comprising the step of injecting the non-carbon sorbent material and the halogen or halide promoter into the mercury containing gas.

[0011-c] Another embodiment of the invention relates to the method defined hereinabove, wherein said halogen or halide promoter and the non-carbon sorbent material are injected into the mercury containing gas at the same location.

[0011-d] Another embodiment of the invention relates to the method defined hereinabove,

wherein said halogen or halide promoter and the non-carbon sorbent material are injected into the mercury containing gas at separate locations.

[0011-e] Another embodiment of the invention relates to the method defined hereinabove, wherein said halogen or halide promoter is injected into the mercury-containing gas upstream of the injection of said non-carbon sorbent material.

[0011-f] Another embodiment of the invention relates to the method defined hereinabove, wherein said halogen or halide promoter is injected into a combustion chamber that produces a mercury-containing gas, and the non-carbon sorbent material is injected downstream of the combustion chamber.

[0011-g] Another embodiment of the invention relates to the method defined hereinabove, wherein said halogen or halide promoter is additionally injected downstream of the combustion chamber.

[0011-h] Another embodiment of the invention relates to the method defined hereinabove, wherein said combustion chamber is a boiler and the mercury-containing gas is a flue gas.

[0011-i] Another embodiment of the invention relates to the method defined hereinabove, wherein said halogen or halide promoter and non-carbon sorbent material are injected downstream of a chamber that produces a mercury-containing gas.

[0011-j] Another embodiment of the invention relates to the method defined hereinabove, wherein said chamber is a boiler and the mercury-containing gas is a flue gas.

[0011-k] Another embodiment of the invention relates to the method defined hereinabove, wherein the rate at which said non-carbon sorbent material is injected or the rate at which said promoter is injected or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at a desired level.

[0011-l] Another embodiment of the invention relates to the method defined hereinabove, wherein said non-carbon sorbent material is selected from the group consisting of porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof.

[0011-m] Another embodiment of the invention relates to the method defined hereinabove, wherein said non-carbon sorbent material is a material that reacts with oxidized mercury in the mercury-containing gas to form a second mercury/sorbent chemical composition.

[0011-n] Another embodiment of the invention relates to the method defined hereinabove, wherein said non-carbon sorbent material comprises Lewis basic groups.

[0011-o] Another embodiment of the invention relates to the method defined hereinabove, wherein said non-carbon sorbent material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals.

[0011-p] Another embodiment of the invention relates to the method defined hereinabove, wherein said alkaline-earth metals comprise Group I and Group II alkaline-earth metals.

[0011-q] Another embodiment of the invention relates to the method defined hereinabove, wherein said non-carbon sorbent material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

[0011-r] Another embodiment of the invention relates to the method defined hereinabove, wherein said promoted non-carbon sorbent comprises metastable complexes formed between said promoter and inorganic species on the non-carbon sorbent.

[0011-s] Another embodiment of the invention relates to the method defined hereinabove, wherein said inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof.

[0011-t] Another embodiment of the invention relates to the method defined hereinabove, wherein said promoted non-carbon sorbent comprises metastable complexes formed between said promoter and metal-oxygen-metal structures on the non-carbon sorbent.

[0011-u] Another embodiment of the invention relates to the method defined hereinabove, wherein said promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof.

[0011-v] Another embodiment of the invention relates to the method defined hereinabove,

wherein said promoted non-carbon sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof.

[0011-w] Another embodiment of the invention relates to the method defined hereinabove, wherein said interaction between promoted non-carbon sorbent and said mercury-containing gas stream comprises:

mercury diffusing from the gas phase onto a surface of said non-carbon promoted sorbent; and

reacting with activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on a sorbent surface.

[0011-x] Another embodiment of the invention relates to the method defined hereinabove, further comprising pretreating said non-carbon sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof on said sorbent.

[0011-y] Another embodiment of the invention relates to the method defined hereinabove, wherein pretreating said non-carbon sorbent comprises chemical treatment, thermal treatment, vacuum treatment, and combinations thereof.

[0011-z] Another embodiment of the invention relates to the method defined hereinabove, wherein said chemical treatment comprises acid treatment and alkaline treatment.

[0011-aa] Another embodiment of the invention relates to the method defined hereinabove, further comprising introducing an alkali component into the mercury-containing gas.

[0011-ab] Another embodiment of the invention relates to the method defined hereinabove, wherein said carbon sorbent or said promoter or combination thereof are introduced into the mercury-containing gas at one or more locations.

[0011-ac] Another embodiment of the invention relates to the method defined hereinabove, wherein the rate at which said carbon sorbent is introduced or the rate at which said promoter is introduced or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at a desired level.

[0011-ad] Another embodiment of the invention relates to the method defined hereinabove, where the promoted halogenated carbon sorbent and the promoted halogenated non-

carbon sorbent comprise 1 to 30 grams of the halogen or halide promoter per 100 grams of the carbon sorbent and the non-carbon sorbent.

[0012] A halogen/halide-promoted sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises any activated carbon and/or non-carbon compound, such as porous or vesicular felsic or basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the promoted sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. Methods for in-flight preparation, introduction, and control of the sorbent, promoter and promoted sorbent into the mercury contaminated gas stream are described.

[0013] When a promoted or a non-promoted base sorbent reacts with elemental or oxidized mercury, a mercury/sorbent chemical composition is formed and, in the case of elemental mercury reacting with the promoted base sorbent, the mercury is oxidized. As discussed in further detail in other portions of the specification, the base sorbent may be either a carbon or a non-carbon material or a combination thereof. Additionally, the mercury/sorbent chemical composition may be comprised of covalent bonds, ionic bonds and/or chemical complexes between the promoted or non-promoted base sorbent and the oxidized mercury. The Lewis basic groups on the non-promoted base sorbent, or the non-promoted portions of a promoted base sorbent, are available for reaction with the Lewis acid groups of already existing oxidized mercury in the mercury containing gas. Thus, mercury may be removed from the mercury containing gas stream through the formation of multiple and various mercury/sorbent chemical compositions even within the same process. For example, multiple sites on a sorbent particulate can form

multiple and various mercury/sorbent chemical compositions in the case where only a portion of the sites on the base sorbent particulate are promoted.

[0014] In some embodiments, a carbon and/or non-carbon promoted sorbent and/or a combination thereof is provided comprising a sorbent structure that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream. The carbon sorbent comprises reactive Lewis acid groups/sites; the non-carbon sorbent comprises reactive Lewis basic groups/sites.

[0015] In an embodiment, a promoted carbon and/or non-carbon sorbent is provided wherein the base sorbent is selected from the group consisting of carbon, activated carbon, porous or vesicular felsic and basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof, with an average particle size similar to that of fly ash produced from a thermal process (combustion or gasification) or greater than that of fly ash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the promoted sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter greater than about 40 micrometers.

[0016] In another embodiment, the promoted sorbent comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced.

[0017] In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt% of the concentration of the promoter on the finished sorbent.

[0018] In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the base sorbent.

[0019] In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor

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form when combined with the base sorbent. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base sorbent. In another embodiment, the promoter and optional secondary component are combined with the base sorbentsubstantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

[0020] In an embodiment, a method is provided comprising providing a granular base sorbent and reacting the base sorbent with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. In another embodiment the reaction product has an average particle-size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment, the reaction product has a mass mean particle diameter greater than about 40 micrometers.

[0021] In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the promoter is in the gas phase when contacting the base sorbent (carbon, non-carbon, or their combination). In another embodiment, the promoter is in an organic solvent when contacting the base sorbent (carbon, non-carbon, or their combination).

[0022] In another embodiment, the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

[0023] In another embodiment, the method further comprises reacting the granular non-carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the non-carbon base sorbent. In another embodiment, the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity,

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mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

[0024] In an embodiment, the promoted sorbent is introduced by direct injection into the flue gas stream. In another embodiment, the base sorbent is promoted within the flue gas stream

[0025] In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a base sorbent, either by injection or in situ creation, into a mercury-containing flue gas stream, collecting greater than 70 wt% of the mercury in the flue gas on the promoted sorbent to produce a cleaned flue gas, and substantially recovering the promoted sorbent from the cleaned flue gas. In embodiments where less than 70 wt% mercury removal is desired, the required removal is attained using less base sorbent as would be required with standard base sorbent. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered promoted sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of base sorbent and promoter. In another embodiment the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

[0026] In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination).

[0027] In another embodiment, the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination), a promoter, and an optional secondary component to enhance the reactivity and capacity of the promoted sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

[0028] In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt% of the promoter content. In another embodiment, the method further comprises adding to the promoted sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2,

CS_2, P_2S_5, and combinations thereof.

[0029] In an embodiment, the method further comprises coinjecting an optional alkaline material, including without limitation alkaline and alkaline-earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce promoted sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

[0030] In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the promoted sorbent. In another embodiment, the promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within the flue gas stream or in a transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination), wherein the rate at which the promoter is added and the rate of promoted sorbent injection are determined by a digital computer based, at least in part, on the monitored mercury content of the cleaned flue gas.

[0031] In an embodiment, a method for reducing the mercury content of a mercury and ash-containing gas stream is provided wherein particulate carbon and/or non-carbon promoted sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the promoted sorbent particles, the promoted sorbent particles are separated from the ash particles on the basis of size, and the promoted sorbent particles are reinjected to the gas stream. In another embodiment, the mercury-containing promoted sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is coinjected into the gas stream. In another embodiment, the promoted sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

[0032] In an embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is disclosed. The method comprises reacting a carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted carbon sorbent; allowing said promoted carbon sorbent to interact with a mercury-containing gas to capture mercury

in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0033] In a further emobodiment, the method comprises reacting a non-carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted non-carbon sorbent; allowing said promoted non-carbon sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the non-carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the non-carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the non-carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0034] In a further embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is presented. The method comprises reacting a base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted sorbent, wherein said base sorbent is selected from the group consisting of a non-carbon material, a carbon material, and combination thereof; allowing said promoted sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas.

[0035] In some embodiments, the base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some

embodiments, the base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In some embodiments, introducing the base sorbent and the promoter comprises injecting the base sorbent and the promoter into the mercury-containing gas. In some embodiments, the promoter is introduced into the mercury-containing gas upstream of the introduction of the base sorbent. In some embodiments, the promoter is introduced upstream of a boiler or a combustion chamber. In an embodiment, the rate at which the base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0036] In an embodiment, the base sorbent for the promoted sorbent is selected from the group consisting of carbon, activated carbon, porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof. In embodiments, the non-carbon material comprises Lewis basic groups and the carbon material comprises Lewis acid groups. In some cases, the non-carbon material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals. The alkaline-earth metals comprise Group I and Group II alkaline-earth metals. In some other cases, the non-carbon material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

[0037] In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and inorganic species on the non-carbon base sorbent. In some embodiments, the inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof. In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and metal-oxygen-metal structures on the non-carbon base sorbent. In some embodiments, the promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof. In an embodiment, the promoted sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof. In some embodiments, the interaction between promoted sorbent and said mercury-containing

gas stream comprises mercury diffusing from the gas phase onto said promoted sorbent surface; and reacting with the activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on the promoted sorbent surface.

[0038] In an embodiment, the method for reducing mercury in a mercury-containing gas to a desired level further comprises pretreating the base sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof. In some cases, the pretreating methods comprise chemical treatment, thermal treatment, vacuum treatment, and combinations thereof. In some embodiments, chemical treatment comprises acid treatment and alkaline treatment, hi an embodiment, the method for reducing mercury in a mercury-containing gas to a desired level further comprises introducing an alkali component into the mercury-containing gas.

[0039] As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from combustion and gasification systems.

[0040] The foregoing has outlined rather broadly the features and technical advantages 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 that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention.

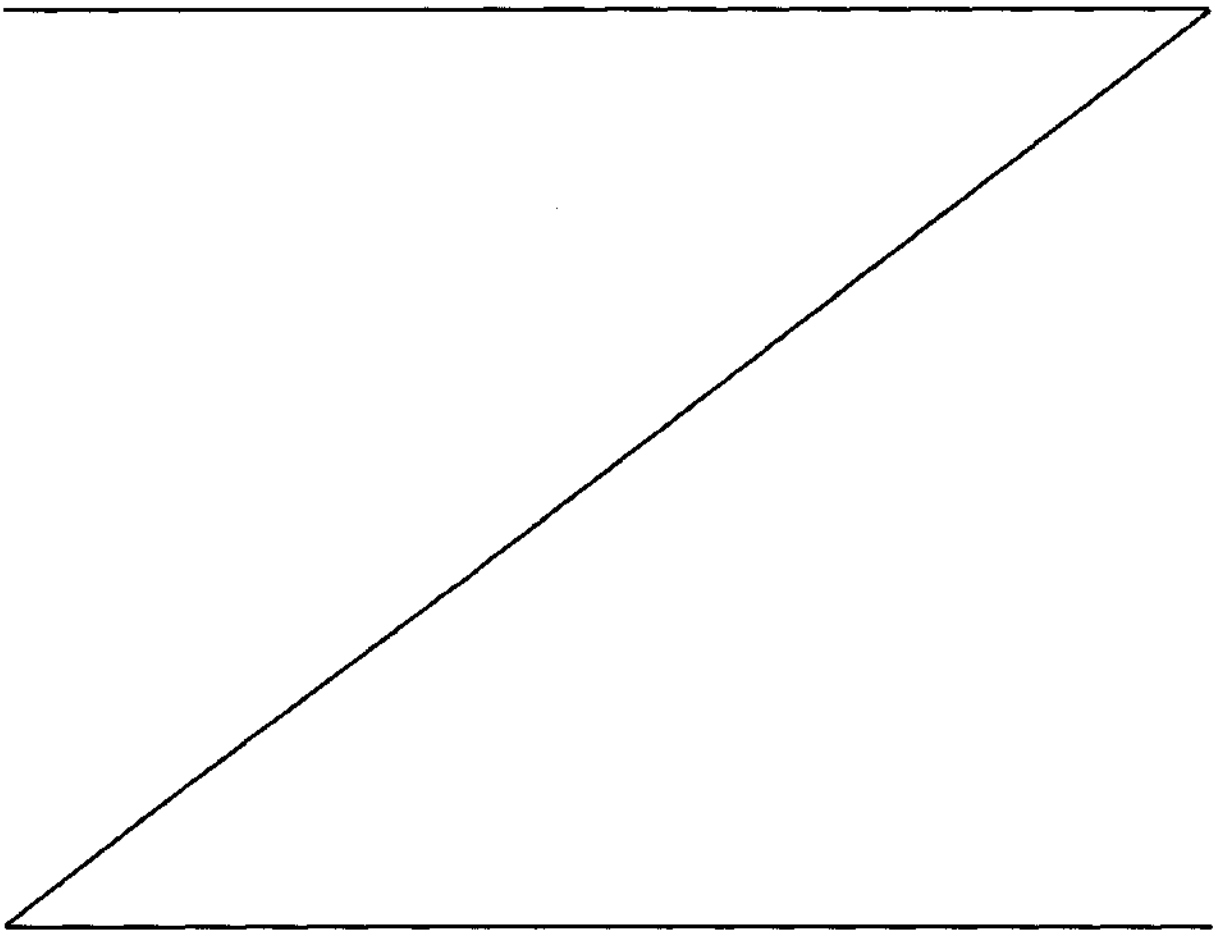
BRIEF DESCRIPTION OF THE DRAWINGS

[0041] For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

[0042] Figure 1 schematically illustrates methods for preparation of promoted carbon and/or non-carbon sorbents in accordance with the present invention.

[0043] Figure 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

[0044] Figure 3 schematically illustrates preparation of promoted carbon and/or non-carbon sorbents and processes for flue gas mercury reduction in flue gases and/or



product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon and/or non-carbon sorbent.

[0045] Figure 4 illustrates a mechanism for promotion of metal oxide base sorbent via formation of a reactive halogen complex sorbent and subsequent capture of elemental mercury on the promoted sorbent.

[0046] Figure 5A schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

[0047] Figure 5B schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

DETAILED DESCRIPTION

[0048] Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

[0049] The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide-promoted sorbents using a bromide (or other halogen/halide) treatment of the promoted sorbent, that capture mercury via mercury–sorbent surface reactions, at very short contact times of seconds or less. The reactivity of the promoted sorbent toward the pollutants (i.e., mercury) is greatly enhanced, and the sorption capacity can be regenerated; i.e., the promoted sorbent may be regenerated, recycled and/or reused.

[0050] The treated base sorbents (carbon, non-carbon, or their combination), treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

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[0051] Hereinafter the disclosure may at times discuss the use of carbon base sorbents in further details; however the use of non-carbon base sorbents and a combination of carbon and non-carbon base sorbents is also contemplated to at least the same degree as carbon base sorbents.

[0052] Referring now to Figure 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture in a mercury containing gas, such as a flue gas and/or product gas from gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base sorbent while block 20 illustrates adding a halogen or halide promoter that reacts with the base sorbent to produce a product-promoted sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A to produce a product-promoted sorbent suitable for injection.

[0053] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base sorbent as shown by block 10, adding a halogen or halide promoter that reacts with the base sorbent, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product-promoted sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A to produce a product-promoted sorbent suitable for injection.

[0054] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base sorbent as illustrated at block 10 and adding a halogen or halide promoter and a secondary component to the base sorbent together, with which they react to produce a product-promoted sorbent as illustrated by block 40. As above, in embodiments where vapor additions are made to the base sorbent, no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A to produce a product-promoted sorbent suitable for injection.

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[0055] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-50 in combination with path 20-50. In this embodiment, a base sorbent as illustrated by block 10 is introduced to the mercury containing gas as illustrated by block 50 while a halogen or halide promoter as illustrated by block 20 is introduced to the mercury containing gas stream. Thus the base sorbent and promoter react at block 50 to produce a product-promoted sorbent. In a similar manner, a secondary component as illustrated by block 30 may be added to the halogen or halide promoter as illustrated by block 20 and introduced into the mercury containing gas as illustrated by block 50. In embodiments where both the halogen or halide promoter and secondary component are added, for example, by vapor, no further steps may be taken. In embodiments where the halogen or halide and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A and/or block 30A.

[0056] Referring still to Figure 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a mercury containing gas stream is treated with product-promoted carbon sorbent prepared as described above.

[0057] In some preferred embodiments, the carbon base sorbent provided may preferably be any of several types, as understood by those skilled in the art. For example, the carbon base sorbent may include powdered activated carbon, granular activated carbon, carbon black, unburned carbon, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product-promoted carbon sorbent, or other types as known in the art.

[0058] In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle size greater than the fly ash in a mercury containing gas, such as a flue gas stream, to be treated.

[0059] In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle-size distribution greater than that of the fly ash or entrained ash in a flue gas stream, or other mercury containing gas, to be treated, such that the activated carbon and ash can be separated by physical means.

[0060] In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the carbon base sorbent may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

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[0061] Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

[0062] Referring now to Figure 4, a theory is illustrated developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure 4, a molecular bromine molecule forms a complex with the surface of the base sorbent comprising a high surface area form of a metal oxide. Complexing with bromine can occur at surface and defect sites on the surface of the glassy amorphous tectosilicates by association with the Lewis basic oxygen lining the interstitial cavities and the alkali actions on the surface. Molecular hydrogen bromide or an electrophilic or Lewis acid bromine compound react to form a similar structure. The precedence for this promotion of a metal oxide surface complex with an acidic species is described in a paper by Stark and Klabunde (Klabunde, K.J. Chem. Mater. 1996, 8, 1913-1918) who showed addition of acids, HCl, SO_3, and NO, to a MgO surface to form a surface complex. In US Patent 6,517,423 to Koper et al. the described surface complexes were active for destroying biological agents and toxins. As shown in Figure 4, addition of halogens to a metal oxide surface (A) can form a complex that could be described as a bromide-oxybromide species (B), in which electrophilic reactivity is maintained, owing to the formation of positive charges on the surface. The electrophilic complex formed on the metal oxide base sorbent comprises an active site for oxidation of elemental mercury. Addition of mercury to the complex results in formation of a mercury oxygen bond and, simultaneously, a mercury bromine bond as shown in complex C in Figure 4. Thus the final structure is a stable oxidized Hg form (D) described as a metaloxymercuric bromide.

[0063] In summary, it has now been found that the formation of the new bromide complex with the metal oxide surface increases the surface reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus as the mercury electrons are drawn toward the positive surface oxygen, the halide anion electrons are pushing in from the other side, stabilizing the

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positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus adding HBr or Br_2 to the appropriate metal oxide forms a similar surface bromide complex, in which the positive oxygen oxidizes the mercury with the assistance of the bromide ion.

[0064] In embodiments, a non-carbon base sorbent with Lewis basic sites/groups comprising metal-oxygen-metal structures is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the metal-oxygen-metal structures of the non-carbon base sorbent form metastable complexes, which are responsible for mercury capture via chemisorption. For example, metastable complexes may form between a halogen promoter and inorganic species on a non-carbon base sorbent, wherein inorganic species include sodium (Na), calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe) compounds, and combinations thereof. In some embodiments, the metastable complexes comprise a dihalogen group, such as Br-Cl, Br-Br, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a halogen atom, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a hydrohalogen group, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a Group V or Group VI halide, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metal-oxygen-metal structures of the base sorbent are complexed with combinations of the functional groups disclosed herein. Without wishing to be limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these metastable complexes.

[0065] In embodiments, a carbon base sorbent with Lewis acid sites/groups comprising graphene sheets is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the grapheme sheets of the carbon base sorbent form stable compounds, which are responsible for mercury capture via chemisorption. Without being limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these stable compounds. As one skilled in the art would appreciate, the versatility of chemistry associated with the base sorbent (carbon, non-carbon, or combination thereof) and the promoter of this disclosure enables versatile applications of the promoted sorbent system for mercury

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capture. This is especially advantageous because mercury content in flue gases varies from facility to facility, from operation to operation, and from day to day.

[0066] Examples of non-carbon base sorbents are amorphous forms of tectosilicates that comprise nanoscale cavities lined with Lewis basic oxygen associated with Group I alkali metals and Group II alkaline-earth metals. Such tectosilicates can be found in naturally occurring minerals, including, but not limited to, perlite and pumacite. Examples of non-carbon base sorbents also include amorphous forms of phyllosilicates. It is appreciated that other minerals may be used and also treated chemically and thermally to increase the activity of the base sorbent materials, such as phyllosilicates in the amorphous forms.

[0067] In some embodiments, bentonites are used as non-carbon base sorbents, including sodium bentonite and calcium bentonite. The use of other types of bentonites is contemplated as is known to one skilled in the art. The application of bentonite base sorbents is by introducing them into the flue gas at a location of the mercury capture system wherein the temperature of that location is below 800°C.

[0068] In some embodiments, the base sorbents are treated chemically and/or thermally to increase their activity. For example, perlite as a base sorbent may go through vacuum treatment and then thermal treatment so as to reduce the moisture contained therein, increase its activity, and potentially alter its morphology. Other treatment processes include chemical treatment, such acid treatment and alkaline treatment. These treatment methods may be combined to achieve desired effects as known to one skilled in the art. One of the desired effects is to increase the number of available Lewis acid sites/groups in the carbon base sorbent and/or the number of available Lewis basic sites/groups in the non-carbon base sorbent for subsequent activation via reaction with a promoter disclosed herein.

[0069] Referring now to Figure 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted base sorbents and flue gas mercury reduction in accordance with preferred embodiments of the present invention. In the exemplary embodiment shown, there is provided a base sorbent reservoir 110, a halogen/halide promoter reservoir 120, a secondary component reservoir 130, and an alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the alkali component reservoir 180, flow control devices 208 and 209 can be used independently, together, or not at all. Further, reservoirs 110, 120, 130 and 180 are optional and can be used in any combination, or not at all, whereby the otherwise stored components can be

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introduced into the system by other means either together or independently. Further, the alkali and secondary components may not be used at all within the system, if so desired.

[0070] As shown, reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in Figure 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

[0071] For clarity, single injection points 116 or 119 are shown in Figure 3, although one skilled in the art will understand that multiple injection points and/or locations are within the scope of the present invention. In the embodiment shown, transport line 15 comprises multiple lines allowing for multiple injections and separate and/or combined injections of base sorbent 110 and promoter 120 and/or 130. One mode of operation, by example, comprises providing base sorbent 110 in a common line which is promoted inline "in-flight" using promoter 120 and/or 130 and injected at point 116. Another mode of operation, by example, comprises transport and injection of a base sorbent 110 in a separate line to a point downstream of the injection of promoter 120 and/or 130 in a line at point 116 which is upstream of injection of base sorbent 110, resulting in in-flight preparation at a promoted sorbent within stream 15.

[0072] In the exemplary embodiment shown, an optional optical density measuring device(s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

[0073] Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more ESPs, or other particulate removal devices as are

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known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at multiple locations upstream and/or downstream of 140 when parallel, sequential, or combinations thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142 and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152 and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

[0074] An optional continuous emission monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35 to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

[0075] In operation, as example, promoted sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25 by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury clean flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, and 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, and 209 can also be adjusted manually or by some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

[0076] Referring still to Figure 3, several embodiments are illustrated for preparation and injection of promoted sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base sorbent from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206.

The halogen/halide may be combined and react with the base sorbent according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base sorbent prior to injection point 116 or downstream at point 116. This results in in-flight preparation of a promoted sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with the base sorbent prior to entering transport line 115. Still further, the halogen/halide may be contacted and react with the base sorbent by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebulliated or flueidized bed of base sorbent, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base sorbent in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in Figure 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to Figure 1.

[0077] Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131b and 131c.

[0078] Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with the base sorbent, promoted sorbent, or optional secondary components. Being able to vary on-site the amount of the optional alkali component relative to base sorbent, promoted sorbent, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

[0079] In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base sorbent. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

[0080] In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebulliated or flueidized

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bed of granular or fibrous base sorbent, with the promoted sorbent so produced removed from the top of the bed via gas entrainment for injection.

[0081] In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted sorbent may comprise from about 1 to about 30 g of halogen/halide per 100 g of base sorbent. In some preferred embodiments, the promoted sorbent may comprise a secondary component in concentration of from about 1 to about 15 wt% of the concentration of the halogen/halide component.

[0082] In still other embodiments, the product-promoted sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

[0083] In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

[0084] Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with hot flue gas components leaves little to react with elemental mercury. The atomic elemental halogen form, which includes the flueorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury, but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

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[0085] The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view, therefore, a halide salt-treated sorbent will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen-Promoted Sorbent Characteristics

[0086] The promoted sorbent described here has a very high initial reactivity for oxidizing mercury and therefore, can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the promoted sorbents produced using the inventive technology. The time interval required for the mercury and the promoted sorbents of the present invention to successfully interact in a flue gas duct, with subsequent collection of the mercury on the promoted sorbent and ash, is very short – less than seconds. Clearly, such collection times require the promoted sorbent to have both high capacity and high reactivity toward mercury. The promoted sorbent can be utilized in a very finely powdered form to minimize mass-transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the promoted sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a promoted sorbent containing a halide component formed on and/or within the base sorbent structure that provides a sorbent that is highly active on initial contact with the mercury-contaminated gas stream, which allows for very effective capture of the mercury.

[0087] The inventive sorbents chemically combine bromine species with Lewis acid/basic sites on the base sorbent. For example, x-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus the promoted sorbent produced from halogen and base sorbent does not represent a molecular halogen form, but rather a new chemically modified structure. This phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of

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mercury. Thus an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury shown in Figure 2. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

[0088] It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the promoted sorbent, typically exceeding that of both the untreated base sorbent and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

[0089] It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio on-site in order to overcome and optimize for a given set of site conditions.

[0090] The synergy that can be gained when coinjecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e., sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants, thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully

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consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury-binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than AC; thus more of it can be used, still resulting in overall lower costs.

In-Flight Sorbent Preparation

[0091] As stated previously, the halogen promoted sorbent can be readily produced in-flight. This is accomplished by, for example, contacting the vapors of any combination of halogens and, optionally, a second component, in-flight, with base sorbent particles. The particles may be dispersed in a stream of transport air (or other gas, such as the flue gas itself), which also conveys the halogen/halide-promoted sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

[0092] Referring to Figures 5A and 5B, process flow diagrams are shown as examples of the process for mercury removal from a mercury containing gas, such as a flue gas. In an embodiment shown at Figure 5A, gas inlet stream 501 passes through chamber 301 and enters air heater 302 as stream 502; then it exits air heater 302 as stream 503 and passes through particulate control device 303 and enters scrubber 304 as stream 504; finally it exits scrubber 304 as stream 505. As shown, chamber 301 is a boiler, however, one skilled in the art will appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection streams 401, 402, 403 and 404, in addition to stream 501, are multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

[0093] Figure 5B shows an embodiment similar to that of FIG. A, but with the position of the scrubber and particulate control device switched. Specifically, gas inlet stream 501' passes through chamber 301' and enters air heater 302' as stream 502'; then it exits air heater 302' as stream 503' and passes through scrubber 304' and enters particulate control device 303' as stream 504'; finally it exits particulate control device 303' as stream 505'. As shown, chamber 301 is a boiler, however, one skilled in the art will

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appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection stream locations 401', 402', 403' and 404', in addition to stream 501', represent multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

[0094] At each of the aforementioned injection stream locations 401, 401', 402, 402', 403, 403', 404 and 404', 501, 501' multiple injection points are contemplated so that promoter and base sorbent may be injected as a single injection stream or as separate injection streams, as further illustrated in the following exemplary embodiments.

[0095] In an embodiment, a promoter is introduced to chamber 301 at location 401. A base sorbent (carbon, non-carbon, or their combination) is introduced at location 402 upstream of air heater 302. In a further embodiment, a promoter is introduced to at location 402 upstream of air heater 302. A base sorbent (carbon, non-carbon, or their combination) is also introduced at location 402 either as a separate stream or as a mixed single stream with the promoter. In another embodiment, a promoter is introduced at locations 401 and 402. A base sorbent (carbon, non-carbon, or their combination) is introduced at location 402 either as a separate stream or as a mixed single stream with the promoter.

[0096] With the aid of this disclosure, one of ordinary skill in the art will be able to configure the process in many different fashions for mercury removal using the promoted sorbent. All these configurations are considered equivalents of the disclosed process and therefore are within the scope of the claimed invention.

Advantages of On-Site Preparation

[0097] In-flight preparation of the halogen/halide-promoted sorbent on location produces certain advantages. For example, the treatment system can be combined with the base sorbent injection system at the end-use site. With this technique, the halogen/halide is introduced to the base sorbent air (or other gas, including to the flue gas or other mercury containing gas) mixture in a transport line (or flue gas duct part of the base sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.

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- The inventive process uses existing hardware and operation procedures.
- The inventive technology ensures that the sorbent is always fresh and, thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- The inventive process allows rapid on-site tailoring of additive–sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when fuels are changed or loads are reduced, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

[0098] With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide-promoted sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g., bromine) to the base sorbent structure.

Sorbent Injection Location

[0099] Some of the preferred embodiments contemplate the use of a halogen-promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen-promoted sorbent comprise a powdered modified AC prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base AC and/or with the use of a halogen-based sorbent and any other combinations of the sorbent technologies provided in this patent. Other embodiments allow for in-flight preparation of promoted sorbents by using and combining the promoters and base sorbents. Alternatively, embodiments include methods wherein the base sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

[00100] Any of the above embodiments of the halogen/halide-promoted carbon and/or non-carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed, and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon and/or non-carbon itself contrasts with the earlier, more expensive, conventional methods of

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adding a reagent (such as peroxide, gold, triiodide, etc.) to a base sorbent. The halogen/halide-promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in copending, commonly owned PCT Patent Application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT".

Sorbent Injection Control Schemes

[00101] Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

EXAMPLES

[00102] To more clearly illustrate the present invention, an example is presented below. This example is intended to be illustrative, and no limitations to the present invention should be drawn or inferred from the example presented herein.

Example 1 - Non-carbon-Promoted Sorbent Tests at Full-Scale Plants

[00103] Full-scale commercial tests were conducted at several coal-burning facilities equipped with ESPs wherein three types of pre-cursers were injected upstream of an ESP at 325°F. In all, more than thirty tests were performed with variations in base sorbent material, base sorbent material injection rates and promoter injection rates. Promoters were halogen-based materials. Base sorbents were clay-based materials such as perlite and pumacite, which are vesicular forms of tectosilicates comprising silicates and aluminate tetrahedra with alkali metals in the interstitual spaces. Each base sorbent was injected upstream from the ESP.

[00104] The flue gas flow rate for the test was approximately 23 million $dsft^3/hr$ with a corresponding mercury flow rate of 0.0097 lbs Hg/hr. Initial mercury concentration in

the flue gas prior to the introduction of the base sorbent or promoted sorbent was approximately 0.000417 lbs Hg/million dsft^3.

[00105] As shown in Table 1, each base sorbent was injected at three different test rates: about 100 lb/hr ("Low"), about 150 lb/hr ("Ave.") and about 200 lb/hr ("High"). At each test rate, the mercury removal rate was measured both with and without the use of a promoter to show the relative benefit of introducing the promoter into the flue gas stream. For the tests where promoter was injected into the flue gas stream, promoter was injected at about 20 lb/hr for the "Low" tests, at about 25 lb/hr for the "Ave." tests and from about 30 to about 50 lb/hr for the "High" tests. The percent mercury removal for each test was calculated based on measurements taken from the inlet flue gas and the outlet flue gas. The results as shown in Table 1 clearly show a significant improvement in mercury capture when a promoter and base sorbent are injected, as compared to the injection of a base sorbent alone.

Table 1. Test Data for Non Carbon-Promoted Sorbents

Base Sorbent Material	Base Sorbent Injection Rate (lb/hr)			Promoter Injection Rate (lb/hr)			Percent Removal of Mercury (%)		
	Low	Ave.	High	Low	Ave.	High	Low	Ave.	High
Perlite	100	150	200	0	0	0	37	40	43
	100	150	200	20	25	35	55	72	74
Pumacite	100	150	200	0	0	0	25	25	25
	100	150	200	20	25	50	52	60	65
Clay-Based Mix of Silica and Alumina	100	150	200	0	0	0	50	52	54
	100	150	200	20	25	30	58	65	74

[00106] While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

[00107] The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

[00108] The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application.

[00109] Although the invention is described herein as a promoted sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described.

WHAT IS CLAIMED IS:

1. A method for separating mercury from a mercury containing gas comprising:

(a) providing a carbon sorbent material and a non-carbon sorbent material, wherein the carbon sorbent material comprises activated carbon;

(b) providing a halogen or halide promoter;

(c) promoting at least a portion of the carbon sorbent material and the non-carbon sorbent material by chemically reacting the carbon sorbent material and the non-carbon sorbent material with the halogen or halide promoter to form a promoted halogenated carbon sorbent and a promoted halogenated non-carbon sorbent;

(d) chemically reacting elemental mercury in the mercury containing gas with the promoted halogenated carbon sorbent and the promoted halogenated non-carbon sorbent to form a mercury/sorbent chemical composition; and

(e) separating particulates from the mercury containing gas to form a cleaned gas, the particulates including ash and the mercury/sorbent chemical composition.

2. The method of claim 1, further comprising the step of injecting the non-carbon sorbent material and the halogen or halide promoter into the mercury containing gas.

3. The method of claim 2, wherein said halogen or halide promoter and the non-carbon sorbent material are injected into the mercury containing gas at the same location.

4. The method of claim 2, wherein said halogen or halide promoter and the non-carbon sorbent material are injected into the mercury containing gas at separate locations.

5. The method of claim 4, wherein said halogen or halide promoter is injected into the mercury-containing gas upstream of the injection of said non-carbon sorbent material.

6. The method of claim 5, wherein said halogen or halide promoter is injected into a combustion chamber that produces a mercury-containing gas, and the non-carbon sorbent material is injected downstream of the combustion chamber.

7. The method of claim 6, wherein said halogen or halide promoter is additionally injected downstream of the combustion chamber.

8. The method of claim 6, wherein said combustion chamber is a boiler and the mercury-containing gas is a flue gas.

9. The method of claim 3, wherein said halogen or halide promoter and non-carbon sorbent material are injected downstream of a chamber that produces a mercury-containing gas.

10. The method of claim 9, wherein said chamber is a boiler and the mercury-containing gas is a flue gas.

11. The method of claim 2, wherein the rate at which said non-carbon sorbent material is injected or the rate at which said promoter is injected or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at a desired level.

12. The method of claim 1, wherein said non-carbon sorbent material is selected from the group consisting of porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof.

13. The method of claim 12, wherein said non-carbon sorbent material is a material that reacts with oxidized mercury in the mercury-containing gas to form a second mercury/sorbent chemical composition.

14. The method of claim 1, wherein said non-carbon sorbent material comprises Lewis basic groups.

15. The method of claim 12, wherein said non-carbon sorbent material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals.

16. The method of claim 15, wherein said alkaline-earth metals comprise Group I and Group II alkaline-earth metals.

17. The method of claim 1 wherein said non-carbon sorbent material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

18. The method of claim 1, wherein said promoted non-carbon sorbent comprises metastable complexes formed between said promoter and inorganic species on the non-carbon sorbent.

19. The method of claim 18, wherein said inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof.

20. The method of claim 1, wherein said promoted non-carbon sorbent comprises metastable complexes formed between said promoter and metal-oxygen-metal structures on the non-carbon sorbent.

21. The method of claim 20, wherein said promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof.

22. The method of claim 1, wherein said promoted non-carbon sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof.

23. The method of claim 1, wherein said interaction between promoted non-carbon sorbent and said mercury-containing gas stream comprises:

mercury diffusing from the gas phase onto a surface of said non-carbon promoted sorbent; and

reacting with activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on a sorbent surface.

24. The method of claim 1 further comprising pretreating said non-carbon sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof on said sorbent.

25. The method of claim 24, wherein pretreating said non-carbon sorbent comprises chemical treatment, thermal treatment, vacuum treatment, and combinations thereof.

26. The method of claim 25, wherein said chemical treatment comprises acid treatment and alkaline treatment

27. The method of claim 1 further comprising introducing an alkali component into the mercury-containing gas.

28. The method of claim 1, wherein said carbon sorbent or said promoter or combination thereof are introduced into the mercury-containing gas at one or more locations.

29. The method of claim 28, wherein the rate at which said carbon sorbent is introduced or the rate at which said promoter is introduced or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at a desired level.

30. The method of claim 1, where the promoted halogenated carbon sorbent and the promoted halogenated non-carbon sorbent comprise 1 to 30 grams of the halogen or halide promoter per 100 grams of the carbon sorbent and the non-carbon sorbent.

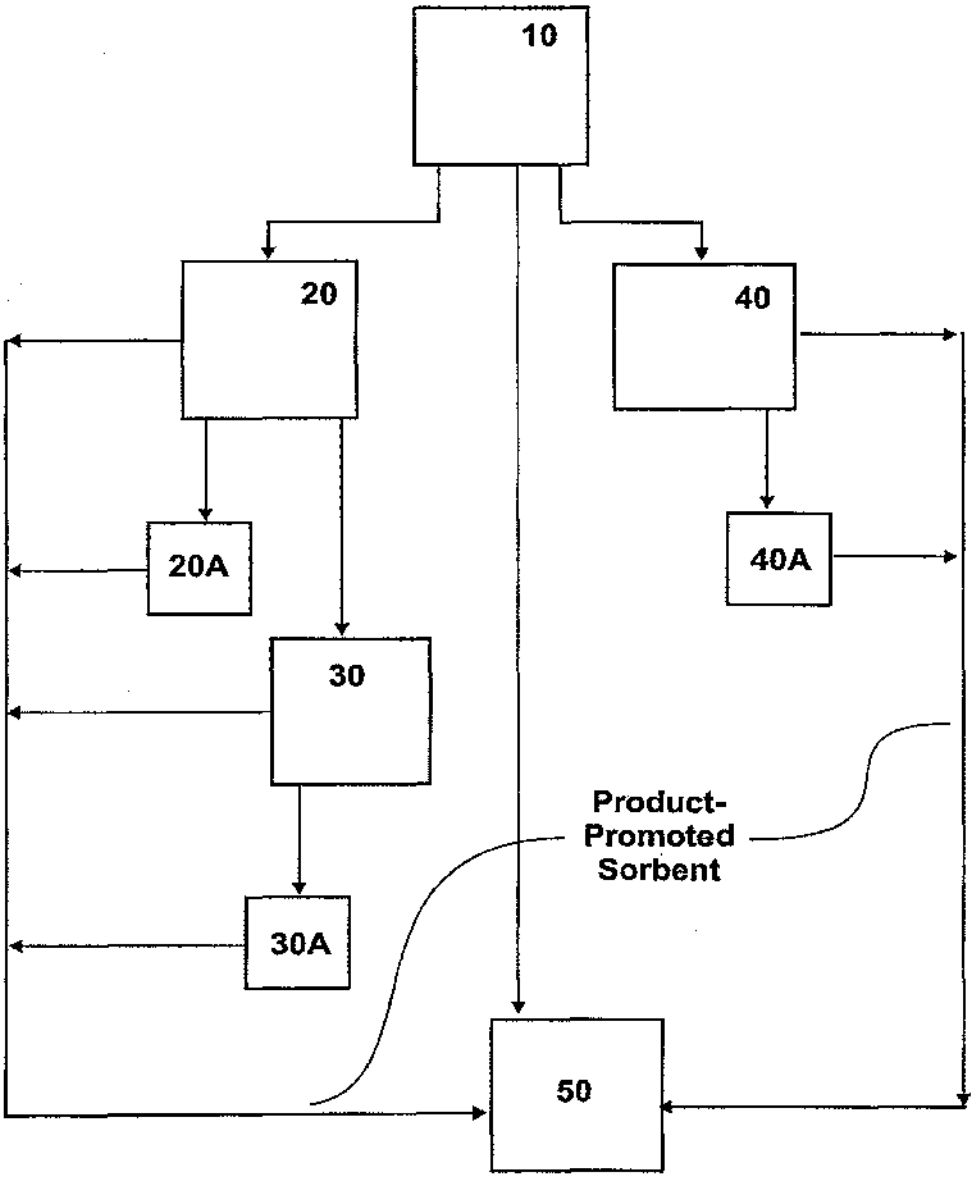


FIG. 1

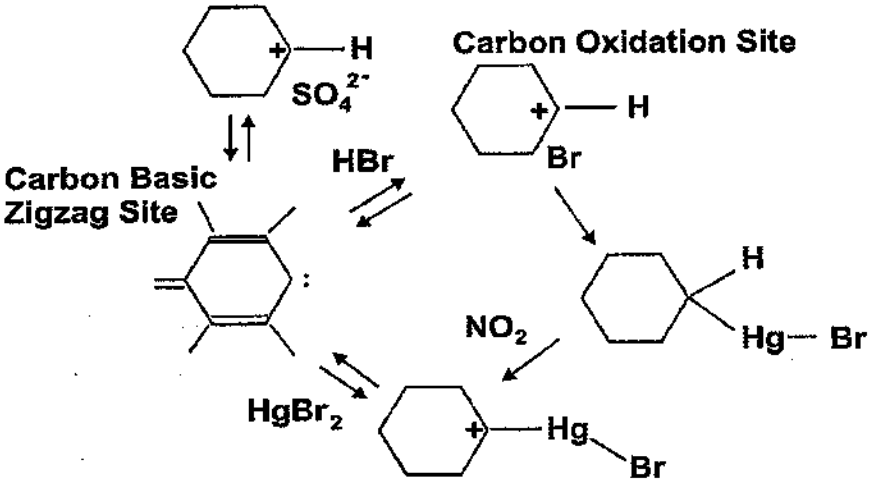

Carbon Oxidation Site
H
SO_4^{2-}
HBr
Carbon Basic
Zigzag Site
Br
H
Hg— Br
NO_2
$HgBr_2$
Hg
Br

FIG. 2

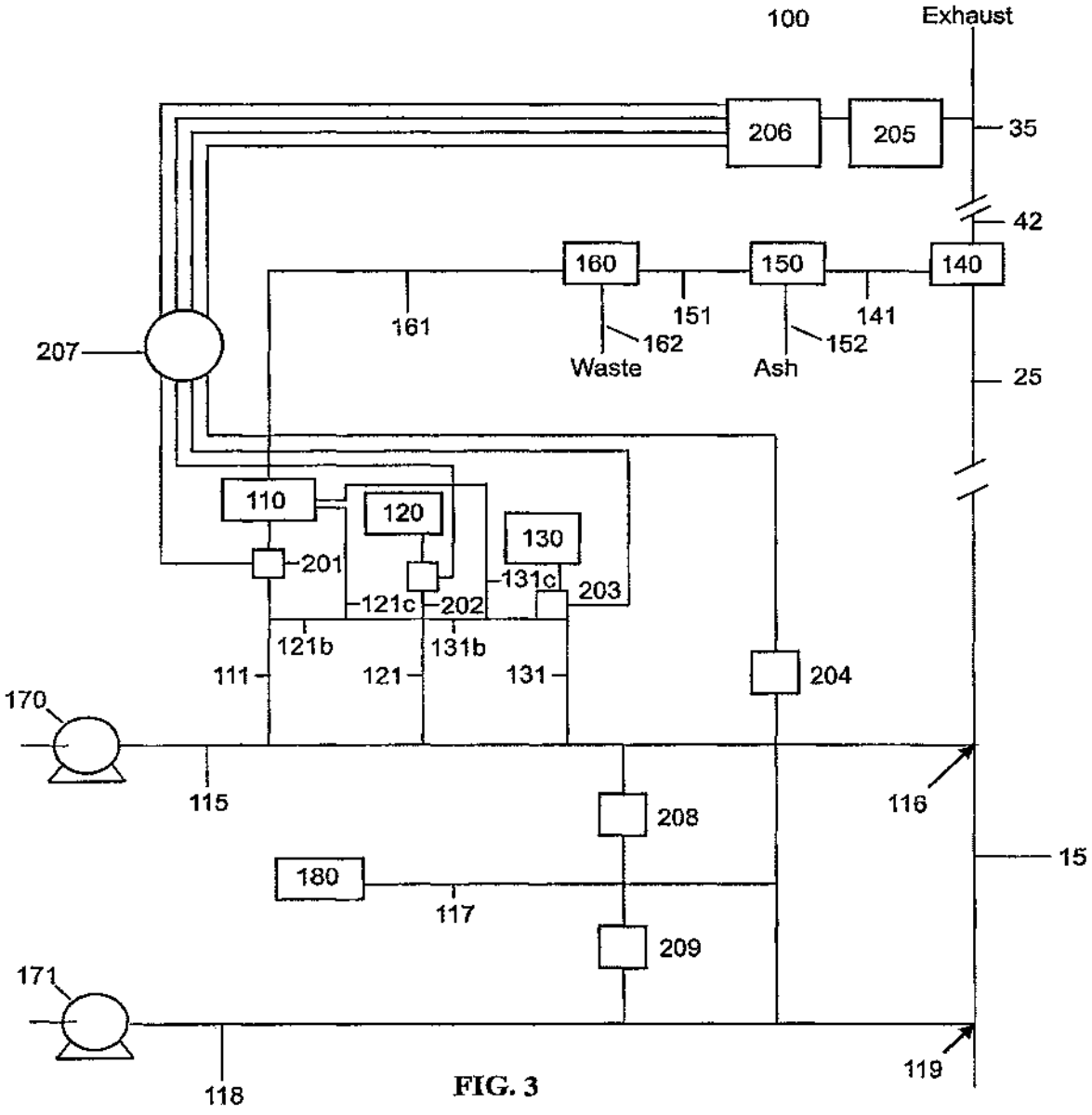

100
Exhaust
206
205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
25
110
120
130
201
131c
121c
202
203
121b
131b
111
121
131
204
170
115
116
208
15
180
117
209
171
118
119

FIG. 3

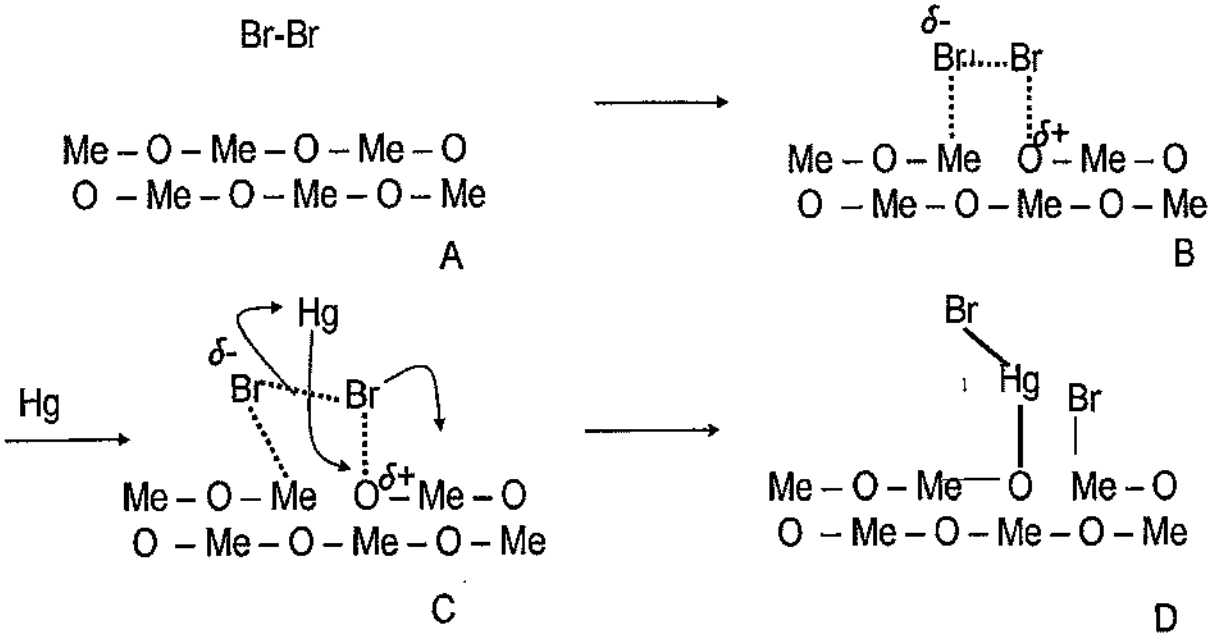

Br-Br
Me – O – Me – O – Me – O
O – Me – O – Me – O – Me
A
δ-
Br
Br
δ+
Me – O – Me
O – Me – O
O – Me – O – Me – O – Me
B
Hg
Hg
δ-
Br
Br
δ+
Me – O – Me
Me – O
O – Me – O – Me – O – Me
C
Br
Hg
Br
Me – O – Me
O
Me – O
O – Me – O – Me – O – Me
D

FIG. 4

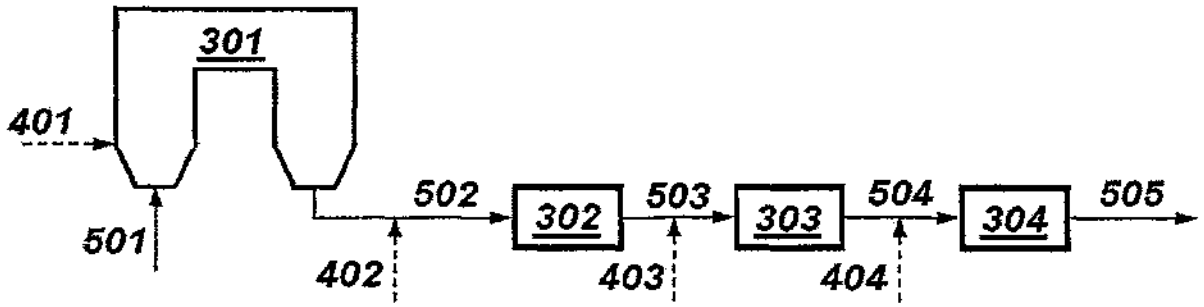

301
401
501
502
402
302
503
403
303
504
404
304
505

FIG. 5A

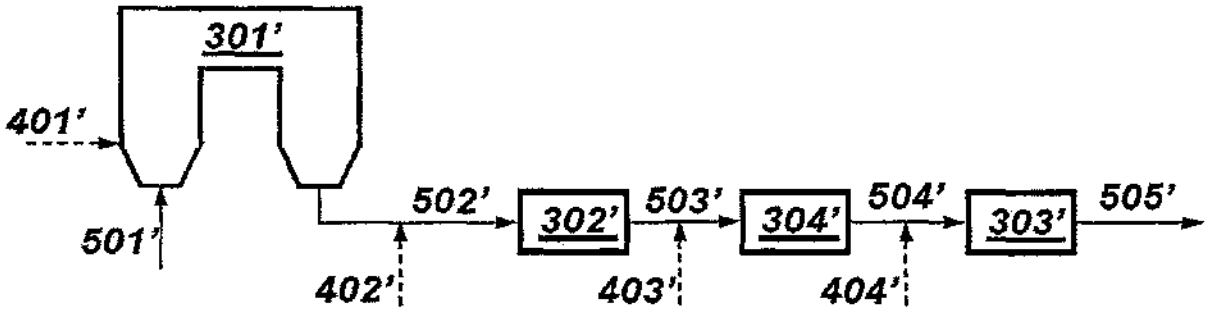

301'
401'
501'
502'
402'
302'
503'
403'
304'
504'
404'
303'
505'

FIG. 5B

Espacenet

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Sorbents for the oxidation and removal of mercury

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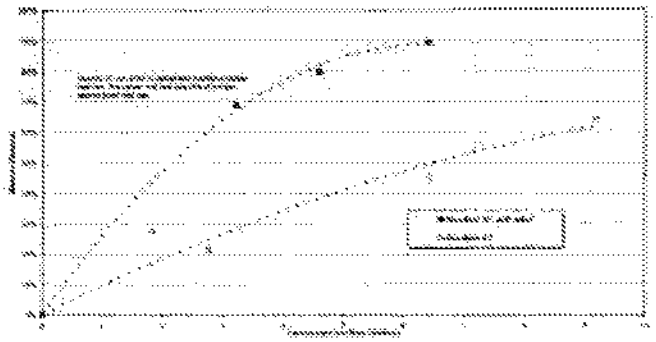
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- cooperative: **B01D53/10**; **B01D53/64**; **B01J20/20**; **B01J20/22**; B01D2253/102; B01D2257/602; Y10S95/901

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Abstract of CN101048218 (A)



A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated

gas stream are described.

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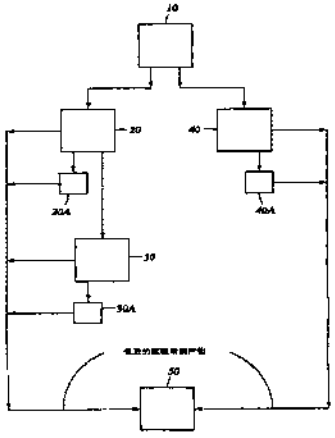
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权利要求书 6 页 说明书 32 页 附图 7 页

[54] 发明名称

用于汞的氧化及清除的吸附剂

[57] 摘要

本发明描述了一种促进的活性炭吸附剂，其用于从烟道气流中高效地清除汞。该吸附剂包括含有活性形式的卤素和卤化物的新改性的碳形式。可以加入任选的组分以提高活性和汞容量。可以将这些任选组分与吸附剂直接加入，或者将这些加入到烟道气中以提高吸附剂性能和/或汞的捕集。得到的汞清除效率超过了常规的方法。吸附剂可以再生及重新使用。还描述了吸附剂处理及制备方法。描述了动态制备、引入及控制活性吸附剂到汞污染的气流中的新方法。



1. 一种促进的碳吸附剂，其包含已与选自卤化物、卤素及其组合的促进剂反应的基体活性碳，从而使反应产物有效用于从气流中清除汞。

2. 权利要求 1 的促进的碳吸附剂，其中基体活性碳选自粉状活性碳、粒状活性碳、碳黑、碳纤维、气凝胶碳、热解炭、平均粒度大于 40 微米的活性碳及其组合，促进剂选自分子态卤素、V 族卤化物、VI 族卤化物、氢卤化物及其组合。

3. 权利要求 2 的促进的碳吸附剂，其中相对于每 100 克的基体活性碳，该吸附剂包含约 1 至约 30 克的促进剂。

4. 权利要求 3 的促进的碳吸附剂，还包括含有卤素或氢卤化物的任选的次级组分，从而提高吸附剂的活性和汞容量。

5. 权利要求 4 的促进的碳吸附剂，还包含选自碱元素、碱土元素、碱盐、碱土盐及其组合的任选的碱性组分。

6. 权利要求 4 的促进的碳吸附剂，其中成品吸附剂中任选的次级组分的浓度范围为成品吸附剂中促进剂浓度的约 1 至约 15 wt%。

7. 权利要求 6 的促进的碳吸附剂，其中任选的次级组分选自 V 族卤化物、VI 族卤化物、HI、HBr、HCl 及其组合。

8. 权利要求 7 的促进的碳吸附剂，其中任选的次级组分选自 I_2、HI 及其组合。

9. 权利要求 8 的促进的碳吸附剂，其中与基体活性碳结合时的促

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进剂基本上是蒸汽形式的。

10. 权利要求 8 的促进的碳吸附剂，其中促进剂在与基体活性碳反应之前与有机溶剂结合。

11. 权利要求 8 的促进的碳吸附剂，其中促进剂和任选的次级组分基本上同时与基体活性碳结合。

12. 权利要求 8 的促进的碳吸附剂，还包含选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5及其组合的汞稳定剂。

13. 权利要求 12 的促进的碳吸附剂，其中促进剂选自 Br_2、HBr 及其组合。

14. 权利要求 3 的促进的碳吸附剂，还包含选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5及其组合的汞稳定剂。

15. 权利要求 14 的促进的碳吸附剂，还包括含碱或碱土元素的任选的碱性组分，其中促进剂选自 Br_2、HBr 及其组合。

16. 一种方法，其包括：提供粒状的活性碳；使活性碳与选自卤素、卤化物及其组合的促进剂反应，从而使反应产物包含有效用于从气流中清除汞的促进的碳吸附剂。

17. 权利要求 16 的方法，其中相对于每 100 克的活性碳，反应产物包含约 1 至约 30 克的促进剂。

18. 权利要求 16 的方法，其中反应产物的平均粒度分布大于约 40 微米。

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19. 权利要求 16 的方法，其中促进剂选自分子态卤素、氢卤化物、V 族卤化物、VI 族卤化物及其组合。

20. 权利要求 19 的方法，其中促进剂与活性碳接触时是在气相中。

21. 权利要求 19 的方法，其中促进剂在接触活性碳时在有机溶剂中。

22. 权利要求 20 的方法，其中促进剂选自 Br_2、V 族溴化物、VI 族溴化物及其组合。

23. 权利要求 18 的方法，还包括提供任选的碱性组分以改善汞清除的有效性。

24. 权利要求 20 的方法，还包括使粒状的活性碳与包括卤素或氢卤化物的任选的次级组分进行反应，从而使吸附剂的活性和汞容量得以提高。

25. 权利要求 24 的方法，还包括提供任选的碱性组分以改善汞清除的有效性。

26. 权利要求 24 的方法，其中促进剂和任选的次级组分同时与活性碳接触。

27. 权利要求 24 的方法，其中任选的次级组分包括 I_2 或 HI。

28. 权利要求 20 的方法，还包括加入选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 及其组合的汞稳定剂。

29. 权利要求 24 的方法，还包括加入选自 S、Se、H_2S、SO_2、H_2Se、

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SeO_2、CS_2、P_2S_5及其组合的汞稳定剂。

30. 一种降低烟道气中的汞的方法，其包括：提供吸附剂，将吸附剂注入到包含汞的烟道气流中，在吸附剂上收集烟道气中超过70wt%的汞以产生清洁的烟道气，以及从清洁的烟道气中基本回收吸附剂。

31. 权利要求30的方法，还包括将任选的碱性组分共注入到含汞的烟道气流中。

32. 权利要求30的方法，还包括监测清洁的烟道气中的汞含量、使回收的吸附剂再生以及应用清洁的烟道气中的监测汞含量来控制吸附剂的注入速率。

33. 权利要求30的方法，其中通过使活性碳与促进剂在气动运输管线内反应来动态地制备注入的吸附剂，反应产物从该管线中注入到含汞的烟道气流中。

34. 权利要求33的方法，其中促进剂选自分子态卤素、卤化物及其组合。

35. 权利要求34的方法，其中促进剂选自Br_2、HBr、V族溴化物、VI族溴化物及其组合。

36. 权利要求35的方法，其中促进剂在气相中或以蒸汽形式进行反应。

37. 权利要求36的方法，其中相对于每100克的活性碳加入约1至约30克促进剂。

38. 权利要求37的方法，其中通过在气动运输管线内使活性碳、

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促进剂和任选的次级组分进行反应来动态地制备注入的吸附剂，从而提高吸附剂的活性和容量，反应产物从该管线中注入到包含汞的烟道气流中。

39. 权利要求 38 的方法，其中任选的次级组分选自碘、氢卤化物、V 族卤化物、VI 族卤化物及其组合。

40. 权利要求 39 的方法，还包括将任选的碱性组分共注入到含汞的烟道气流中。

41. 权利要求 39 的方法，其中任选的次级组分的加入量为促进剂含量的约 1 至约 15 wt%。

42. 权利要求 41 的方法，其中任选的次级组分选自 I_2、HI 及其组合。

43. 权利要求 42 的方法，其中在气相中或以蒸汽形式加入任选的次级组分。

44. 权利要求 41 的方法，还包括在吸附剂中加入选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 及其组合的汞稳定剂。

45. 权利要求 32 的方法，还包括应用清洁的烟道气中的监测汞含量来控制吸附剂的组成。

46. 权利要求 40 的方法，还包括监测清洁的烟道气中的汞含量以及应用监测的汞含量来控制吸附剂的组成和碱与吸附剂的注入比。

47. 权利要求 45 的方法，其中通过使活性碳与促进剂在气动运输管线内反应来动态地制备注入的吸附剂，反应产物从该管线注入到含

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汞的烟道气流中，其中促进剂选自分子态卤素、卤化物及其组合，其中促进剂在气相中或以蒸汽形式进行反应，其中相对于每 100 克的活性碳加入约 1 至约 30 克促进剂，其中至少部分地基于清洁的烟道气中的监测汞含量、通过数字计算机来确定促进剂的加入速率和吸附剂的注入速率。

48. 一种降低气流中的汞含量的方法，其包括以下步骤：将质均粒度>40 μ m 的粉状活性碳吸附剂注入到包含汞及灰分粒子的气流中，从气流中将汞捕集于吸附剂粒子上，将吸附剂粒子与灰分粒子机械分离开，以及将分离的吸附剂粒子再注入到气流中。

49. 权利要求 48 的方法，还包括使吸附剂粒子再生，从而从中基本清除污染物以恢复汞捕集的容量。

50. 权利要求 48 的方法，还包括将选自碱元素、碱土元素、碱盐、碱土盐及其组合的碱性组分共注入到气流中。

51. 权利要求 48 的方法，其中粉状活性碳吸附剂还包含选自卤化物、卤素及其组合的促进剂。

52. 权利要求 51 的方法，还包括将选自碱元素、碱土元素、碱盐、碱土盐及其组合的碱性组分共注入到气流中。

53. 权利要求 48 的方法，其中微粒活性碳吸附剂具有的质均粒度>60 μ m。

54. 权利要求 52 的方法，其中微粒活性碳吸附剂具有的质均粒度>60 μ m。

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用于汞的氧化及清除的吸附剂

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发明背景

发明技术领域

本发明涉及用于从气化系统的产物气或者烟道气中清除污染物的方法及材料。具体而言，本发明涉及通过高活性的可再生吸附剂从化石燃料的燃烧或气化期间产生的气流中清除汞。

发明背景

诸如煤炭的化石燃料的燃烧和气化能产生包含源自于燃料的汞及其它痕量元素的烟道气。必须通过使用吸附剂、涤气器、过滤器、沉降器以及其它清除技术来控制汞(和其它污染物)向环境中的排放。在燃烧和气化期间汞最初以元素态的形式存在。在诸如燃烧系统的管道及烟道的下游工艺部分中，一些元素态的汞被氧化。被氧化的量取决于烟道气中酸性气体的存在量以及其它的因素。汞的量随燃料不同而变化，但煤炭燃烧的烟道气流中汞的浓度通常为每十亿份中低于 5 份(ppb)。诸如电力设施的大型煤炭燃烧设备每天可能排出一磅的汞或更多。汞清除的应用领域包括但不限于煤炭(或其它化石燃料)燃烧中的烟道气、废物焚烧、气化中的产物气以及矿物加工、金属提炼、干馏、水泥制造、氯碱工厂、牙科设施和火化场中的尾气。

汞吸附剂技术

已经研究了几种类型的用于烟道气中汞的控制方法，包括将细吸附剂粒子注入到烟道气管道内，并使烟道气通过吸附剂床。细粒子注

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入吸附剂包括活性碳、金属氧化物吸附剂、硫化钠粒子和碱性硅酸盐或氧化物吸附剂。当采用粒子注入时，在袋滤室或静电沉降器(ESP)中将捕集到吸附剂粒子上的汞从气流中清除并与灰分微粒一起收集起来。硫化物和碱性硅酸盐及氧化物粒子仅对氧化态的汞是有效的，且与碳粒子相比，金属氧化物吸附剂显示出降低的捕集动力学性能。此外，将细碳粒子注入到烟道气流内来清除汞，尤其是清除元素态的汞，仅仅是部分成功，在使用 FF(织物过滤器)以收集碳和灰分的某些应用中，仅仅达到约 60%的有效清除。当使用 ESP 来收集碳时，因为碳与气体的接触时间非常短，观察到得到甚至更低的清除比率。

现有的碳注入系统的主要问题是，吸附剂初始为非活性的，只有在烟道气中长时间地暴露以后吸附剂才能具备有效的适应性，并提供对气体中汞的增强活性。因此，为了有效地捕集汞，必须以较大的量、较高的吸附剂/汞比例使用这些吸附剂。这些吸附剂往往相对昂贵，不易从灰分中分离出来以再生及重新使用。灰分中碳的收集也造成了固体废物处理的问题，用过的吸附剂可能污染收集的灰分，妨碍其在各种应用当中的用途。

因此，需要有一种更加经济和有效的汞清除技术。本发明提供包含汞的污染物的成本有效清除方法，其使用吸附剂增强添加剂和/或高活性吸附剂，接触时间为若干秒(或更短)，且可以再生及重新使用。

发明概述

因此，本发明的目的是克服现有技术的不足，从而提供新的和经济的方法，用于在利用化石燃料而产生的气体中清除汞。

本发明描述了一种卤素/卤化物促进的活性碳吸附剂，其用于高效地从烟道气流中清除汞。该吸附剂含有新的卤化物改性碳形式，其包含由溴(或卤化物或其它卤素)与碳反应生成的活性化合物。可以加入任选的次级组分和碱以进一步提高活性及汞容量。得到的汞清除效率超

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过或相当于常规的方法，还具有附加的益处例如成本降低。任选地，可以再生及重新使用吸附剂。还描述了吸附剂处理和/或制备方法。描述了活性吸附剂的动态(in-flight)制备、引入到汞污染的气流中以及控制的新方法。

在一些实施方案中提供了促进的碳吸附剂，其包含已经与选自卤化物、卤素及其组合的促进剂反应的基体活性碳，从而使反应产物可有效用于从气流中清除汞。

在一个实施方案中提供了促进的碳吸附剂，其中基体活性碳选自粉状活性碳、粒状活性碳、碳黑、碳纤维、气凝胶碳、热解炭、平均粒度大于所产生的飞灰的活性碳(从而可以从中物理地分离出来) 以及它们的组合。促进剂选自分子态卤素、第 V 族(全部采用 CAS 术语)卤化物、第 VI 族卤化物、氢卤化物以及它们的组合。在一个实施方案中，基体活性碳可以具有这样的质均粒径，使得可以基本上通过物理方法将其从气流中夹带的含有欲清除的汞的灰分中分离出来。在一个实施方案中，基体活性碳可以具有大于约 40 微米的质均粒径。

在另一个实施方案中，对于每 100 克的基体活性碳而言，吸附剂包含约 1 至约 30 克的促进剂。另一实施方案中还包含任选的包括卤素或氢卤化物的次级组分，从而提高吸附剂的活性和汞容量。

在另一个实施方案中，成品吸附剂中任选次级组分的浓度范围在成品吸附剂中促进剂浓度的约 1 至约 15 wt%以内。

在另一个实施方案中，优选可以加入任选的碱性组分以通过该碱与初级吸附剂的组合提供协同效应。

在另一个实施方案中，任选的次级组分选自 V 族卤化物、VI 族卤化物、HI、HBr、HCl 以及它们的组合。在另一个实施方案中，与基体

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活性碳结合时的促进剂基本上是蒸汽形式的。在另一个实施方案中，促进剂在与基体活性碳反应之前与有机溶剂结合。在另一个实施方案中，促进剂和任选的次级组分基本上同时与基体活性碳结合。另一个实施方案中还包括加入选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 以及它们的组合的汞稳定剂。另一个实施方案中还包括加入任选的碱性组分。

在一个实施方案中提供了一种方法，其包括：提供粒状的活性碳；使活性碳与选自卤素、卤化物以及它们的组合的促进剂反应，使反应产物包含能从气流中有效清除汞的促进的碳吸附剂。在进一步的实施方案中，相对于每 100 克活性碳，反应产物中包含约 1 至约 30 克促进剂。在另一个实施方案中，反应产物具有的平均粒度分布大于欲清除汞的气流中夹带的灰分粒子的平均尺寸，从而使得可以通过物理方法将反应产物从夹带的灰分粒子中基本移出。在另一个实施方案中，反应产物具有大于约 40 微米的质均粒径。

在另一个实施方案中，促进剂选自分子态卤素、氢卤化物、V 族卤化物、VI 族卤化物以及它们的组合。在另一个实施方案中，促进剂在接触活性碳时是在气相中。在另一个实施方案中，促进剂在接触活性碳时在有机溶剂中。

在另一个实施方案中，促进剂选自 Br_2、V 族溴化物、VI 族溴化物以及它们的组合。

在另一个实施方案中，所述方法还包括使粒状的活性碳与任选的次级组分进行反应，所述次级组分包括卤素或氢卤化物，从而使吸附剂的活性和汞容量得以增加。在另一个实施方案中，促进剂和任选的次级组分同时与活性碳接触。在另一个实施方案中，所述方法还包括加入选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 以及它们的组合的汞稳定剂。在一个实施方案中提供了一种以较低的清除速率控制烟

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道气中汞的方法，所述方法对吸附剂的要求充分的低。通过吸附剂活性的增强，每克吸附剂的汞清除量也增加，因此，通过降低对吸附剂的要求可以降低投资和操作成本。

在一个实施方案中提供了一种减少烟道气中的汞的方法，所述方法包括提供吸附剂、将吸附剂注入到包含汞的烟道气流内、在吸附剂上收集超过 70 wt%的烟道气中的汞以产生清洁的烟道气以及从清洁的烟道气中基本回收吸附剂。在期望汞的清除低于 70 wt%的实施方案中，优选可以通过使用低于采用标准(非增强的)碳时所需碳量的一半的碳来达到所需的清除 。在进一步的实施方案中，所述方法还包括监测清洁的烟道气中的汞含量、使回收的吸附剂再生及应用监测的清洁的烟道气中的汞含量来控制吸附剂的注入速率。在另一个实施方案中，通过使活性碳与促进剂在气动的运输管线内反应来动态地制备注入的吸附剂，反应产物从该管线中注入到包含汞的烟道气流内。

在另一个实施方案中，促进剂选自分子态卤素、卤化物以及它们的组合。在另一个实施方案中，促进剂在气相中或以蒸汽形式进行反应。在另一个实施方案中，相对于每 100 克的活性碳加入约 1 至约 30 克促进剂。

在另一个实施方案中，通过在气动的运输管线内使活性碳、促进剂和任选的次级组分进行反应来动态地制备注入的吸附剂，从而增加吸附剂的活性和容量，反应产物从该管线中注入到包含汞的烟道气流内。

在另一个实施方案中，任选的次级组分选自碘、氢卤化物、V 族卤化物、VI 族卤化物以及它们的组合。在另一个实施方案中，任选的次级组分的加入量为促进剂含量的约 1 至约 15 wt%。在另一个实施方案中，所述方法还包括在吸附剂中加入选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 以及它们的组合的汞稳定剂。

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在一个实施方案中，所述方法还包括共注入任选的包括但不限于碱和碱土组分的碱性物质，从而通过捕集被氧化的汞和/或捕集可能会降低吸附剂容量的气态组分来改善汞捕集效率。在另一个实施方案中，任选的碱性物质优选可以包括氧化钙、碳酸钠等等，如在本领域中已知的那些。

在另一个实施方案中，所述方法还包括应用监测的清洁的烟道气中的汞含量来控制吸附剂的组成。在另一个实施方案中，通过使活性碳与促进剂在气动的运输管线内反应来动态地制备注入的吸附剂，反应产物从该管线中注入到包含汞的烟道气流内，其中促进剂选自分子态卤素、卤化物以及它们的组合，其中促进剂在气相中反应或以蒸汽形式进行反应，其中相对于每 100 克的活性碳加入约 1 至约 30 克促进剂，其中至少部分地基于清洁的烟道气中的监测汞含量，通过数字计算机来确定促进剂的加入速率和吸附剂注入速率。

在一个实施方案中，提供了减少包含汞及灰分的气流中的汞含量的方法，其中将质均尺寸大于 40 μm 的微粒活性碳吸附剂注入到气流中，通过吸附剂粒子从气体中清除汞，基于尺寸大小使吸附剂粒子与灰分粒子分离，将吸附剂粒子再注入到气流中。在另一个实施方案中，使包含汞的吸附剂粒子再生，从而清除一些或基本上所有的汞。在另一个实施方案中，将碱性组分共注入到气流中。在另一个实施方案中，吸附剂可以还包含促进剂。促进剂优选可以包含卤化物、卤素，或包含它们二者。

如以下将更详细描述的那样，本发明从而提供了优于以前已知技术的若干优点，包括对流出气体显著更有效及经济性的汞吸附剂，可以有利地适用于燃烧设备及气化系统的气流处理。

为了可以更好地理解随后对本发明的详细描述，前述内容已经相

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当广泛地概括了本发明的特点和技术优势。以下将描述本发明另外的特点及优势，其构成本发明的权利要求的主题。本领域技术人员应该理解的是，可以很容易地利用所公开的概念和具体实施方案为基础，修改或设计出其它的结构以实现与本发明相同的目的。本领域技术人员还应该意识到，这种等价的构造并不偏离随附的权利要求中限定的本发明的实质和范围。

附图说明

本发明优选实施方案的更详细描述可参考所给出的附图。

图 1 示意性地例示根据本发明的促进的碳吸附剂的制备方法。

图 2 例示了提出的导致汞氧化及捕集的化学反应的机理模型。

图 3 示意性地例示根据本发明的促进的碳吸附剂的制备以及降低气化系统的产物气和/或烟道气中的烟道气汞的方法，包括促进的碳吸附剂的动态制备。

图 4 为例示 5 wt/wt %溴化 NORIT Darco FGD 吸附剂(37 mg+113 mg 砂) 在低-HCl (1 ppm) 合成烟道气中的穿透曲线的图示。

图 5 为例示非卤化 NORIT Darco FGD 吸附剂(37 mg+113 mg 砂) 在低-HCl (1 ppm) 合成烟道气中的穿透曲线的图示。

图 6 为例示中试规模汞清除结果的条形图表，包括大尺寸吸附剂的结果。

图 7 为例示对于 ESP 和织物过滤器而言的吸附剂尺寸和注入速率对汞清除的影响的图示。

图 8 为例示具有惰性砂的溴化 NORIT Darco FGD 吸附剂的穿透曲线的图示。

图 9 为例示具有共注入碱性物质的溴化 NORIT Darco FGD 吸附剂的穿透曲线的图示。

图 10 为具有和不具有共注入的碱性物质时的汞清除对碳注入速率的图示。

优选实施方案的详细描述

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此处将详细描述本发明具体的优选实施方案，须理解的是，应该认为此处的公开内容为本发明原理的例证，并不意味着将本发明限制在此处例示和描述的内容上。本发明容许不同形式或次序的优选实施方案，不应该认为限制在具体表述的方法或本文所包含的组分上。特别而言，本发明各种优选的实施方案提供了本发明方法、成分以及它们的用途的许多不同构造和应用。

本发明提供利用异常活性的卤素/卤化物促进的碳吸附剂来捕集污染物的成本有效的方法，所述吸附剂使用溴化物(或其它卤素/卤化物)处理的碳，其在若干秒或更短的接触时间内通过汞-吸附剂表面反应来捕集汞。与常规的活性碳吸附剂不同，该吸附剂不需要在气流中的原位活化以达到较高的活性（没有诱导期）。吸附剂对污染物的活性大大增加，可以恢复吸附容量， 可以再生、再循环和/或重新使用促进的吸附剂。

除了对于燃烧系统的烟道气之外，此处讨论的处理的碳、处理技术以及任选的添加剂对于产物气或排出气或者气化系统、合成气发生炉的气体以及其它含汞气流中的汞控制也具有适用性。因此，应该理解的是，本说明书中全文中使用的术语燃烧系统和烟道气可同样地应用于气化系统以及合成气或燃料气，如本领域的技术人员将会理解的那样。

现在参考图 1，显示的是例示本发明方法的一些优选实施方案的方框流程图，用来制备用于从气化系统流的产物气和/或烟道气中捕集汞的促进的吸附剂。在一个由路径 10-20 例示的优选实施方案中，方框 10 例示的是提供基体活性碳，方框 20 例示的是加入与碳反应的卤素或卤化物促进剂，以生成产物促进的碳吸附剂。在以例如蒸汽的形式加入卤素或卤化物的实施方案中，可不需要有另外的步骤。在以例如溶剂的形式加入卤素或卤化物的实施方案中，则可以期望采用如方框 20A 例示的溶剂清除。

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仍然参考图 1，路径 10-20-30 例示了本发明方法的另一个优选的实施方案，包括如方框 10 表示的提供基体活性碳、方框 20 例示的加入与碳反应的卤素或卤化物促进剂以及方框 30 例示的加入与方框 20 的产物反应的次级组分，以生成产物促进的碳吸附剂。在卤素或卤化物促进剂以及次级组分均以例如蒸汽形式加入的实施方案中，可以无需另外的步骤。在以例如溶剂的形式加入卤素或卤化物促进剂和/或次级组分的实施方案中，则可以期望采用如方框 30A 例示的溶剂清除。

仍然参考图 1，路径 10-40 例示了本发明方法的另一个优选的实施方案，其包括如方框 10 表示的提供基体活性碳、方框 40 例示的将卤素或卤化物促进剂以及次级组分一道加入至与之反应的活性碳中，生成产物促进的碳吸附剂。如上所述，在采用蒸汽加入至活性碳的实施方案中，可以无需另外的步骤。在以溶剂形式加入一种或多种组分的实施方案中，则可以需要提供如方框 40A 例示的溶剂清除步骤。

仍然参考图 1，其还例示了优选实施方案，其中如方框 50 所例示，采用如上所述制备的产物促进的碳吸附剂来处理烟道气流。

本领域技术人员可以理解的是，在一些优选的实施方案中，所提供的活性碳优选可以为若干类型中的任何种类。例如，活性碳可以包括粉状活性碳、粒状活性碳、碳黑、碳纤维、碳蜂窝或板状结构碳、气凝胶碳薄膜、热解炭、源于产物促进的碳吸附剂的再生活性碳或本领域中已知的其它类型。

本领域技术人员可以理解的是，在一些优选的实施方案中，所提供的活性碳优选可以为若干类型中的任何种类。例如，活性碳可以包括粉状活性碳、粒状活性碳、碳黑、碳纤维、碳蜂窝或板状结构碳、气凝胶碳薄膜、热解炭、质均粒度大于欲处理烟道气流中的飞灰的活性碳或再生活性碳。

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本领域技术人员可以理解的是，在一些优选的实施方案中，所提供的活性碳优选可以为若干类型中的任何种类。例如，活性碳可以包括粉状活性碳、粒状活性碳、碳黑、碳纤维、碳蜂窝或板状结构碳、气凝胶碳薄膜、热解炭、活性碳或再生活性碳，所述活性碳或再生活性碳的质均粒径优选大于 40 微米，更优选大于 60 微米，或者粒度分布比欲处理的烟道气流中的飞灰或夹带灰分更大，从而使得可以通过物理方法来分离活性碳和灰分。

作为例示而非限制，在一些优选的实施方案中，加入到基体活性碳中并与之反应的卤素或卤化物促进剂优选可以包括：蒸汽或气体形式的分子态卤素；在有机溶剂中的分子态卤素；蒸汽、液体或溶液形式(但不在含水溶剂中)的 V 族或 VI 族卤化物，例如分别是 PBr_3 或 SCl_2。

还提供了这样的实施方案，其中有机溶剂优选可以包括氯代烃如二氯甲烷，例如包括石油醚、轻石油、戊烷、己烷、甲苯和苯的烃溶剂，二硫化碳，废弃溶剂，醚，再循环溶剂，超临界溶剂如超临界 CO_2，水(但不是在 V 族或 VI 族卤化物的情况下)，以及对于本领域的技术人员显而易见的其它溶剂。

现在参考图 2，其例示了由科学性的论据导出的理论，用以解释促进性化合物的性质。例如，如图 2 所例示，溴化氢与活性碳的不饱和结构发生反应。仅作为例示而言，这可以是位于碳的石墨烯(graphene)片层结构的边缘上的碳烯物质。分子态溴或溴化合物的反应可形成类似的结构，带有对汞的氧化具有活性的正碳，随后被吸附剂所捕集。

现在已经发现，与碳形成新的溴化合物增大了它们对于汞和其它污染物的活性。另外，所得到的溴化合物对于促进汞的氧化具有独特的适用性。氧化的有效性显然是源于卤化物对氧化期间在汞上逐渐发展的正电荷产生的促进效果，这在化学领域中被认为是特定催化效应。

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因此，当汞的电子被拉向正碳时，卤化物阴离子的电子则从另一侧推进，使在汞上逐渐发展的正电荷稳定化，降低氧化过程所需的能量。溴化物是特别有活性的，这是由于其离子的外层 4p 轨道上的可高度极化的电子的缘故。因此，在碳上加入 HBr 或 Br_2 形成类似的碳溴化物，其中正碳在溴离子的协助下将汞氧化。

现在参考图 3，提供了汞控制系统 100 的示意流程图，依照本发明优选的实施方案，其包括制备促进的碳吸附剂和降低烟道气中的汞。提供了基体活性碳储槽 110、任选的卤素/卤化物促进剂储槽 120、任选的次级组分储槽 130 和任选的碱性组分储槽 180，它们的每一个都带有各自相应的流动控制装置 201、202、203 和 208/209。对于任选的碱性组分储槽 180，可以独立地使用任选的流动控制装置 208 和 209，或一起使用它们，或者不使用它们。

储槽 110、120、130 和 180 通过它们各自的流动控制装置经由相关的管道连接至运输管线 115。任选的碱性组分储槽 180 也可以通过各自的流动控制装置经由相关的管道连接至运输管线 118。通过气体源 170 将空气、氮或其它运输气体源提供至运输管线 115，使之夹带从储槽 110、120、130 和 180 中排出的物料，并经由注入点 116 将这种物料注入到污染的烟道气流 15 之内。可以通过气体源 171 将空气、氮或其它运输气体源提供至运输管线 118，使之夹带从储槽 180 中排出的物料，并经由注入点 119 将这种物料注入到烟道气流 15 之内。根据需要，气体源 170 和 171 可以相同或不同。或者，可以通过气体源 170 将运输气体提供至运输管线 115 和 118 两者(从源 170 至管线 118 的连接未示出)。虽然在图 3 中显示的气体源 170 和 171 为压气机或鼓风机，但本领域的技术人员将会意识到，本领域中已知的任何运输能量源都是可以接受的。

为清楚起见，在图 3 中显示了单一注入点 116 或 119，本领域的技术人员可以理解的是，多重注入点也在本发明的范围之内。光密度

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测量装置 204 连接至运输管线 115 和/或 118，从而提供代表运输管线 115 和/或 118 内部的光密度的信号，其为时间的函数。

注入点 116 和 119 的下游提供了微粒分离器 140。以说明而非限制性的方式，微粒分离器 140 可以包括一种或多种织物过滤器、一种或多种静电沉降器(以下称“ESP”)或本领域中已知的其它微粒清除装置。还应该指出的是，可以存在顺序配置或并列配置的一个以上微粒分离器 140，当存在并列配置、顺序配置或它们的组合配置时，注入点 116 和 119 可以在 140 的上游和/或下游的位置。微粒分离器 140 至少产生主导性的气态(“清洁”) 流 142 和包含分离的固体物质的流 141。吸附剂/灰分分离器 150 将流 141 分离成大体为灰分的流 152 和大体为吸附剂的流 151。然后优选可以使流 151 通过任选的吸附剂再生器 160，其产生再生吸附剂流 161 和废物流 162。

在废气流 35 中提供任选的汞连续排放监测器(以下称“CEM”) 205，用以提供代表废气流 35 中汞浓度的电信号，其为时间的函数。任选的汞 CEM205 与流动控制器 201、202、203、208 和 209 经由任选的线路 207(或无线地)电连接至任选的数字计算机(或控制器) 206，其接收和处理信号，并优选控制促进的碳吸附剂的制备及其向污染的烟道气流 15 内的注入。

在操作中，将促进的碳吸附剂和/或任选的碱性组分注入到污染的烟道气流 15 内。在注入的物质与污染的烟道气流 15 接触以后，注入的物质使汞的浓度降低，将污染的烟道气转变为汞降低的烟道气 25。通过分离器 140 从烟道气 25 中清除注入的物质，分别地将其处理掉或通过任选的分离器 150 进行进一步的分离，再处理掉或通过任选的再生器 160 进行再生。然后，汞降低的“清洁”烟道气流 142 中采用任选的 CEM205 监测汞含量，其向任选的计算机/控制器 206 提供相应的信号。然后，依照本领域中熟知的控制算法，使来自 206 中的逻辑及最优化信号调节流动控制器 201、202、203、208、209，从而保持废气

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流 35 中汞浓度在期望的限度以内。流动控制器 201、202、203、208、209 也可以是手动调节的或某些其它的自动化装置，从而依照本领域中熟知的控制算法以保持废气流 35 中汞浓度在期望的限度以内。

仍然参考图 3，例示了依照本发明的促进的碳吸附剂和/或碱性组分的制备及注入的若干优选的实施方案。流 111 提供从储槽 110 的基体活性碳的引入，这通过流动控制器 201 手动地或者在计算机 206 的指令下进行计量。根据任何所提供的若干方法，可以使卤素/卤化物和基体活性碳结合并与之进行反应。卤素/卤化物优选可以经由管线 121 直接结合到运输管线 115 内，在其内于注入点 116 之前和基体活性碳接触并与之反应。依照本发明，该选择为本文所指的促进的碳吸附剂的“动态”制备的一种形式。进一步地，卤素/卤化物在进入运输管线 115 之前可以经由管线 121b 与基体活性碳结合。更进一步地，卤素/卤化物可以通过经由管线 121c 引入到储槽 110 内而和基体活性碳接触并与之反应。当例如储槽 110 包括基体活性碳的沸腾床或流化床时，卤素/卤化物在其中以气体的形式或作为蒸汽流动，该选择是优选采用的。当然，如前面讨论到的那样，卤素/卤化物也可以优选以液体的形式或在溶剂中与基体活性碳接触，然后，如果需要的话，如参考图 1 所讨论的实施方案所提到的那样，可以提供溶剂清除(图 3 中未示出)。

类似地，任选的次级组分可以经由管线 131、或任选地如上面所描述的卤素/卤化物那样经由管线 131b 和 131c 而直接在运输管线 115 中接触与反应。

类似地，180 中任选的碱性组分既可以直接加入到运输管线 115 中，或者也可以通过运输管线 118 单独地注入，在下游结合到烟道气 15 中，与基体活性碳、促进的碳或任选的次级组分产生协同效应。能够相对于基体活性碳、促进的碳或任选的次级组分而原位地改变任选的碱性组分的量，这是克服位置特异性操作及烟道气条件并优化之的一个关键性特征。

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在一些其中组分之间的接触及反应是在液体或溶剂相中进行的优选实施方案中，可以提供对这种液体和/或浆料混合物的搅拌。在其它的实施方案中，优选可以溶液的形式将卤素/卤化物促进剂和任选的次级组分喷射到基体活性碳之内或之上。在一些这样的实施方案中，然后可以提供干燥、过滤、离心、沉降、倾析或本领域中已知的其它溶剂清除方法。

在其中卤素/卤化物促进剂为气体或蒸汽形式的实施方案中，可视情况将其在空气、氮或其它气体中进行稀释。可以使例如气态 HBr 或 Br_2 的卤化物/卤素气体通过粒状或纤维状活性碳的沸腾床或流化床，经由气体夹带将如此生成的促进的碳吸附剂从床的顶部移走，用于注入。

在一些实施方案中，次级组分优选可以包括碘或其它卤素，氢卤化物，包括但不限于 HI、HBr、HCl，V 族或 VI 族元素与分子态卤素，例如 SCl_2 及其它。在一些优选的实施方案中，相对于每 100 g 基体活性碳，促进的碳吸附剂可以包含约 1 至约 30 g 的卤素/卤化物。在一些优选的实施方案中，促进的碳吸附剂可以包含次级组分，其浓度为卤素/卤化物组分浓度的约 1 至约 15 wt%。

还在其它的实施方案中，可以将产物促进的碳吸附剂施加到基材上。在其它的实施方案中，为了达到降低汞的目的，可以使这样制备的基材与污染的烟道气或气化系统的产物气流接触。这样的基材可以是单片的(monolithic)、旋转的，或者以本领域技术人员已知的任何方式暴露于气流中。

在一些实施方案中，提供了这样的方法，其中汞稳定剂加入到促进的碳吸附剂中，从而产生双功能吸附剂。可以在卤素/卤化物的加入及反应之前或之后顺序地加入这种稳定剂。在一些优选的实施方案中，卤素/卤化物优选包括 Br 或 HBr，汞-稳定剂可以包括 S、Se、H_2S、SO_2、

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H_2Se、SeO_2、CS_2、P_2S_5以及它们的组合。

汞的捕集中的卤素

在使用卤素来处理烟道气的方法学上已经产生一些问题，这是由于它们对其它气体及金属具有的活性，导致腐蚀及健康方面的问题。“卤素”定义为一系列的非常活跃的元素，包括周期表中的 VIIA 族(通篇使用 CAS 命名；VIIA 族(CAS)对应于 VIIB 族(IUPAC))。分子态元素形式的卤素，包括 F_2、Cl_2、Br_2和 I_2，其与热烟道气组分的反应后，几乎没有剩余可与元素汞反应。原子态元素的卤素形式包括氟、氯、溴和碘原子，其对汞的反应活性要大出约一百万倍，但原子态形式的浓度通常是极低的。在大部分的电业煤炭燃烧设施中，其浓度通常不足以使显著量的汞被氧化。

此处采用的术语“卤化物”定义为由卤素与另一种元素或基团反应形成的化合物。一般地，卤化物比起分子态卤素来讲活性要低得多，具有较低的化学势。卤化物被认为是不能单独氧化其它化合物的还原态形式。因此在传统的观点当中，卤化物-盐-处理的活性碳不能有效地将元素态的汞氧化及捕集元素态的汞。

卤素促进的吸附剂特性

这里描述的吸附剂对于汞的氧化具有非常高的初始活性，因此使用非常少的量就可以得到非常高的捕集效率，从而降低操作成本，减少废物处理的问题。此外，对采用本发明技术生成的吸附剂进行再生及重新使用可以获得进一步的处理减少。汞与本发明的促进的碳吸附剂在烟道气导管中顺利地相互作用以及随后汞在吸附剂和灰分上的收集所需的时间间隔非常短，不到几秒钟。很显然，这样的收集时间需要吸附剂对汞既具有高容量又具有高活性。可以非常细的粉末形式利用促进的碳吸附剂，从而使传质限制最小化。但此外，活性应该非常之高，从而捕集细粒子所遇到的所有的汞。另外，采用这些增强技术可以容许得到对更大吸附剂粒子而言的有效捕集，而更大的吸附剂粒

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子使得吸附剂能从灰分中分离，从而能够进行随后的再生以及灰分的利用。本发明的一个特点在于制备含有在碳结构上形成的卤化物的吸附剂的方法，其提供与汞污染的气流初始接触时具有高度活性的吸附剂，这使得能非常有效地捕集汞。

看起来本发明的吸附剂用活性碳(边缘位置)例如从溶液中与分子态溴化学地结合。X 射线光电子能谱法已经确定，溴、氯、HBr 或 HCl 的加入在碳结构中形成了化学的化合物。因此，由卤素和活性碳生成的吸附剂不再是分子态卤素的形式，而是一种新的化学改性的碳(或卤化碳)结构。除卤化物离子外，在低活性的碘中可能不出现这种现象，其中 I_2 分子络合物可能存在于碳基面上。在溴的情况下，改性的阳离子碳具有使汞氧化的高化学势。因此而给出了溴处理的碳对汞的活性的全新模型。优选可以通过加入溴、溴化氢或如本文中描述的溴与其它元素的组合来产生活性的碳形式。卤素处理产生具有更高活性的碳，因为卤化物(特别是溴化物和碘化物)阴离子通过使在氧化的过渡态中汞上逐渐发展的正电荷稳定化而有效地促进氧化。基于该模型而产生若干创新、价廉、活性增强的特点。

任选的次级组分

已经证实，除了溴以外任选的次级组分的加入导致吸附剂活性和容量的改善，通常超过了未处理的碳和溴化的碳。次级化合物或者包括次级卤素，或者包括次级卤素衍生的化合物，例如 HI。因此，除了存在具有活性的碳形式外，次级组分产生 Lewis 碱，其具有更强的能力以使在汞上逐渐发展的正电荷稳定化。因此，次级组分为具有更大程度极化电子(4p 和 5p)的元素。

任选的碱性组分

已经证实，在基体活性碳或促进的活性碳中加入任选的碱性组分可以导致汞捕集的改善，通常要超过未处理的碳和促进的碳。测试数据表明，烟道气污染物、烟道气成分(SO_2、NO_x、HCl 等)、操作温度、

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汞的形式以及汞的浓度可以影响到碱加入的有效性。这就暗示需要能够原位地调节及定制碱与活性碳的比率，从而能克服给定的原位条件并优化之。

可以如下地解释当共注入两种材料时得到的协同。首先，测试表明，活性碳(以下称作“AC”)上的结合位置可以被氯物质、硫物质(即硫酸盐)和其它的烟道气污染物(砷酸盐、硒酸盐等)所消耗。加入的任选碱材料将与这些物质/污染物相互作用及反应，从而使它们对于 AC 汞的结合位置的消耗最小化。其次，测试还表明，即使结合位置完全被消耗，标准 AC 也将继续进行汞的氧化。然后该被氧化的汞可以与碱性物质反应，并随后被粒子控制装置所捕集。因此，任选的碱性组分的加入起到保护汞结合位置及捕集被氧化的汞的作用，从而导致在更低成本下的汞降低的改善。与活性碳相比，碱成本通常要低得多(差了~一个数量级)，因此可以更多地使用，而总体成本仍然较低。

“动态的”吸附剂制备

此外，已经证实可以容易“动态地”生成卤素促进的碳吸附剂。这可以通过以下来实现，例如，使卤素和任选次级组分的任意组合的蒸汽动态地与非常细的碳粒子接触。粒子可以被分散在运输空气(或其它气体)流中，该气流也将卤素/卤化物促进的碳吸附剂粒子输送至烟道气导管或其它污染的气流中，然后汞从那里被清除。对于该接触没有特别的温度要求。该技术的实施显然非常简单，并在很大程度上导致将该技术用于汞捕集的设备成本的节省。

原位制备的优点

在原位置动态地制备卤素/卤化物促进的碳吸附剂具有某些优点。例如，处理系统可以在最终使用位置上与碳注入系统结合。采用此技术时，卤素/卤化物被引入到运输管线(或吸附剂存储及注入系统的其它部分)中的碳-空气(或其它气体)混合物中。这提供了如下优于现有的离位处理吸附剂的常规概念的益处：

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●排除了处理设施的投资设备成本

●排除了操作处理设施的的成本

●没有关于将碳和添加剂运输到处理设施的成本

●本发明方法使用现有的硬件及操作步骤

●本发明技术确保吸附剂始终是新的，因此更具有活性

●没有引入新的处理方面的问题

●没有从处理系统中清除碳的成本

●本发明方法可以容许添加剂-吸附剂比的快速原位定制，从而可以适应例如当改变燃料或减少负载时可能需要的烟道气变化的要求，因此可进一步优化经济性

●本发明技术使需处理的用过的吸附剂量减少

考虑到前述内容以及其它特点，根据本发明，提供了以下实施方案，包括制备和再生卤素/卤化物促进的碳吸附剂的方法，通过将卤素(例如溴)加入到碳结构中增强其汞捕集的活性。

吸附剂注入位置

一些优选实施方案设想以粉末形式使用卤素促进的吸附剂，其在清除灰分微粒之前或之后注入到烟道气流中。本发明其它实施方案的卤素促进的碳吸附剂的组成包括通过加入 Br_2 或 HBr 和任选的次级组分而制备的粉状改性活性碳。其它实施方案容许与基体活性碳协同地加入任选的碱性组分、和/或使用卤素基吸附剂，以及本专利中提供的吸附剂技术的任意其它的组合。或者，实施方案包括这样的方法，其中吸附剂在由含有一种或多种上列组成的粒子或纤维组成的移动接触器上。

吸附剂再生

可以很容易地使任何上述实施方案的卤素/卤化物促进的碳吸附剂再生；优选清除烟道气中的毒害性污染物，加入便宜的促进剂，从而恢复汞吸附活性。该促进碳本身的活性的方法与在吸附剂中加入试剂(例如过氧化物、金、三碘化物等)的早期更昂贵的常规方法形成对比。

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本发明的卤素/卤化物促进的碳吸附剂是用溴和/或任选组分处理的，是非腐蚀性的。吸附剂再生技术的详细实例描述于标题为“PROCESS FOR REGENERATING A SPENT SORBENT”的共同未决、共有的PCT专利申请No. PCT/US04/12828中，现将其全文引入以供参考。

吸附剂注入控制方案

本发明另一优点涉及使用反馈系统来更有效地利用本发明的某些方面。在可能和期望的情况下，本发明的汞控制技术优选可以利用汞排放的连续测量作为反馈，协助控制吸附剂注入速率。可以这样地达到吸附剂和任选组分水平的更严格控制，这将保证汞清除的条件符合最低的物质要求，从而使相关成本最小化。在一个实施方案中，在注入位置的下游，优选在烟道的废气中连续测定汞排放。

促进的碳吸附剂

卤素和酸性物质与活性碳吸附剂上的碱性结合位置的反应产生了将汞氧化的位置。诸如硼、锡、砷、镓、Sb、Pb、Bi、Cd、Ag、Cu、Zn的其它金属离子或其它污染物也将与碳上产生的氧化位置进行反应。

根据我们的模型，将溴试剂中的溴或卤化氢酸中的质子加入到碳边缘结构上的碱性碳烯位置上，以形成碳正离子，其接受中性汞原子中的电子，形成结合到吸附剂表面上的氧化了的汞物质。活性位置还可以在碳的活性位置上产生活性的溴基或碳基。因此活性碳用于使溴稳定化，但能提供高度活性的含溴试剂，该试剂可以使汞氧化并促进其在活性碳上的捕集。预计包含溴的吸附剂比相应的包含氯的吸附剂活性大，且比包含碘的吸附剂便宜得多。

实施例

为了更清楚地例示本发明，下面给出若干实施例。这些实施例是作为例示目的的，本文中给出的实施例不应该理解或推断为对本发明

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的限制。

实施例 1-制备及测试卤化的碳(及比较例)

气相卤化

将细的粉末活性碳(例如 NORIT Darco FGD，NORIT Americas，Inc.，Marshall，Tex.(USA)，尽管如本领域技术人员可认识到的那样，也可适用其它的)置于带有侧叶片的旋转式塑料桶(5 ft^3 (0.14 m^3) 水泥搅拌器)中，其上安装有紧密的塑料盖以防止在制备期间细粉末的损失。在一个单独的容器中，气相溴的制备是通过使氮流流过被暖热至约 40℃-50℃的已称重量的液体溴来实现的。溴的蒸汽压力使得产生的暗红色气体流出发生器。气态溴发生器的出口经由一个 1/4 英寸(0.64 cm)的塑料胶管连接至固定的金属管，所述金属管通过法兰插入到塑料盖的中心并穿入到桶的中心内部。法兰不是空气密闭的，当溴被传递至翻转的碳上之后，过剩的氮被释出。如此，溴气流不断地流入到旋转桶的内部，在那里与翻转的碳接触。然后操作该单元，直到期望数量的溴与碳结合。通常是，0.4 至 1 kg 的溴对 20 kg 的碳(2-5 wt. %)。当反应完毕时，称量碳的重量。处理过的碳是无嗅的，不会产生皮肤刺激性，因为溴已经完全与碳反应而生成了溴化的碳。

XPS 光谱表明，溴化的碳包含与碳键合的(有机)共价溴化物以及阴离子溴化物。产物中包含的湿度与初始存在于活性碳中的相同(5-17 wt %)，但无需进一步的干燥即可使用。在更高的温度下(>150℃)湿度被去除，直到非常高的温度时才会释放出溴。

汞的氧化及捕集效率的实验室规模测试

使用基于以上描述的实验室规模的装置和步骤测试若干促进的活性碳吸附剂的初始活性及容量， 所述吸附剂使用粉状碳，包括由多种碳制备的含溴活性碳，包括商业上可得到的吸附剂、气凝胶膜吸附剂和初始前体碳用于比较。

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文献 Dunham，G.E.；Miller，S. J. Chang，R.；Bergman，P. *Environmental Progress* **1998**，17，203 提供了装置及其操作的详细描述，在此全文引入以供参考。用细粉(-400 目)状吸附剂(37 mg)与 113 mg 砂混合，装填在石英过滤器(2.5 英寸(6.35 cm))中，进行烟道气组合物中的实验室规模汞吸附剂测试。在模拟的烟道气流(30 SCFH (标准立方英尺/小时)或 0.79 NCMH (标准立方米每小时))下将装填的过滤器和支架于炉中(125℃)加热，所述模拟的烟道气流包含如下成分：O_2 (6%)、CO_2 (12%)、SO_2 (600 ppm)、NO (120 ppm) NO_2 (6 ppm)、HCl (1 ppm)、Hg^0(11 μ g/m^3)、H_2O (15%)和 N_2 (余量)。通过置于双夹套玻璃冷凝器中并加热至所期望温度的标准渗透管源提供元素汞。使用连续汞排放监测器(Sir Galahad 汞 CEM，制造商 P.S. Analytical Deerfield Beach FL USA)确定气流中的汞浓度，并使用 $SnCl_2$ 池将被氧化的物质转变为元素态，从而可以获得对于从吸附剂床的流入及流出浓度的元素态及被氧化的汞的浓度数据。根据采用的流速校准汞浓度。对用过的吸附剂进行汞的分析以确定质量平衡。

现在参考图 4，给出作为流入汞百分数的流出汞浓度数据对时间的图示。卤化的吸附剂所得到的曲线(穿透曲线)显示流出物中最初有 0%-1%的 Hg(99+% 捕集)，仅在 30-60 分钟(穿透点)之后有所增加，这取决于吸附剂情况。图 4 例示的是对于 5 wt/wt %溴化的 NORIT Darco FGD 吸附剂(37 mg÷113 mg 砂)与包含 1 ppm HCl 的合成烟道气的穿透曲线。流出物中总 Hg(实心圆)和元素态 Hg(实心方框)给出为入口 Hg 的百分数。“EOT”表示测试的终点(后面显示的数据点用于校准核对)。

图 5 给出的是依照合成烟道气中的 HCl 浓度情况，通常起始为 5%-50%入口汞时相应的非卤化吸附剂的比较穿透曲线，由此表明了非卤化吸附剂具有相当低的汞氧化及捕集活性。无论是卤化或非卤化的吸附剂，在穿透以后，流出物中大部分的汞为被氧化的汞。

实施例 2 -流态化碳的气相卤化

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通过氮流使由玻璃棉塞支撑在垂直管中的活性碳床流态化。流化床管的顶部与用于吹出管顶部的碳细粒的捕集器连接。如实施例 1 中描述的溴气体发生器与流化碳床相连，使期望数量的气态溴流到床内。然后将捕集器中的内含物与床内的物质混合并称重。得到的溴化的碳表现出与实施例 1 中溴化的碳类似的性能。

实施例 3 -液相(水)卤化

将 50 g 溴小心地加入到 1 升冷水中，制备溴的 5%水溶液。将一 kg 的活性碳加入到大金属罐里的溴溶液中。在加入的期间用大桨叶片对得到的浆料搅拌，经短时间后，直到红色消失表明所有的溴已经与碳反应。然后用布氏漏斗真空过滤浆料。将过滤器中收集到的潮湿碳在 110℃炉中干燥若干小时至恒重。如在实施例 1 中那样，碳中还仍然留有一定湿度。然后使干燥的碳在旋转桶中翻转，利用金属片破碎及疏解(fluff)碳。

实施例 4 -任选次级卤化物组分的加入

通过类似于根据实施例 3 所描述的溶液相溴化生成溴化的碳。然而在过滤之前，将氢碘酸(HI)溶液加入到浆料中，其量等于溴量的 10%。搅拌浆料以完成反应，然后如实施例 3 中描述的那样进行过滤及干燥。

实施例 5-液相磷卤化

在大金属罐中搅拌三溴化磷(500 g)的轻石油(10 升)溶液，加入 10 kg 的活性碳。用大桨叶片在环境温度下对所得到的浆料进行搅拌以完成反应。以若干批次在大的布氏漏斗中真空过滤浆料。湿滤饼在 110 ℃炉中干燥至恒重。干燥的产物如在实施例 3 中所描述的那样在旋转桶中疏解。

实施例 6-更大粒子碳的制备及其上的吸附

燃烧次烟煤炭，用中试规模的燃烧器进行测试，通过注入大于正常尺寸的处理的活性碳来评估汞的控制。标准 AC 吸附剂通常为细尺寸

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的，平均粒径小于 20 微米，这也是煤粉燃烧产生的飞灰的典型尺寸。因此，由于标准 AC 与飞灰的尺寸类似，两者的分离是困难的。通常不考虑注入更大尺寸的 AC，因为吸附剂的有效性随尺寸而降低。在使注入的碳再循环的方案中，从飞灰中分离出碳。基于尺寸分级的分离需要处理的更大粒子的吸附剂。为了验证这种观点，开发、制备和测试了处理的更大尺寸的(>60 μ m)吸附剂。

处理-气相卤化

研磨粒状活性碳(Calgon F400)并用常规网筛进行筛分。收集-170至+240 的网目尺寸部份(相当于约 60 至约 88 微米)并置于如上面实施例 1 中描述的旋转容器中。也如在实施例 1 中描述的那样，在单独的容器中，气相溴的产生是通过使氮流在被暖热至约 40℃-50℃的已称重量的液体溴之上流过来实现的，该气态溴发生器的出口经由一个 1/4 英寸(6.35 mm)的塑料胶管连接至固定的金属管，所述金属管通过法兰插入到盖的中心并穿入到旋转容器的中心内部。操作该单元，直到期望量的溴与碳结合，在这里是 0.05 kg 的溴与 1 kg 的碳(5 wt.%)。当反应完毕时，称量碳的重量。如上面已经描述的那样，处理的碳是无嗅的。

PTC 装置

中试规模燃烧器即已知的“微粒测试燃烧器”(以下称作“PTC”)，其为 550,000-Btu/hr(约 161 kW)的粉煤(“PC”)燃烧单元，其用来产生燃烧烟道气性能以及飞灰，用以代表大规模动力锅炉所产生的那些物质。使燃烧器垂直定向以使壁上沉积最小化。耐火衬里有助于保证完全燃烧的足够火焰温度，并阻止聚结或凝结的飞灰的迅速淬灭。基于表观气体速度，粒子在燃烧器中的平均滞留时间为大约 3 秒钟。PTC 的煤炭喷嘴从燃烧器的底部轴向地向上燃烧，以紊流混合将次级空气同心式地引入初级空气中。经由螺旋进料机和喷射器将煤炭引入到初级空气流中。使用电空气预热器精确控制燃烧空气温度。最初，PTC 使用冷水环形热交换器对集尘室(也指的是“织物过滤器”)或静电沉降器(ESP)提供烟道气的温度控制。然而，对从热交换器中收集到的灰分

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沉积物的分析表明，一些汞积聚在管道壁上。为了使这种影响最小化，对热交换器进行改进以提供更高的管道壁温度。

PTC 仪器设备容许连续地监测系统温度、压力、流速、烟道气成分浓度以及微粒控制装置(集尘室、高级混合式粒子收集器/AHPC™ 和/或静电沉降器/ESP)的操作数据并用数据记录器记录。

PTC 步骤

烟道气样本的选取为三个可取的系统样本点—炉子出口、粒子控制装置入口、粒子控制装置出口—中两个的组合。将烟道气通过样本调节装置以去除水分之后，通常对烟道气中的 O_2、CO、CO_2、SO_2 和 NO_x 进行分析。通常使用两个分析仪同时在炉子出口和粒子控制装置出口对每种成分进行分析。连续记录所有仪器上的浓度值。此外，以设定的时间间隔手动记录数据。使用一对 Rosemount Analytical NO_x 化学发光分析仪确定 NO_x。使用一对 Ametek Instruments 光度气体分析仪测定 SO_2。通过一对 Rosemount Analytical 多气体连续排放监测器对其余的气体进行测定。定期校准及维护各自的这些分析仪，从而提供准确的烟道气浓度测量。

集尘室容器为 20 英寸(50.8 cm)(ID)热跟踪及隔绝的腔室，引入的烟道气在底部附近。在 300℉(约 150℃)下燃烧器生成约 200 ACFM(实际立方英尺每分钟；约 5.7 实际 m^3/min)的烟道气，因此，三个 13 英尺 x5 英寸(3.96 m x12.7 cm)的袋子提供 4 英尺/min (1.22 m/min)的气布比。每个袋子随其自身的隔膜脉冲阀的操作而单独地进行清洁。为了对不同测试条件下压降的差值定量化，袋子的清洁是基于时间的，而不是基于压降引发的清洁周期。一旦引发袋子的清洁，以快速的顺序性在线对所有三个袋子进行脉冲。

还用单线式管状 ESP 代替织物过滤器进行了测试。设计 ESP 单元以使在 300℉(150℃)下提供的比收集面积为 125。因为 PTC 的烟道气

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流速为 130 SCFM(标准立方英尺每分钟；约 3.7 NCMM (标准 m^3/min))，则通过 ESP 的气体速度为 5 英尺/分钟(约 1.52 m/min)。ESP 单元的板距为 11 英寸(27.9 cm)。ESP 的设计要有利于各测试之间的彻底清洁，从而使所有的测试能具有相同的基础。

PTC 结果

结果例示于图 6 中。在图 6 中观察到，即使测试的吸附剂粒度显著地大于正规的吸附剂粒子，所处理的大于正规尺寸(即>60 微米)的活性碳吸附剂对于汞的捕集也相当有效。当在中试规模 ESP 前注入更大尺寸处理的 AC 时，大约 75%的汞被捕集，而当在中试规模织物过滤器(“FF”)前注入时，大约 85%的汞被捕集。注意在图 6 中(以及通篇中)，“Macf” (及“MACF”)表示百万实际立方英尺(1 MACF 为约 0.028 百万实际立方米或“MACM”)。

现在参考图 7，可以观察到，在相同的配置下，当在中试规模 ESP(菱形记号)前注入时，更大尺寸处理的 AC 表现出的性能优于更细的标准 AC(三角形)。作为比较，当在织物过滤器(FF) 前注入时，更大尺寸处理的 AC(方形)表现出从类似到稍微更差的性能。然而，对于这种应用而言，更大尺寸处理的 AC 可以从更小的飞灰粒子中物理地分离出来，然后可以将吸附剂再生、再循环及重新使用。这将充分地改善总利用性及经济性。这些数据因而说明，大于正规尺寸的吸附剂可以提供有效的汞控制，飞灰与 AC 的分离也容易，因此可以保留飞灰的销售及有益用途的特性。相应地，由于已经成功地证明了>60 μ m 的吸附剂粒子，因而使用>40 μ m 的粒子可以获得优异的汞控制，依照所使用的吸附剂粒子/灰分分离系统的情况，在一些应用中使用 40 μ m 的粒子是优选的。注意在图 7 中(以及通篇中)，“Macf” (及“MACF”)表示百万实际立方英尺。

实施例 7-液相(有机溶剂)卤化

将 50 g 溴小心地加入到 1 升冷的轻石油中，制备溴在轻石油中的

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5%溶液。将 1 kg 的活性碳加入到大金属罐里的溴溶液中。在加入的期间用大桨叶片搅拌浆料，经短时间后，直到红色消失表明所有的溴已经与碳反应。用布氏漏斗真空过滤浆料。将过滤器中收集到的碳饼在110℃炉中干燥若干小时，直到其显示为干燥并达到恒重。如在实施例1中那样，碳中还仍然留有一定湿度。然后使干燥的碳在旋转桶中翻转，利用金属片破碎及疏解碳。

实施例 8-促进的活性碳吸附剂

采用基于上面描述的实验室规模的步骤来测试若干促进的活性碳吸附剂的初始活性及容量，所述吸附剂使用粉状碳，包括由商业上可得到的吸附剂制备的含溴活性碳和气凝胶碳膜吸附剂，以及初始前体碳用于比较。将粉状活性碳前体浸渍于搅拌的溶液中制备溴处理的碳，所述搅拌的溶液是溴在四氯化碳或二氯甲烷或者在 HBr 水溶液中的溶液，接着在环境温度下于空气中干燥，在 100℃炉中于空气或氮气氛下干燥。还可以使气体流过活性碳前体的旋转干燥床，从而从气相中浸渍溴来制备溴处理的碳。结果表明在溶液中加入次级组分改善了吸附剂的容量。

碳的初始测试在加热床上进行，其中包含元素态汞(11 μg/m^3)的合成烟道气流通过该床。流出气体中总的及元素态 Hg 的浓度用 Sir Galahad 汞 CEM(“连续排放监测器”) (制造商 P S Analytical，Deerfield Beach，FL，USA)来确定。在测试期间粉状吸附剂负载在石英过滤器上，以三层形式测试其它吸附剂。对初始的商业级粉状碳吸附剂、与该吸附剂在用 0.1 N HBr 处理之后离心收集粉末并干燥作了比较，表明汞捕集的活性从在入口处约 50% Hg 的初始捕集效率增大至 100%捕集。吸附剂在随后用 HBr 再生的比较表明，其不仅能够以与以前同样(100% 捕集)的水平捕集汞，而且其容量还延长若干分钟，因此是增强了的。如上面所描述的那样在溶液中或在干燥床中用分子态溴处理碳膜和碳纤维吸附剂得到类似的结果。

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实施例 9-流化/沸腾床制备

通过使气体流过与碳的流化床或沸腾床串联的液体溴储槽的方式，由包含分子态溴的气体组合物来进行分子态溴的浸渍，通过如此处理碳来制备活性碳吸附剂。依照所使用的比例，每 100 g 活性碳中碳吸收的溴量范围从(在一个实施例中的)<1 至约 30 g。

实施例 10-大规模测试

在该实施例中，使用集尘室(织物过滤器)或 ESP 来收集大规模商业粉煤燃烧设备的废气中的微粒。同时使用涤气器和吸附剂床从烟道气流中将不期望的成分在被送料到烟道之前清除掉。在该实施例中，在锅炉之后将卤素/卤化物促进的碳吸附剂注入到烟道气内。然而，一般来讲，可以将本发明的吸附剂注入到期望的位置(例如，在锅炉之前、之后或之内)。

在燃烧褐煤的设备上进行的一个示范测试中，烟道气相中汞(元素态) 浓度为 10 至 11 μ g/m^3。在 350℉至 375℉(约 175-190℃)下在集尘室中收集灰分和注入的碳。以 1.0 lb/MACF 的速率(“MACF”和“Macf”代表百万实际立方英尺；1.0 lb/MACF 为约 16 kg/MACM(百万实际立方米))注入商业级活性碳粉末(未处理的)，得到 3.8-4.2 μ g/m^3 的汞流出浓度结果(分别代表气体中 62%-58%的汞清除)，速率 2.0 lb/MACF(约 32 kg/MACM)时，给出 74%-71%的清除。以 1.0 lb/MACF 速率注入溴处理的碳给出 73%-69%的清除结果，速率 2.0 lb/MACF 给出 86%-84%的清除。因此，使用本发明的溴促进的碳吸附剂表现出汞捕集的显著增加。

实施例 11A-任选的碱性组分的加入—实验室规模

为了捕集可能从吸附剂中释放的任何被氧化的汞，或者捕集烟道气中可能对吸附剂容量具有不利影响的某些硫或硒的氧化物，通过使用碱性物质与活性碳的共注入可以明显地改善活性碳的汞捕集效率。

制备由 37 mg 溴化的活性碳与 113 mg 氧化钙混合组成的过滤器，

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进行实验室规模测试。如在实施例 1 中描述的那样进行测试，并与带有惰性稀释剂的相同碳吸附剂进行比较。溴化的(2%) NORIT Darco FGD 吸附剂与惰性砂的混合物的穿透曲线示于图 8 中，与 CaO 的混合物的穿透曲线示于图 9 中。可以看到，与 CaO 的混合物的 50%穿透点增至 65 分钟，而与砂的混合物仅为 48 分钟。

实施例 11B-任选的碱性组分的加入—中试规模

在参考上面实施例 6 描述的中试规模的 PTC 燃烧器上进行测试，燃烧 Texas 褐煤，通过在织物过滤器上游共注入标准活性碳(本文也称为“AC”) 和碱性物质来评价汞控制。典型结果例示在图 10 中。如图 10 所示，石灰与活性碳的共注入大大地增加了汞的清除。使用共注入吸附剂达到了大约 90%的汞清除，而即使在高得多的注入速率下，单独使用标准 AC 时只达到不到 60%的清除。类似测试的数据显示，注入类似量的碳酸钠与 AC 以及石灰与 AC，分别给出大约 80%以及 87%的汞清除结果。这些数据暗示，也可以用其它碱与 AC 共注入来改善汞的清除。其它数据显示，烟道气温度可以影响碱加入的有效性。进一步的测试数据表明，烟道气污染物、烟道气成分(SO_2、NO_x、HCl 等)、操作温度、汞的形式以及汞的浓度可以影响到碱加入的有效性。这表明理想的是能够原位地调节及定制碱与 AC 的比率，从而能在设定的原位条件下使清除最优化。

虽并不打算束缚于任何特定的理论，但可以如下地解释当两种物质共注入时在性能改善当中观察到的协同。首先，测试表明，AC 上的结合位置可以被硫物质和其它污染物所消耗。碱材料与这些物质相互作用及反应，从而使它们对于 AC 上汞结合位置的消耗最小化。其次，其它工作已经表明，即使结合位置完全被消耗，标准 AC 也将继续进行汞的氧化。然后该被氧化的汞可以与碱性物质反应，并随后被微粒控制装置捕集。因此，碱与处理的和/或未处理的 AC 的结合将协同地利用这两种机理，导致在降低的成本下的汞捕集的改善。

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实施例 12-用于气化燃料气体的溴化处理碳吸附剂 5% Br2W-AC 的制备

采用类似于实施例 3 中的步骤，制备溴在水中的 2.5 wt/vol % 溶液。将粒状的 Calgon F400 加入到溴溶液中，得到 5 wt/wt %溴化的碳产物。在加入期间及之后用大桨叶片搅拌溴溶液，直到水中的红色消失。用大布氏漏斗真空过滤悬浮液。滤饼在空气中干燥，然后在 110 ℃炉中干燥，直到获得稳定的重量，湿度减少到 15%。

5% Br2D-AC 的制备

如在实施例 7 中所描述的那样由在溶剂中加入 Br_2 制备溴化的吸附剂，不同的是，使用二氯甲烷代替轻石油作为溶剂，使用粒状的 Calgon F400。

5% PBr3-AC 的制备

采用实施例 5 中描述的方法由 PBr_3 制备磷卤化的吸附剂，不同的是，使用粒状的 Calgon F400。

氢气氛下的测试—步骤

为了模拟从煤炭气化的合成气或受热燃料气中捕集汞，采用使氮中包含 10% vol/vol 氢的气流以 500 cc/min 速率通过吸附剂来进行测试。气流中包含来自市售汞渗透源的 26.9 微克/m^3 的元素态汞。

在测试中，将吸附剂(0.5 g) 置于 0.39 英寸(1 cm, 内径)的玻璃管中，所述玻璃管配有中等熔块(medium frit)烧结玻璃滤片，从而在气流中保持吸附剂。包含吸附剂床的管与气体入口管连接，用于引入包含汞蒸汽的气流，在管连接的出口与检测器连接。检测器为 Semtech 2000 连续汞排放监测器。在环境温度下使管在氮气流(450 cc/min)中平衡 5 分钟以使系统稳定化。检测器显示在吸附剂床的流出物中汞的浓度为 0。(没有吸附剂的空白运转时的读数为 26.9 微克/m^3)。然后在选定的温度下将管置于炉中进行测试(250℃至 400℃)。收集检测器中的流出汞浓

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度数据，直到检测器显示恒定的读数有 5 分钟。然后在气流中加入氢(50 cc/min)，每 5 min 读取检测器的读数。根据温度及吸附剂的情况，在达 3 小时时段的不同时间段中，在几个炉温下进行测试。如在实施例 1 中那样，元素态汞浓度数据绘制为入口汞浓度的百分数对时间的图形。流出物中所有的汞为元素态的，因此单一检测器就足够了，无需用 $SnCl_2$ 捕集器来转化至元素态汞(如在实施例 1 中那样)。然后由穿透曲线确定 50%穿透的时间(达到 50%捕集的时间)。

结果

对于未溴化的吸附剂(Calgon F-400)、溴化的吸附剂(5% Br2W-AC 和 5% BrD-AC) 及磷溴化的吸附剂(5% PBr3-AC)，结果示于(以下)表 1 中。对于表 1 最后一栏中表示的时间段而言，每次运行在流出物中得到的最大汞浓度也记录在表 1 中。

在还原的氢条件下，未溴化的吸附剂立即穿透，仅 6.5 min 之后就耗尽。这种彻底失效的出现是因为氢在 100℃以上的任何温度下使未溴化的吸附剂中捕集的汞还原。两种溴化的吸附剂在高至至少 400℃的所有温度下均展示出极好的活性和良好的容量。磷溴化的吸附剂在高至至少 400℃的所有温度下展示出优异的活性和容量。

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表 1

50%穿透的时间

观察到的吸附剂最大 Hg 浓度

(10% 氢流)

吸附剂	温度(℃)	50%穿透(min)	最大[Hg] ($\mu g/m^3$)	时间(min)
F-400	250	6	20.3	6.5
5% Br2W-AC	250	>150	1.4	150
5% Br2W-AC	300	>180	4.3	180
5% Br2W-AC	350	160	15.1	180
5% Br2W-AC	400	60	13.9	65
5% PBr3-AC	250	>140	0.4	140
5% PBr3-AC	300	>150	0.5	150
5% PBr3-AC	350	>150	1.4	150
5% Br2D-AC	350	>180	2.1	180
5% Br2D-AC	400	>180	10.9	180

虽然已经给出和描述了本发明优选的实施方案，本领域的技术人员在不偏离本发明的实质和教导的情况下可以对其作出各种修改。本文中描述的实施方案仅为示范性的，不意味着具有限制性。文中公开的本发明的种种变化及修改也是可行的，也在本发明的范围之内。因此，保护范围不限于上面说明书给出的内容，而仅由随后的权利要求所限定，该范围包括权利要求主题的所有等同方案。

公开文本中提供的实施例仅为例示和解释的目的，不意味着对权利要求或本发明实施方案的限制。虽然已经给出和描述了本发明优选的实施方案，本领域的技术人员在不偏离本发明的实质和教导的情况下可以对其作出各种修改。基于本文的公开内容，本领域的技术人员可以很容易地确定出本发明给定实施中的方法标准、设备等。本文描述的实施方案仅为示范性的，不意味着具有限制性。文中公开的本发明的多种变化及修改也是可行的，也在本发明的范围之内。关于本发

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明中的任何要素使用的术语“任选的”意味着表明该主题要素是需要的或者不需要的。两种选择方案均意味着落于本发明的范围之内。

背景部分中对参考文献的讨论并不是承认其为本发明的在先技术，特别是公布日期可能在本申请的优先权日期之后的任何参考文献。据此将本文引用的所有专利、专利申请及出版物的公开内容全部全文引入到本文中以供参考，其引入的范围对本文中的陈述内容提供示范性的、程序性的或其它详细的补充。

虽然本文描述的本发明为吸附剂材料以及其制备和用途的相关方法，但并不意味着局限于所描述的细节，在不偏离本发明实质的情况下可以做出各种修改及结构变化，这都在权利要求的等同方案的范围之内。

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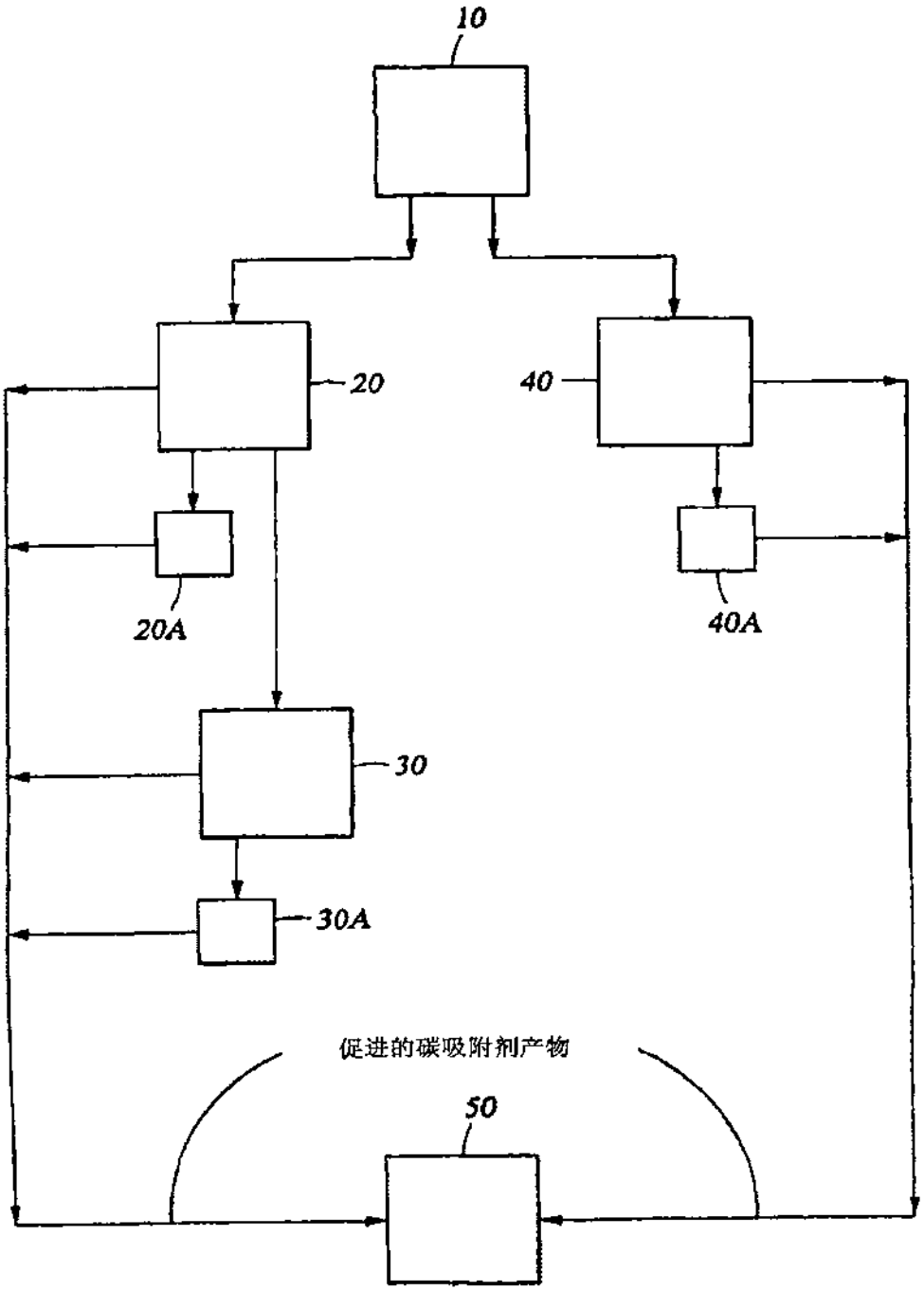


图1

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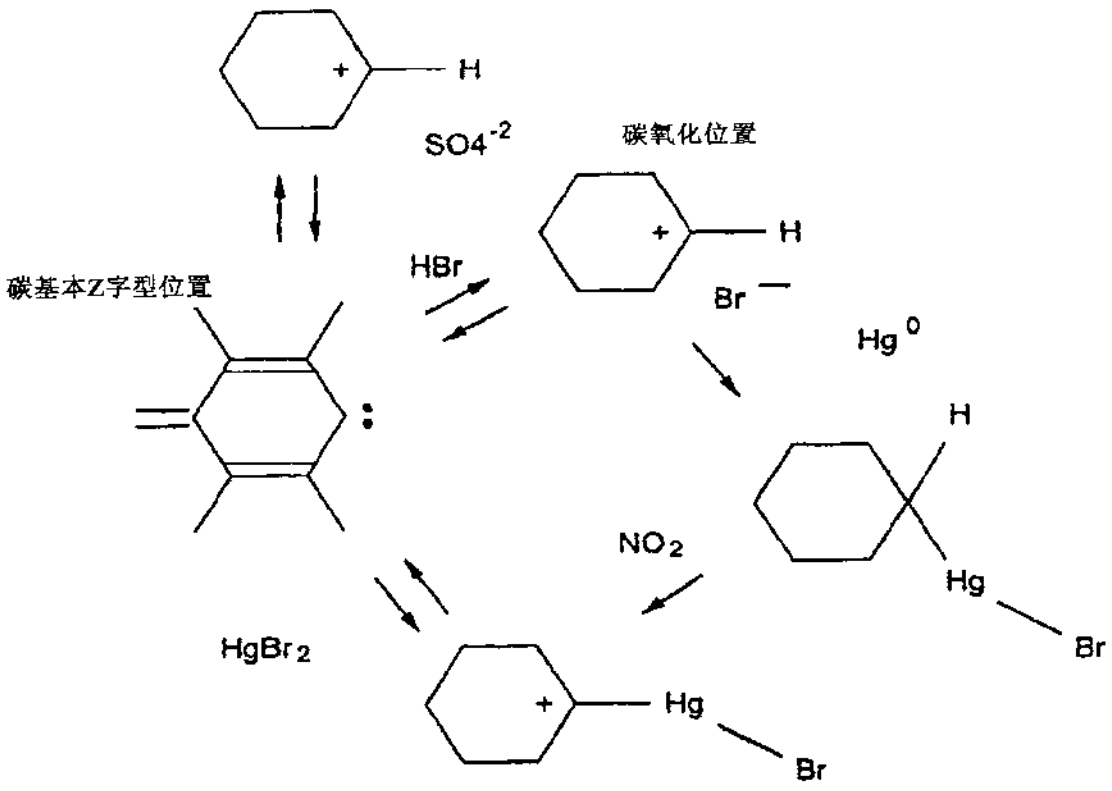


图2

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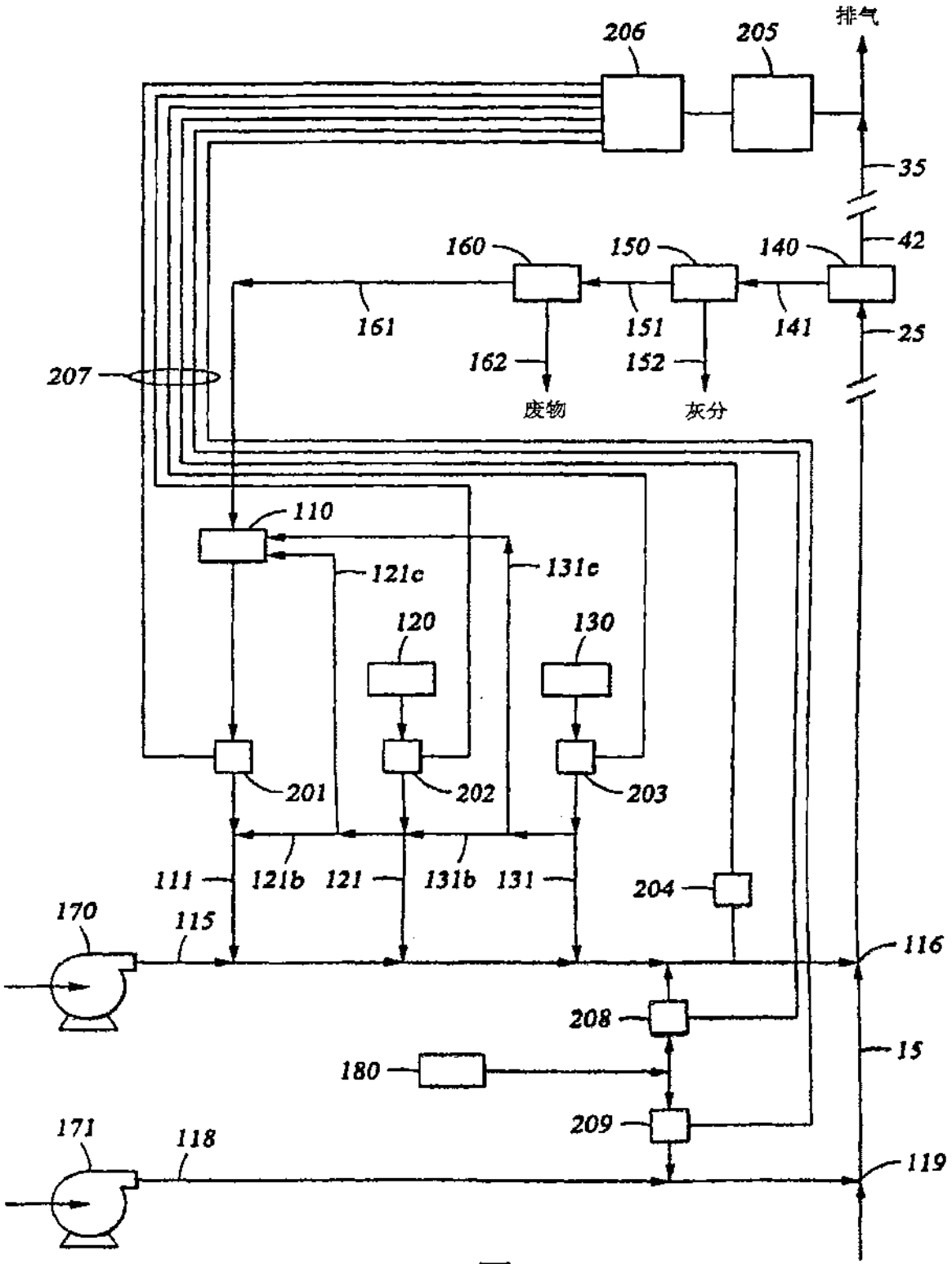


图3

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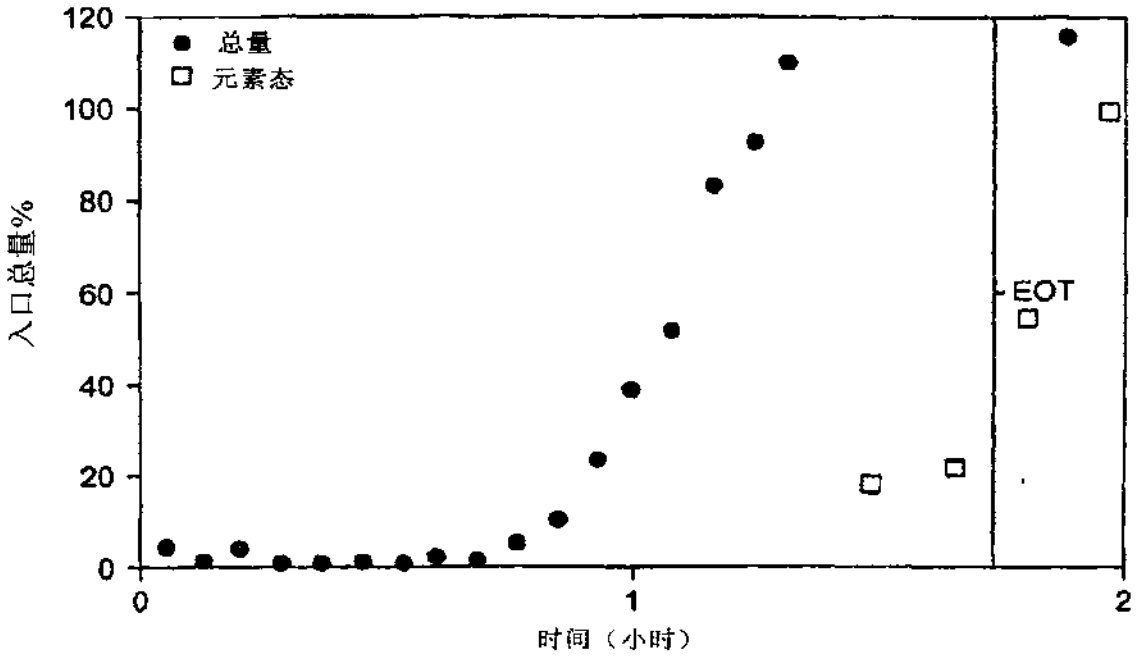


图4

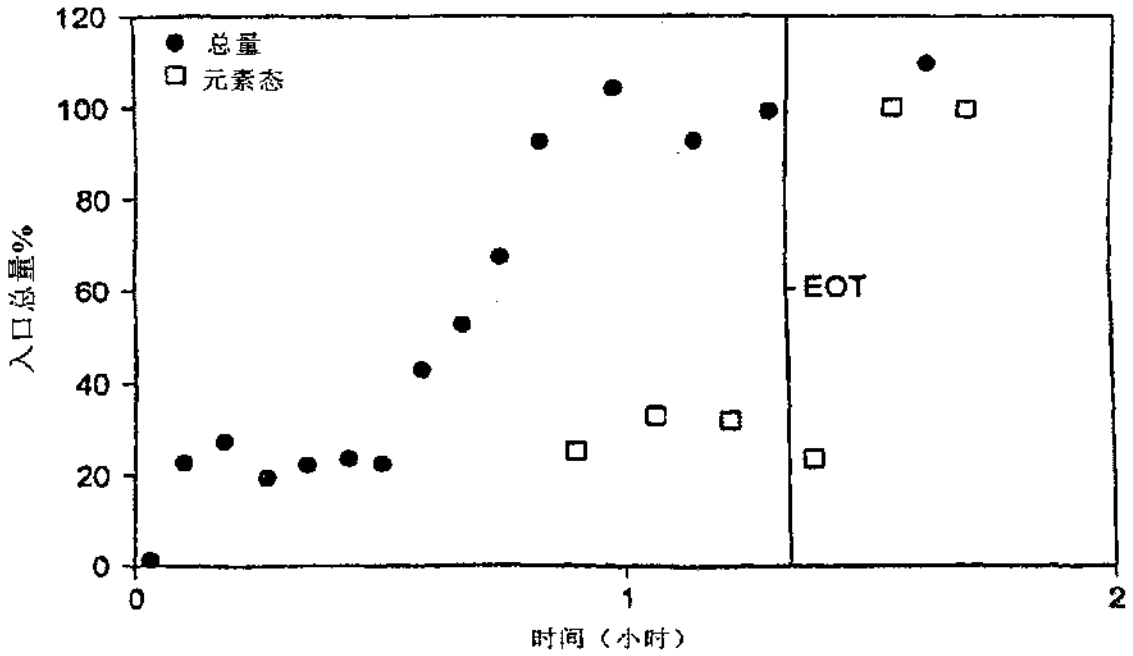


图5

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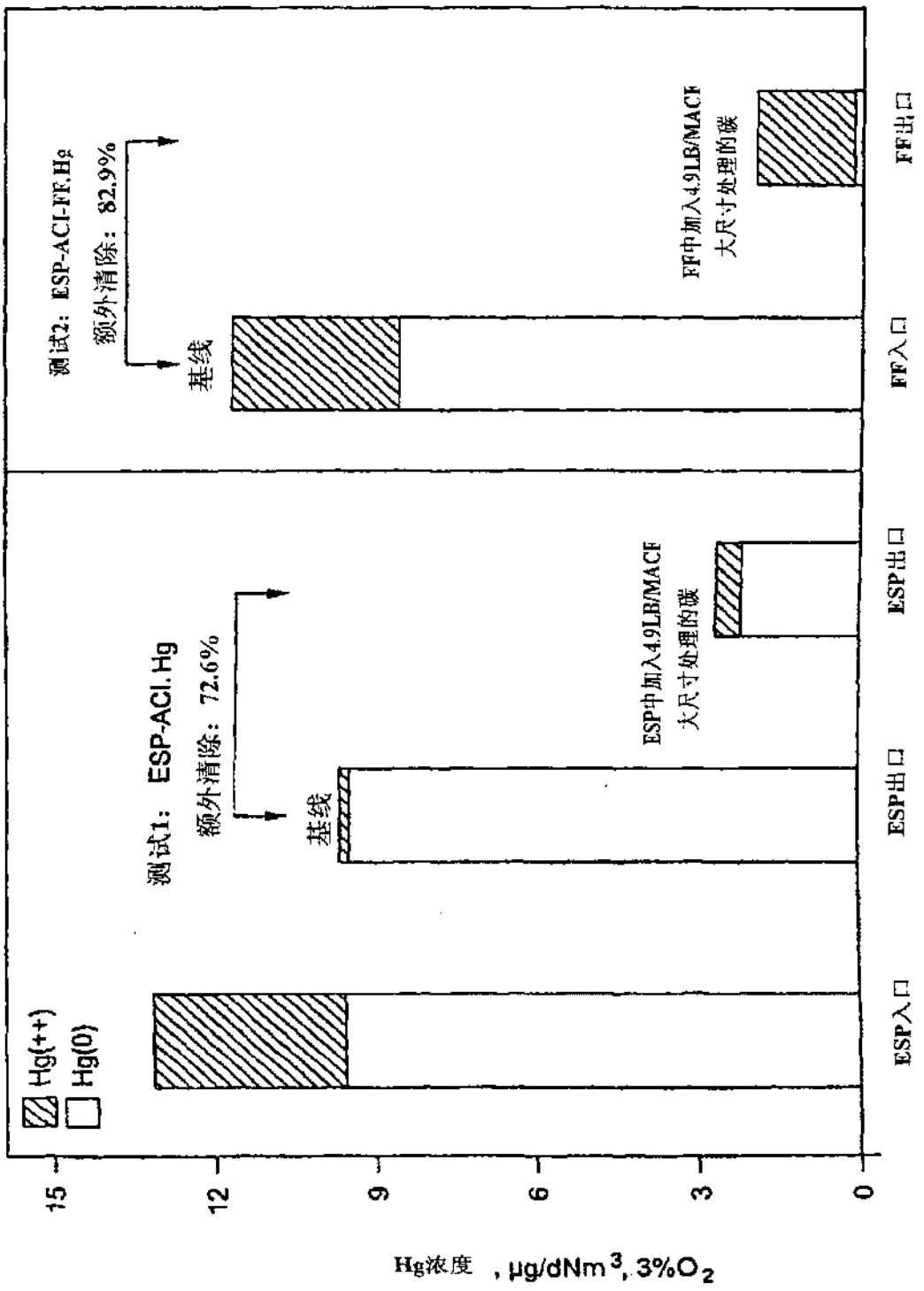


图6

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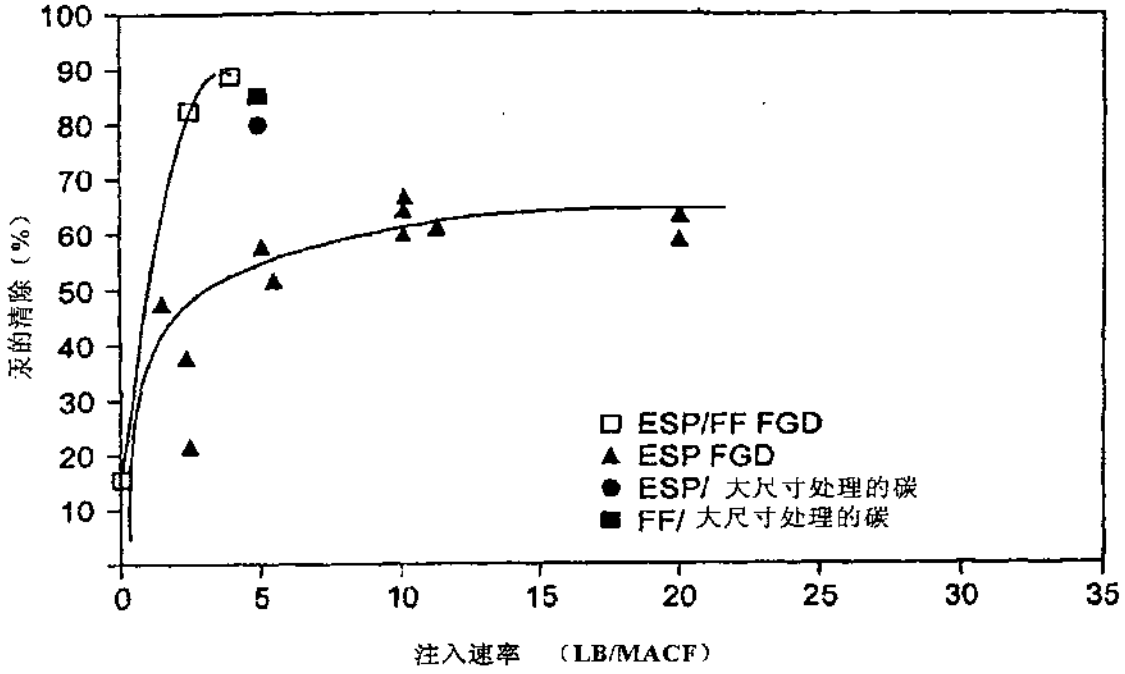


图7

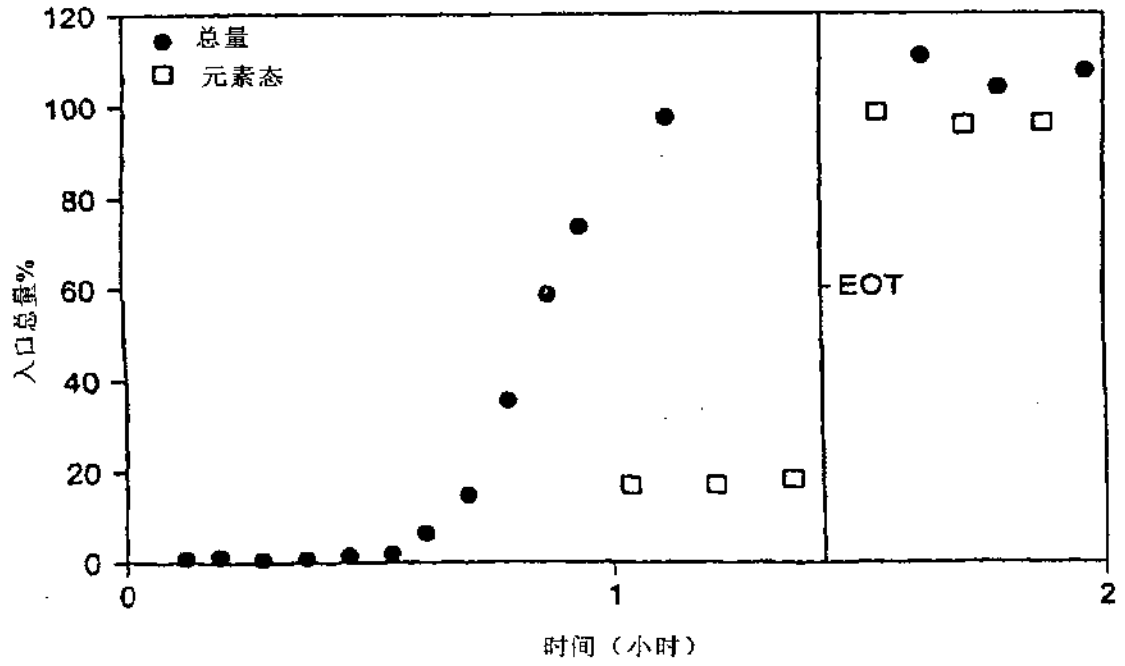


图8

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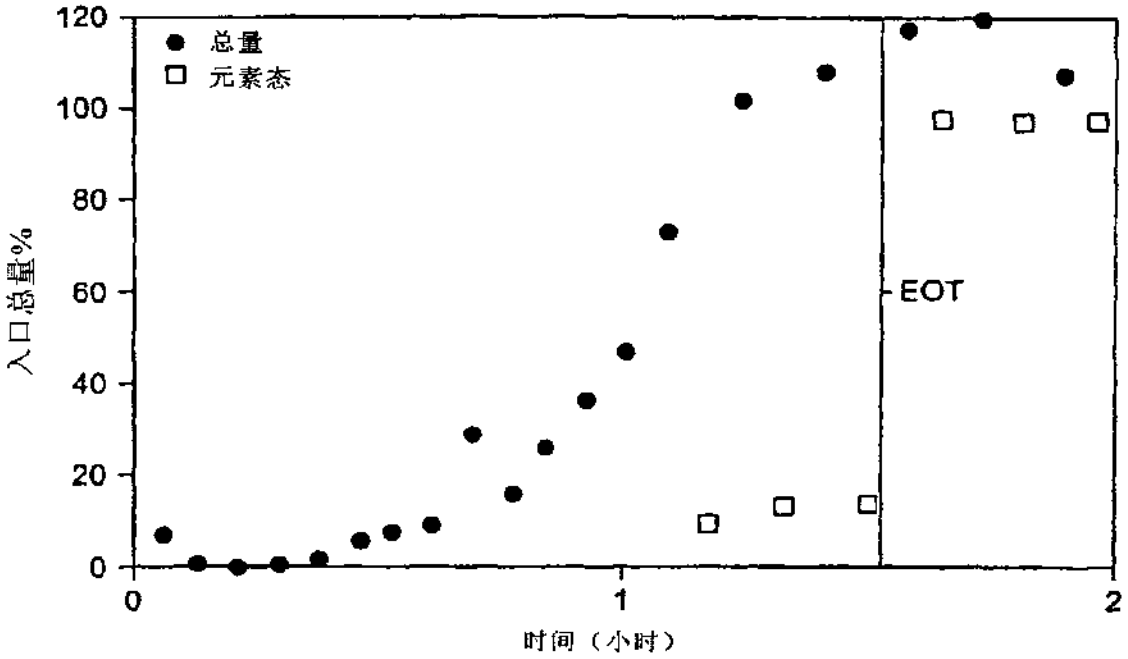


图9

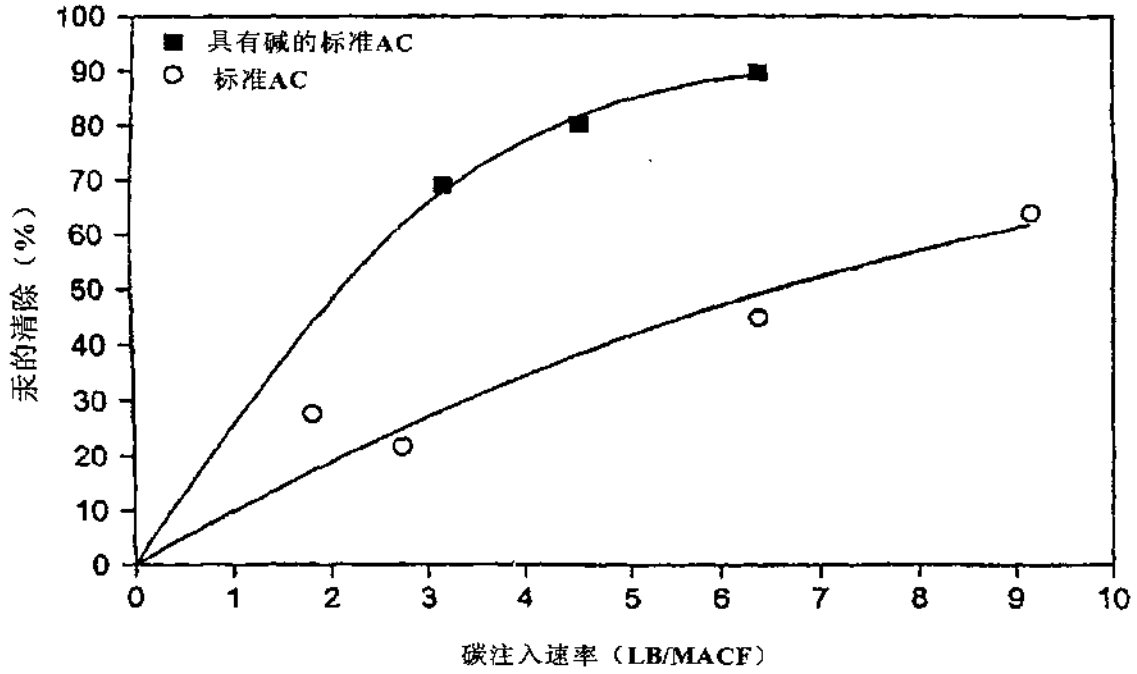


图10

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Organic complex supported activated carbon adsorbent and its preparation method and application

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Abstract of CN101053820 (A)

The invention relates to an organic complex supported activated carbon adsorbent, which has activated carbon as a carrier and organic complex distributed on a pore path of the activated carbon. The preparing method comprises: immerging the activated carbon treated by vacuumizing in a maceration extract; removing solvent by vacuumizing; leaching the sample using an eluate while vacuum filtrating; and washing the the sample using deionized water while vacuum filtrating. The adsorbent is applicable for purifying peroxide (H2O2) solution by a way of: adding the adsorbent into the peroxide solution, absorbing and filtering the mixture to effectively remove organic matter impurity from the peroxide solution as well as remove various metallic iron impurities such as Al, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Rb, Sr, Mo, Ag, Sb, W, Au, Hg, etc., thus the aim of purification is achieved.; Accordingly, the adsorbent of the invention is suitable for purifying of peroxide solution, in particular commercial grade peroxide solution having more organic matter impurity.

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权利要求书 2 页 说明书 9 页

[54] 发明名称

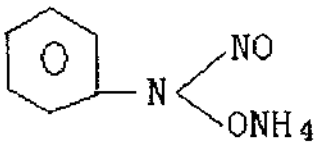
有机络合物负载型活性炭吸附剂及其制备方法和应用

[57] 摘要

本发明涉及一种有机络合物负载型活性炭吸附剂，是以活性炭为载体，有机络合物主要分布在活性炭的孔道上；其制备方法包括：经抽真空处理的活性炭浸没在浸渍液中；抽真空脱除溶剂；用淋洗液对样品边淋洗边进行真空抽滤；用去离子水对样品边冲洗边进行真空抽滤；所述吸附剂可用于纯化过氧化氢(H_2O_2)溶液，即将吸附剂加入到过氧化氢溶液中，进行吸附，过滤，可有效地脱除过氧化氢溶液中的有机物杂质，以及可对 Al、Ti、Cr、Mn、Fe、Ni、Cu、Zn、Ga、Rb、Sr、Mo、Ag、Sb、W、Au、Hg 等多种金属离子杂质进行同时脱除，从而达到净化的目的；本发明的吸附剂适用于过氧化氢溶液，特别是含有机物杂质较多的工业级过氧化氢溶液的纯化。

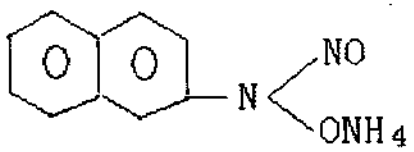
1、一种有机络合物负载型活性炭吸附剂，以活性炭为载体，有机络合物采用浸渍法负载到活性炭载体上，其特征在于有机络合物主要分布在活性炭的孔道上，负载的有机络合物占负载型活性炭吸附剂重量的0.05～8.0%；

所述有机络合物为N－亚硝基苯基羟胺的铵盐（Ⅰ）、N－亚硝基萘基羟胺的铵盐（Ⅱ）中的一种或两种；其中N－亚硝基苯基羟胺铵盐的化学结构式为



（Ⅰ），

N－亚硝基萘基羟胺铵盐的化学结构式为



（Ⅱ）。

2、按照权利要求1所述的有机络合物负载型活性炭吸附剂，其特征在于负载的有机络合物占负载型活性炭吸附剂重量的0.5～6.0%。

3、按照权利要求1或2所述的有机络合物负载型活性炭吸附剂，其特征在于所述活性炭的BET法比表面积为600～1300 m^2/g，孔径分布在0.5～100 nm，主要峰值在1.2～1.5 nm处。

4、按照权利要求3所述的有机络合物负载型活性炭吸附剂，其特征在于所述活性炭的孔径分布在1～30 nm。

5、权利要求1～4之一所述的有机络合物负载型活性炭吸附剂的制备方法，其特征在于包括以下步骤：

（1）配制有机络合物浸渍液：有机络合物溶于有机溶剂中；所述溶剂为乙醇、丙酮、四氢呋喃中的一种或几种。

（2）用有机溶剂和去离子水配制成有机溶剂的浓度为0.2～10.0%重量的水溶液，得到淋洗液；所述溶剂为乙醇、丙酮或者四氢呋喃中的一种或几种；

（3）经抽真空处理的活性炭浸没在浸渍液中0.1～72小时，浸渍液中的有机溶剂与活性炭的质量比为2.0～3.0∶1。

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（4）抽真空脱除溶剂；

（5）用淋洗液冲洗步骤（4）所得的样品，对样品边淋洗边进行真空抽滤、每次淋洗所用淋洗液与活性炭的质量比为 2.5～4.0∶1；

（6）用去离子水对样品边冲洗边进行真空抽滤，去离子水与活性炭的质量比为 2.5～4.5∶1，干燥，得到有机络合物负载型活性炭吸附剂。

6、根据权利要求 5 所述的方法，其特征在于步骤（3）所述的抽真空处理的活性炭由下述方法得到：活性炭先用浓度为 5～20%重量的稀酸溶液在 40～50℃下进行浸泡、清洗、滤干，然后再用去离子水反复洗涤，烘干待用，所用稀酸可为盐酸或硝酸；然后在真空度为 9.5×10^{4}Pa 或以上，保持 2～4 小时。

7、根据权利要求 5 或 6 所述的方法，其特征在于步骤（4）中，在 45～60℃下，真空度为 9.5×10^{4}Pa 或以上，保持 0.5～4 小时脱除溶剂。

8、根据权利要求 7 所述的方法，其特征在于步骤（6）所述干燥是真空干燥，条件为温度 50～70℃，真空度在 9.8×10^{4}Pa 或以上，保持 1～72 小时。

9、权利要求 1～4 之一所述有机络合物负载型活性炭吸附剂用于纯化过氧化氢溶液的方法，其特征在于将吸附剂加入到过氧化氢溶液中，进行吸附，过滤；所述吸附剂的用量占过氧化氢溶液质量的 0.05～2.0%，过氧化氢溶液的浓度为 20～55%质量；所述吸附是在 5～40℃下缓慢搅拌 0.1～24 小时。

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有机络合物负载型活性炭吸附剂及其制备方法和应用

技术领域

本发明涉及有机络合物负载型活性炭吸附剂及其制备方法。

本发明还涉及该吸附剂用于纯化过氧化氢（H_2O_2）溶液的方法。

背景技术

过氧化氢（H_2O_2）可用作氧化剂、漂白剂、消毒剂、聚合引发剂和交联剂等，在化工、电子、军工及航天等许多领域发挥着重要的作用。根据应用范围的不同，H_2O_2 分为工业级、试剂级、医药级和电子级四种级别，而电子级过氧化氢又可分为常规半导体级（各种金属离子含量低于 100ppb）、精细电子级 SEG（各种金属离子含量低于 10ppb）和超高纯级别 RGS（各种金属离子含量低于 1ppb）产品等。一般的使用，对过氧化氢中的杂质没有特别的要求。但在试剂和半导体制造工业中，特别是在半导体工业上，由于过氧化氢作为一种重要的加工试剂，常用于大规模集成电路的清洗工艺（湿化学处理过程）。该过程要求这些加工助剂（或试剂）具有极高的纯度，包括有极低的有机物含量（TOC）和极小的金属离子和各种阴离子浓度，否则将造成废品率高的情况。

目前，过氧化氢的工业生产主要采用的是蒽醌法。这种方法生产的过氧化氢溶液中往往带有残留的烷基蒽醌及其衍生物，$C_{8\sim10}$的重芳烃、磷酸酯、稳定剂等多种有机物杂质，以及由设备、管线等带来的各种金属离子杂质。由于过氧化氢分子所具有的非对称链状结构及过氧键的存在，使过氧化氢分子易于自发分解。杂质、PH 值、温度、辐射、容器的粗糙表面等均会加快过氧化氢分解。因而过氧化氢在生产、应用、储存和运输过程中都是种极不稳定的化学品。

过氧化氢溶液中含有的有机杂质通常用总有机碳（TOC）来表示。而除去有机杂质的方法主要有蒸馏、树脂吸附、吸附剂吸附、膜分离等。

一般而言，用蒽醌法生产的过氧化氢，用传统的蒸馏法精制，可以除去大多的无机杂质，但其能耗高，受热时间长，而过氧化氢受热分解及其所含有的有机物使得精制过程存在一定的安全隐患，挥发性的有机物也不易有效除去，另外过氧化氢的得率也不高。

用树脂精制过氧化氢溶液的方法用的最多。使用阴、阳离子交换树脂脱除过氧化氢溶液中的阴、阳离子是广为人知的技术。但用一般的离子交换树脂对溶液中的有机物杂质是

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很难有效去除的。用于溶液中的有机物的吸附常常使用的是吸附树脂。这类树脂一般不含离子交换基团，是内部形成交联网络结构的高分子吸附剂，具有一定的孔结构和比表面积，理化性质稳定，耐酸、碱，对有机溶剂也有一定的承受力。可分为非极性、弱极性、极性和强极性四大类。由于不带有酸、碱功能基，故不能发生离子交换反应。其吸附性是由于范德华引力或氢键力的结果。另外，由于吸附树脂孔结构的不同，所造成分子扩散的空间效应可用来选择吸附某些特定的有机物。但是，基于吸附树脂这类高分子材料的结构的特点，对于象过氧化氢溶液中有机物的脱除，要对包括不同的分子结构、不同极性的有机物一起吸附的情况，其效果就受到一定的限制。此外，由于树脂吸附容量比较小，而且溶液中的有机物还很容易造成树脂的污染，降低树脂的吸附和交换能力，对于 TOC 量大的情况下吸附则显得不合适。此外，由于树脂吸附或离子交换系统一般都是在密闭空间中（如吸附柱和离子交换柱）进行，由于过氧化氢的不稳定性，有机物在树脂上的累积还容易造成安全隐患。

活性炭是广泛使用的吸附剂。一般而言，由于其具有发达的孔隙结构及大的比表面积，因而对气相和液相中的有机物都具有极好的吸附作用。但是对于象过氧化氢溶液这样的体系，研究表明，活性炭会加剧过氧化氢的分解，关于过氧化氢催化分解机理的论述众多，有链式反应、氧化还原反应、游离基反应、过氧化合物中间物形成原理、扩散机理、吸附机理等等。活性炭孔道中残存的一些金属元素（如 Fe、Mn、Cu 等）以及过氧化氢水溶液中存在的一些痕量的金属离子，也会加快过氧化氢分解。除金属离子引起过氧化氢均相催化分解外，金属固体微粒及离子还可能引起过氧化氢的多相催化分解和络合物催化分解，此外，在活性炭存在的情况下，一些阴离子也可能使过氧化氢催化分解。这是活性炭基吸附剂的最大缺点。

此外还有膜分离法、萃取法和重结晶法的过氧化氢的精制过程。膜分离法虽然能去除有机物，设备及工艺简单，生产条件温和、操作可靠简便。但对膜材料质量要求高，使用寿命短。萃取法操作简单，有机杂质去除率高，物耗、能耗较低，但对设备要求高、投资较大。而重结晶法可获得高浓度、高纯产品，但须在低温冷冻条件下进行，耗能极高。

发明内容

本发明的目的在于针对现有活性炭基吸附剂会促进过氧化氢分解且对多种金属离子一起脱除效率低的不足的问题，提供一种有机络合物负载型活性炭吸附剂，通过添加有机络合组分对所选活性炭的负载改性，来抑制活性炭对过氧化氢的分解促进作用，同时能较好地保持对过氧化氢溶液中各种有机物的吸附能力，而添加的有机络合物对过氧化氢溶液

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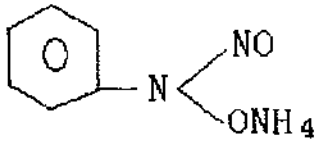
中的多种金属离子能形成络合物或沉淀并吸附在有机络合物负载型活性炭吸附剂上，从而使得过氧化氢溶液得到纯化。

本发明的目的还在于提供所述有机络合物负载型活性炭吸附剂的制备方法。

本发明的另一个目的是提供所述吸附剂用于过氧化氢溶液的纯化方法，通过用本发明的有机络合物负载型活性炭吸附剂进行吸附，过滤操作后，即可对过氧化氢溶液中的有机杂质和多种金属元素进行有效脱除，从而达到净化的目的。

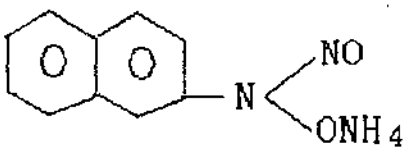
本发明的有机络合物负载型活性炭吸附剂，以活性炭为载体，有机络合物采用浸渍法负载到活性炭载体上，其特点是有机络合物主要分布在活性炭的孔道上，负载的有机络合物占负载型活性炭吸附剂重量的 0.05～8.0%；优选 0.5～6.0%

所述有机络合物为 N—亚硝基苯基羟胺的铵盐（Ⅰ）、N—亚硝基萘基羟胺的铵盐（Ⅱ）中的一种或两种；其中 N—亚硝基苯基羟胺的铵盐的化学结构式为



（Ⅰ），

N—亚硝基萘基羟胺铵盐的化学结构式为



（Ⅱ）。

负载的有机络合物占负载型活性炭吸附剂重量的 0.5～6.0%。

所述活性炭的 BET 法比表面积为 600～1300 m^2/g，优选 900～1100 m^2/g；孔径分布在 0.5～100 nm，且集中分布在 1～3nm；峰值在 1.2～1.5 nm 处。

所述活性炭的孔径分布在 1～30 nm。

所述的有机络合物负载型活性炭吸附剂的制备方法包括以下步骤：

（1）配制有机络合物浸渍液：有机络合物溶于有机溶剂中；所述溶剂为乙醇、丙酮或者四氢呋喃中的一种或几种。

（2）配制淋洗液：有机溶剂和去离子水配制成有机溶剂的浓度为 0.5～10.0%重量的水溶液作为淋洗液，所述溶剂为乙醇、丙酮或者四氢呋喃中的一种或几种；

（3）经抽真空处理的活性炭浸没在浸渍液中 0.1～72 小时，浸渍液中的有机溶剂与活性炭的质量比为 2.0～3.0∶1，优选 2.2～2.5∶1。

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（4）抽真空脱除溶剂；

（5）用淋洗液冲洗步骤（4）所得的样品，对样品边淋洗边进行真空抽滤、每次淋洗所用淋洗液与活性炭的质量比为 2.5～4.0∶1；

（6）用去离子水对样品边冲洗边进行真空抽滤，去离子水与活性炭的质量比为 2.5～4.5∶1，干燥，得到有机络合物负载型活性炭吸附剂。

步骤（3）所述的抽真空处理的活性炭由下述方法得到：活性炭先用浓度为 5～20%重量（优选 8～12%）的稀酸溶液在 40～50℃下进行浸泡、清洗、滤干，然后用去离子水反复洗涤，烘干待用；所用稀酸可为盐酸或硝酸；然后在真空度为 9.5×10^4Pa 或以上，保持 2～4 小时。

步骤（4）所述抽真空脱除溶剂是在 45～60℃下，真空度为 9.5×10^4Pa 或以上，保持 0.5～4 小时脱除溶剂。

步骤（6）所述干燥是真空干燥，条件为温度 50～70℃，真空度在 9.8×10^4Pa 或以上，保持 1～72 小时。

所述有机络合物负载型活性炭吸附剂用于纯化过氧化氢溶液的方法，包括：将吸附剂加入到过氧化氢溶液中，进行吸附，过滤；所述吸附剂的用量占过氧化氢溶液重量的 0.05～2.0%（优选 0.3～1.2%，最佳在 0.5～1.0%），过氧化氢溶液的浓度为 20～55%重量；吸附是在 5～40℃下缓慢搅拌 0.1～24 小时；得到纯化的过氧化氢溶液。

本发明与现有技术相比具有如下优点：

（一）选择本发明所述的具有一定孔隙结构和比表面的活性炭，先通过稀酸除去活性炭中的无机杂质，然后通过抽真空再浸渍的方法将所选有机络合物组分均匀分布在活性炭的大部分的孔道上，特别是分布在较小的孔道里。既对活性炭孔道中残存的的金属元素如 Cu、Fe、Mn、Ni 等离子进行络合，抑制这些金属离子杂质对过氧化氢的分解作用，也可对过氧化氢溶液中多种金属离子杂质进行络合并沉积在吸附剂的孔道内，从而达到纯化的目的。此外，还能较好地保持活性炭对多种有机物良好的吸附功能。

（二）通过步骤（5）、步骤（6）的处理，尽量减少本发明所述有机络合物组分在所选活性炭载体颗粒外表面上的分布量，使得有机络合物组分主要分布在活性炭颗粒的内孔上，形成类似“蛋黄”型的分布。从而使得负载的有机络合物和过氧化氢溶液中的各种金属离子形成络合物或沉淀的过程主要发生在活性炭内表面上。另外，还可以防止有机络合物扩散到过氧化氢溶液中去，造成有机络合剂典型的显示特征颜色的现象出现，造成对过氧化氢溶液形成的新的有机物污染。

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（三）使用本发明的有机络合物负载的活性炭吸附剂，在室温下对过氧化氢溶液进行吸附，再过滤除去吸附剂，即可对过氧化氢溶液中的有机物杂质及多种金属离子进行有效的脱除，从而达到对过氧化氢溶液进行净化的目的。

（四）上述对过氧化氢溶液纯化的方法和传统的蒸馏、树脂吸附、离子交换树脂交换等工艺相比，操作简单、能耗低，安全性高；和过去公开的专利所提及的活性炭吸附工艺相比，除了也能较好地脱除有机物外，还能较好地抑制过氧化氢的分解，而且还可以对过氧化氢溶液中的多种金属离子同时进行络合吸附脱除，具多重的功能。

（五）本发明的有机络合物负载活性炭吸附剂适用于过氧化氢溶液，特别是含有机物杂质较多的工业级过氧化氢溶液的纯化。

具体实施方式

本发明实施例中，过氧化氢溶液的总有机物含量（TOC）数据由 OI Analytical 1020 型 TOC 测定仪（美国）测定，金属元素含量则由 Elan 6100 型 ICP－MS 电感耦合等离子质谱仪（美国 PE 公司）检测。过氧化氢含量按照 GB/T 6684-2002 测定。所用去离子水（纯水）由 Milli－Q （美国）纯水制备仪制备。

实施例 1

按下述步骤制备本发明的有机络合物负载型活性炭吸附剂，并进行过氧化氢溶液的吸附纯化的操作。

（1）取具有本发明所要求的宏观结构的活性炭 10g 作为载体，用 100ml 浓度为 10% 重量的稀盐酸溶液在 50℃下浸泡 2 小时、清洗、滤去酸液、然后用 1000ml 的去离子水分 5 次反复浸泡、洗涤，滤干，在 120℃下烘干；

（2）称取 N－亚硝基苯基羟胺的铵盐（Ⅰ）0.21g 溶于 30ml 丙酮中，制得浸渍液；

（3）配制 2.0%重量丙酮水溶液作为淋洗液，备用；

（4）将按步骤（1）预处理过的活性炭置于带搅拌的密闭容器内，抽真空 3 小时，真空度保持在 9.5×10^{4}Pa 或以上；

（5）在常温下，吸入按步骤（2）制得的浸渍液，并保持浸渍液能浸没密闭容器内的活性炭。关闭真空，使密闭容器内压力回复至常压，保持缓慢搅拌 3 小时，然后静置过夜；

（6）抽真空、真空度保持在 9.5×10^{4} Pa 或以上，逐渐升温至 50℃，保持 3 小时，脱除溶剂丙酮；

（7）将步骤（6）所得的样品置于带真空抽滤的过滤漏斗中，取步骤（3）配制的淋

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洗液 40ml，边淋洗边抽真空过滤，滤去淋洗液。

（8）将步骤（7）得到的滤饼再重复步骤（6）、步骤（7）两次；

（9）在真空抽滤装置中，用 40 ml 去离子水快速冲洗样品，同时真空抽滤，滤去水分。共冲洗 3 次。

（10）升温至 60℃，保持真空度在 9.8×10^4 Pa 或以上进行真空干燥 20 小时，获得 N－亚硝基苯基羟胺的铵盐负载型活性炭吸附剂，其中 N－亚硝基苯基羟胺的铵盐占吸附剂约 2 %重量；

(11)在 20 ℃下，取 1.0g 按上述方法制得的有机络合物负载型活性炭吸附剂，分散缓缓加入到 100 ml 浓度为 35.6%重量的工业过氧化氢溶液中，缓慢搅拌，吸附过程保持 3 小时。

（12）过滤，除去有机络合物负载型活性炭吸附剂，得到纯化了的过氧化氢溶液。

实施例 2～3

仅改变实施例 1 中(2)步骤，分别称取 0.42g、0.62g 的 N－亚硝基苯基羟胺铵盐（Ⅰ），其余步骤按照实施例 1 进行。制成 N－亚硝基苯基羟胺的铵盐分别占吸附剂约 4%、6%重量的 N－亚硝基苯基羟胺的铵盐负载型活性炭吸附剂，然后用于过氧化氢溶液的纯化。

实施例 4

仅改变实施例 1 中（2）步骤，称取 0.21g N－亚硝基萘基羟胺铵盐（Ⅱ），其余步骤按照实施例 1 进行。制成 N－亚硝基萘基羟胺铵盐占吸附剂约 2%重量的 N－亚硝基萘基羟胺铵盐负载型活性炭吸附剂，然后用于过氧化氢溶液的纯化。。

实施例 5

仅改变实施例 1 中（2）步骤，分别称取 0.21g N－亚硝基苯基羟胺铵盐（Ⅰ）和 0.21g N－亚硝基萘基羟胺铵盐（Ⅱ）并进行混合，其余步骤按照实施例 1 进行。制成两种有机络合物共占吸附剂约 4%重量的有机络合物负载型行活性炭吸附剂，然后用于过氧化氢溶液的纯化。

比较例 1

取浓度为 35.6%重量的某工业级过氧化氢原液作为比较样品。

比较例 2

取 1g 具有本发明所要求的宏观结构的活性炭作为吸附剂，按照实施例 1 中步骤(11)和步骤（12）进行吸附、过滤操作，得到处理后的过氧化氢溶液作为比较样品。

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采用上述的吸附剂对过氧化氢溶液进行处理后所得的结果见表 1、表 2 和表 3。其中表 1 是对过氧化氢溶液中 H_2O_2 分解的影响；表 2 是对过氧化氢溶液中 TOC 的脱除影响；表 3 是对工业过氧化氢溶液中各金属离子的络合吸附脱除的影响。

表 1 中的结果表明了单纯的活性炭载体在净化过程中对过氧化氢造成的分解率高，达到 12.75%（见比较例 2），而采用本发明的有机络合物活性炭吸附剂对过氧化氢溶液中过氧化氢的分解有明显的抑制作用，实施例 2 和实施例 5 可将分解率降至 6%以下。

表 1

项目	实施例 1	实施例 2	实施例 3	实施例 4	实施例 5	比较例 1	比较例 2
H_2O_2 浓度/%	32.16	33.50	33.32	32.24	33.65	35.6	31.06
H_2O_2 的分解率/%	9.66	5.90	6.40	9.44	5.48	-------	12.75

注：①工业过氧化氢（H_2O_2）溶液原液的浓度为 35.6%重量。

② H_2O_2 分解率 $= \dfrac{H_2O_2 \text{ 溶液原液的浓度} - \text{处理后 } H_2O_2 \text{ 溶液的浓度}}{H_2O_2 \text{ 溶液原液的浓度}} \times 100\%$

表 2 的结果表明，本发明的络合物负载型活性炭吸附剂对过氧化氢溶液中的有机物（以 TOC 数值表示）的脱除保持了较好的脱除率。

表 2

项目	实施例 1	实施例 2	实施例 3	实施例 4	实施例 5
TOC/ppm	24.42	33.62	35.80	21.95	30.28
TOC 的脱除率/%	82.74	76.24	74.70	84.49	78.60

注：①工业过氧化氢（H_2O_2）溶液原液的 TOC 为 141.49 ppm 。

②总有机物脱除率 $= \dfrac{H_2O_2 \text{ 溶液原液的 TOC} - \text{处理后 } H_2O_2 \text{ 溶液的 TOC}}{H_2O_2 \text{ 溶液原液的 TOC}} \times 100\%$

表 3 的结果表明，采用本发明的络合物负载型活性炭吸附剂及其应用，对过氧化氢溶液中的 Al、Ti、Cr、Mn、Fe、Ni、Cu、Zn、Ga、Rb、Sr、Mo、Ag、Sb、W、Au、Hg 等金属离子能同时进行络合脱除，使得过氧化氢溶液得以纯化。

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表 3

	经吸附剂处理后 H_2O_2 溶液中阳离子浓度 / ppb						
离子	实施例 1	实施例 2	实施例 3	实施例 4	实施例 5	比较例 1	比较例 2
Li	1.57	0.93	1.53	0.48	0.90	0.28	1.26
Be	0.69	0.52	0.69	0.34	0.73	1.67	0.29
Na	9974.96	9960.62	9925.89	10318.11	10930.34	10201.50	10564.71
Mg	118.34	109.54	109.73	104.08	121.91	89.45	140.99
Al	48.22	49.72	50.26	36.85	57.64	71.79	54.25
Si	0.31	0.27	0.24	0.19	0.00	0.00	0.00
K	1556.01	1534.84	1485.12	1296.85	1434.87	1160.56	1504.62
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sc	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	27.90	16.73
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	23.90	0.00
Mn	36.17	35.06	37.45	36.44	39.52	40.41	36.33
Fe	0.00	0.00	0.00	0.00	0.00	282.11	134.06
Co	1.57	1.32	0.14	0.96	2.21	1.77	1.36
Ni	26.54	22.53	25.73	22.91	25.35	38.20	38.10
Cu	4.02	0.90	13.55	4.42	4.28	22.17	10.00
Zn	52.34	38.28	55.45	38.93	82.42	171.89	131.39
Ga	0.00	0.00	0.00	0.00	1.45	1.91	1.36
Ge	0.00	0.00	0.00	0.00	0.00	0.20	0.00
As	0.47	0.65	0.59	0.00	0.44	0.62	0.45
Se	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Br	0.04	0.04	0.06	0.09	0.00	0.00	0.00
Rb	0.00	0.00	0.00	0.00	0.00	1.15	10.89
Sr	5.24	4.35	5.96	4.87	5.83	6.26	6.95
Y	0.00	0.00	0.00	0.00	0.01	0.07	0.00
Zr	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Nb	0.00	0.00	0.00	0.00	0.86	0.84	0.43
Mo	0.20	0.12	0.18	0.11	0.08	3.64	0.57
Ru	0.00	0.00	0.00	0.00	0.00	0.06	0.06
Rh	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Pd	0.00	0.00	0.00	0.00	0.05	0.13	0.00
Ag	0.00	0.00	0.00	0.00	3.70	6.02	4.24
Cd	0.00	0.00	0.00	0.00	0.00	0.42	0.00
In	0.00	0.00	0.00	0.00	0.37	0.12	0.00
Sn	0.00	0.00	0.00	0.00	0.08	928.53	0.00
Sb	0.00	0.00	0.00	0.00	0.00	9.02	11.23
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cs	0.04	0.06	0.05	0.04	0.03	0.03	0.24
Ba	78.97	79.25	85.55	77.23	26.66	51.58	50.40
La	0.00	0.00	0.00	0.00	0.00	0.07	0.00
Ce	0.02	0.01	0.03	0.02	0.01	0.15	0.01

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Pr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nd	0.00	0.00	0.00	0.00	0.00	0.04	0.00
Sm	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eu	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Gd	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Tb	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dy	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ho	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Er	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Tm	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yb	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lu	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hf	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ta	0.00	0.00	0.00	0.00	0.00	0.00	0.00
W	0.60	0.46	0.51	0.39	0.28	2.30	2.44
Re	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Os	0.01	0.00	0.01	0.00	0.06	0.00	0.02
Ir	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pt	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	5.76	4.39	4.37	4.07	5.82	6.71	6.89
Hg	0.00	0.00	0.00	0.00	0.03	0.95	0.64
Tl	0.00	0.00	0.01	0.01	0.01	0.00	0.01
Pb	3.61	4.18	4.92	5.47	4.27	6.20	1.71
Bi	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Th	0.00	0.00	0.00	0.01	0.00	0.01	0.00
U	0.02	0.02	0.04	0.01	0.06	0.02	0.05

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Watersoluble polyurethane adsorption agent containing sulfhydryl group for removing hydrargyrum and preparation method thereof

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Abstract of CN101293196 (A)

The present invention pertains to the technical field of wastewater treatment, in particular to hydrophilic polyurethane absorbent containing sulfhydryl for removing Hg and a preparation method thereof. The present invention takes water and volatile non-water solvent as the mixed solvent, introduces chloromethyl thiirane monomer as the cross linking agent into hydrophilic polyurethane dispersion dope and finally carries out coating and solidification, thus obtaining the hydrophilic polyurethane absorbent containing sulfhydryl. The present invention has the advantages of simple and convenient technique, high production efficiency, high product quality and low cost. The composition of the prepared absorbent is controllable with the size of 50 to 250mm, the prepared absorbent has the advantages of large specific surface area, strong Hg-ion absorption capacity and rapid absorption rate.; In addition, the present invention with excellent high-concentration Hg-ion absorption capacity and trace Hg-ion absorption capacity, good mechanical property and damage ratio lower than 0.5 percent after being used for a plurality of times can be applied to Hg, lead, cadmium and other heavy metal industrial wastewater treatment within a more extensive concentration range.

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[54] 发明名称

一种除汞用含巯基水性聚氨酯吸附剂及其制备方法

[57] 摘要

本发明属废水处理技术领域，具体为一种除汞用含巯基水性聚氨酯吸附剂及其制备方法。本发明以水和挥发性非水溶剂为混合溶剂，将环硫氯丙烷单体作为交联剂引入到水性聚氨酯分散体涂料中，最后进行涂膜和固化处理，而制得含巯基水性聚氨酯吸附剂。本发明方法工艺简便、生产效率高、产品质量高、成本低廉。所制备的吸附剂组成可控，尺寸在 50～250nm 之间，比表面积大，对汞离子的吸收能力强，吸收速度快；具有优异的高浓度汞离子吸附性能，和优异的痕量汞离子吸附性能，并且力学机械性能良好，多次使用后其破损率低于 0.5%，可应用于浓度范围更广泛的含汞、铅、镉等重金属工业污水的处理。

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1、一种除汞用含巯基水性聚氨酯吸附剂，其特征在于由下述方法制备获得：以水和挥发性非水溶剂为混合溶剂，将环硫氯丙烷单体作为交联剂引入到水性聚氨酯分散体涂料中，最后进行涂膜和固化处理，制得一种含巯基水性聚氨酯吸附剂。

2、一种除汞用含巯基水性聚氨酯吸附剂的制备方法，其特征在于具体步骤如下：

(1) 将二异氰酸酯、聚酯多元醇、2，2’-二羟甲基丙酸、催化剂以及有机溶剂以 100：300～400：10～50：0.05～5：300～500 的重量比例混合均匀，升温反应一定时间，使反应趋于完成，即得以异氰酸酯封端的聚氨酯预聚物；将上述异氰酸酯封端的聚氨酯预聚物、扩链剂、催化剂以及有机溶剂，按以 100：1～50：0.5～2：50～200 的重量比例搅拌混合均匀，温度控制在 58～65℃，反应持续 4～12 小时，温度降低至 45～55℃，再加入 0.5～5g 三乙胺，反应 15～60 分钟；量取 50～300mL 去离子水，缓慢滴加入到上述混合物中，保持整个滴加时间为 30～60 分钟，温度为 45～50℃；滴加完毕后，温度为 30～38℃，再继续反应 15～45 分钟，真空抽滤除去有机溶剂后，得到一种水性聚氨酯分散体涂料，固含量为 25～55%；

(2) 采用 20~200 mL 水和 20~200 mL 挥发性非水溶剂为混合溶剂，其中水和挥发性非水溶剂的体积比为 1：0.5~5；称取 50~150 g 上述水性聚氨酯分散体涂料，用 20~200 mL 水-挥发性非水溶剂混合溶剂浸泡 2～24 小时，加入 5~50 g 环硫氯丙烷，其中环硫氯丙烷浓度保持在 5~15%；45~90℃下反应 2~12 小时，然后加入氢氧化钠溶液调节 pH 值至 10~14，再继续反应 6~36 小时；最后制得一种含巯基水性聚氨酯涂料，固含量为 25～55%，聚氨酯涂料中巯基的含量在 1.15×10^{-4}~6.0×10^{-3}mmol/g；

(3) 将上述含巯基水性聚氨酯涂料均匀涂于基体表面，进行热固化处理或 UV 固化处理后，制备得到一种除汞用含巯基水性聚氨酯吸附剂。

3、根据权利要求 2 所述的除汞用含巯基水性聚氨酯吸附剂的制备方法，其特征在于，所述所说的二异氰酸酯是甲苯-2,4-二异氰酸酯、甲苯-2,6-二异氰酸酯、4,4’-二苯基甲烷二异氰酸酯、1,5-萘二异氰酸酯、乙苯二异氰酸酯、4,6-二甲苯二异氰酸酯、3,3’-二甲基联苯-4,4’-二异氰酸酯或 3,3’-二甲基-4,4’-二苯基甲烷二异氰酸酯，或者是己二异氰酸酯、六亚甲基二异氰酸酯、环己基二异氰酸酯、4,4’-二环己基甲烷二异氰酸酯或异佛儿酮二异氰酸酯；所说的聚酯多元醇是己二酸聚酯多元醇、苯酐聚酯多元醇、聚己内酯多元醇、高分子量聚酯多元醇、带侧基的特种聚酯多元醇或聚碳酸酯二元醇；所说的催化剂是二丁基锡二月桂酸酯、辛酸亚锡、N－甲基吗啉或者三亚乙基二胺；所述的扩链剂是乙二胺、丙二胺、

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1,4-丁二胺、己二胺等，可以是乙二醇、丙二醇、1,3-丁二醇、1，4-丁二醇、新戊二醇、1，2-戊二醇、1,5-戊二醇、1,6-己二醇、2-乙基-1,3-己二醇、3-氯-1,2-丙二醇或癸二醇。

4、根据权利要求2所述的除汞用含巯基水性聚氨酯吸附剂的制备方法，其特征在于，所说的有机溶剂是丙酮、丁酮、甲苯、二甲苯、乙酸乙酯、N-甲基吡咯烷酮、N,N-二甲基甲酰胺或N,N-二甲基乙酰胺；所说的挥发性非水溶剂是乙醇、四氢呋喃、二氧六环或乙腈，或其中几种的混合物。

5、根据权利要求2所述的除汞用含巯基水性聚氨酯吸附剂的制备方法，其特征在于，所述基体为无机或有机基体，无机基体为多孔玻璃、硅藻土、活性炭、石英砂、硅胶、玻璃纤维布、Al_2O_3多孔陶瓷、Al_2O_3微滤或超滤膜，有机基体为聚乙烯膜、聚四氟乙烯板、棉花、涤纶布、锦纶布、尼龙布或无纺布。

6、根据权利要求2所述的除汞用含巯基水性聚氨酯吸附剂的制备方法，其特征在于，所说的热固化处理，是将涂覆后的成型品放入恒温箱内，使成型品被远红外线照射或热风加热固化，温度控制在60～100℃；所说的UV固化处理，是被涂覆后的成型品在特定波长的紫外线照射下，利用光化学反应使涂膜固化。

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一种除汞用含巯基水性聚氨酯吸附剂及其制备方法

技术领域

本发明属废水处理技术领域，具体涉及一种除汞用含巯基水性聚氨酯吸附剂及其制备方法。

背景技术

汞在造纸、涂料、化妆品、防腐剂、温度计、压力表、荧光灯和电池等工业领域中的应用越来越广泛，同时，汞也会带来一种严重的环境污染问题。在所有工业重金属污水排放中，汞是对环境影响最大的一种污染物质。据估计，全球每年自然界、人为和海洋喷射等新增加的汞污染高达 5500 吨，因此含汞废水的处理，直接关系到人类的身心健康。如何高效的处理汞，成为了人类面临的极为重要的难题。

传统的含汞废水的处理方法主要有化学沉淀法、金属还原法、吸附法、离子交换法、膜分离法、微生物法等。

化学沉淀法是应用较普遍的一种含汞废水的处理方法，该法具有工艺简单、操作方便、经济实用等优点。常见的沉淀剂为石灰、硫化物、聚合硫酸铁、碳酸盐，以及它们的混合物。化学沉淀法易于快速去除大量的汞金属离子，但由于受沉淀剂和环境条件的影响，出水浓度往往达不到排放要求，因此还需进一步处理，产生的沉淀物必须很好的处理处置，否则会造成二次污染。

离子交换法处理含汞废水，净化程度高，无二次污染，但该法受废水中杂质的影响以及交换剂品种、产量和成本的限制。

电渗析是膜分离技术的一种，它是在直流电场作用下，以电位差为推动力，利用离子交换膜的选择性，把电解质从溶液中分离出来，从而实现溶液的淡化、浓缩、精制或纯化的目的。处理含汞废水的其它膜技术还有：反渗透法、液膜法、超滤等。但是膜在处理废水时选择性比较高，不同的废水必须研究与之相匹配的膜，废水的成分也必须比较稳定才行，膜组件的设计也是一个难题，膜法处理废水的投资也比较高，这些都影响了膜的应用。

吸附法是利用多孔性的固体物质，使水中的一种或多种物质被吸附在固体表面而除去的方法。可用于处理含汞废水的吸附剂有：活性炭、风化煤、磺化煤、高炉矿渣、沸石、壳聚糖、硅藻土、改良纤维、活性氧化铝、蛋壳等。这些吸附剂处理含汞废水的机理不尽相同，有的是物理吸附占主导，有的是化学吸附占主导，有的吸附剂既起吸附作用，又起

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絮凝作用。吸附法具有去除率高、设备相对简单等特点。吸附剂处理含汞废水的控制条件比较多，如吸附剂的粒度、吸附剂的添加量、废水的成分、废水的含铬浓度、pH 值、吸附时间等。因此，仍然需要开发高效、成本低廉和使用方便的新型吸附剂材料体系及其制备技术。

基于上述原因，吸附法对于处理含汞废水效果良好。关键是制备出工作容量大、制备工艺简单、无二次污染、环境协调性优越、性能价格比高、利于回收的吸附剂，从而提供控制和防治含有高浓度或微痕量汞离子浓度污染的新工艺和新技术。

目前国内外还没有关于一种除汞用含巯基水性聚氨酯吸附剂的制备方法的公开文献报道和专利申请。

发明内容

本发明的目的在于克服现有技术存在的不足，提供一种工作容量大、制备工艺简单、无二次污染、利于回收的除汞用含巯基水性聚氨酯吸附剂及其制备方法。

本发明将环硫氯丙烷单体作为交联剂引入到水性聚氨酯分散体涂料中，再将之均匀涂覆于基体表面制备一种除汞用含巯基水性聚氨酯吸附剂。由于该含巯基水性聚氨酯吸附剂中带有的大量功能性基团如巯基、聚硫醚、氨基以及酰胺基等所产生的对汞重金属离子的多重吸附作用，从而对含高浓度汞离子或微痕量汞离子的废水，产生极强的吸附效果，达到净化水体的目的。本发明的制备方法具有简单工艺方便、无污染、环境友好、涂膜质量高、投入产出比高、成本低廉和应用前景广泛等优点，

本发明提出的除汞用含巯基水性聚氨酯吸附剂，由下述方法制备获得：以水和挥发性非水溶剂为混合溶剂，将环硫氯丙烷单体作为交联剂引入到水性聚氨酯分散体涂料中，最后进行涂膜和成型处理，制得一种含巯基水性聚氨酯吸附剂。

本发明提出的一种含巯基水性聚氨酯吸附剂的制备方法，具体步骤如下：

(1) 将二异氰酸酯、聚酯多元醇、2，2’-二羟甲基丙酸、催化剂以及有机溶剂以 100：300～400：10～50：0.05～5：300～500 的重量比例混合均匀，升温反应一定时间，使反应趋于完成，即得以异氰酸酯封端的聚氨酯预聚物。将上述异氰酸酯封端的聚氨酯预聚物、扩链剂、催化剂以及有机溶剂，按 100：1～50：0.5～2：50～200 的重量比例搅拌混合均匀，温度控制在 58～65℃，反应持续 4～12 小时，温度降低至 45～55℃，再加入 0.5～5g 三乙胺，反应 15～60 分钟。量取 50～300mL 去离子水，缓慢滴加入到上述混合物中，保持整个滴加时间为 30～60 分钟，温度为 45～50℃。滴加完毕后，温度为 30～38℃，再继续反应 15～45 分钟，真空抽滤除去有机溶剂后，得到一种水性聚氨酯分散体涂料，固含

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量为25～55%。

(2) 采用20~200 mL水和20~200 mL挥发性非水溶剂为混合溶剂，其中水：挥发性非水溶剂 = 1：0.5~5（体积比）。称取50~150 g上述水性聚氨酯分散体涂料，用20~200 mL水-挥发性非水溶剂混合溶剂浸泡2～24小时，加入5~50 g环硫氯丙烷，其中环硫氯丙烷浓度保持在5~15%。45~90 ℃下反应2~12小时，然后加入2%氢氧化钠溶液调节pH值至10~14，再继续反应6~36小时，最后制得含巯基水性聚氨酯涂料，固含量为25～55%，聚氨酯涂料中巯基的含量在1.15×10^{-4}~6.0×10^{-3}mmol/g。

(3) 将上述含巯基水性聚氨酯涂料均匀涂于基体表面，进行热固化处理或UV固化处理，即制备得到除汞用含巯基水性聚氨酯吸附剂。最后进行汞吸附性能测试。

本发明提出的除汞用含巯基水性聚氨酯吸附剂的制备方法中，所说的二异氰酸酯，可以是是芳香族二异氰酸酯，如甲苯-2,4-二异氰酸酯、甲苯-2,6-二异氰酸酯、4,4'-二苯基甲烷二异氰酸酯、1,5-萘二异氰酸酯、乙苯二异氰酸酯、4,6-二甲苯二异氰酸酯、3,3'-二甲基联苯-4,4'-二异氰酸酯或3,3'-二甲基-4,4'-二苯基甲烷二异氰酸酯，或者脂肪族二异氰酸酯，如己二异氰酸酯、六亚甲基二异氰酸酯、环己基二异氰酸酯、4,4'-二环己基甲烷二异氰酸酯或异佛尔酮二异氰酸酯等。所说的聚酯多元醇，可以是己二酸聚酯多元醇、苯酐聚酯多元醇、聚己内酯多元醇、高分子量聚酯多元醇、带侧基的特种聚酯多元醇或聚碳酸酯二元醇等；所说的催化剂，可以是二丁基锡二月桂酸酯、辛酸亚锡、N一甲基吗啉或者三亚乙基二胺，用量为0.1%－2%重量；所说的有机溶剂，可以是丙酮、丁酮、甲苯、二甲苯、乙酸乙酯、N-甲基吡咯烷酮或N,N-二甲基甲酰胺和N,N-二甲基乙酰胺等。所述的扩链剂，采用二元胺或者二元醇，可以是乙二胺、丙二胺、1,4-丁二胺、己二胺等，可以是乙二醇、丙二醇、1,3-丁二醇、1，4-丁二醇、新戊二醇、1，2-戊二醇、1,5-戊二醇、1,6-己二醇、2-乙基-1,3-己二醇、3-氯 1,2 丙二醇或癸二醇等。所说的挥发性非水溶剂，采用低沸点、高极性的有机溶剂，可以是乙醇、四氢呋喃、二氧六环或乙腈，或其中几种的混合物。

本发明提出的除汞用含巯基水性聚氨酯吸附剂的制备方法中，所述基体包括无机和有机基体，无机基体包括多孔玻璃、硅藻土、活性炭、石英砂、硅胶、玻璃纤维布、Al_2O_3多孔陶瓷、Al_2O_3微滤或超滤膜等，有机基体包括聚乙烯膜、聚四氟乙烯板、棉花、涤纶布、锦纶布、尼龙布或无纺布等。

本发明提出的除汞用含巯基水性聚氨酯吸附剂的制备方法中，所说的热固化处理，可以是：将涂覆后的成型品放入恒温箱内，使成型品被远红外线照射或热风加热固化。通常温度控制在60～100℃左右。所说的UV固化处理，可以是：被涂覆后的成型品在特定波长的紫外线（UV）照射下，利用光化学反应使聚氨酯涂膜固化的方法。

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本发明提出的除汞用含巯基水性聚氨酯吸附剂，它不仅能保证吸附剂具有足够的力学强度和尺寸稳定性等物理与力学性能，而且它能显著提高该聚合物材料在高浓度汞离子存在下对汞离子的吸附性能，和在微/痕量汞离子环境下对汞离子的有效吸收性能。

本发明提出的除汞用含巯基水性聚氨酯吸附剂，其制备方法简便易行，合成效率高，硫醇、硫醚、氨基以及酰胺基等活性吸附基团数量多，所制备吸附剂的汞离子吸附性能优异，应用范围广泛，尤其在含汞、铅、镉等重金属工业废水处理方面有广泛应用前景。

本发明的优点在于：（1）该方法制备的聚氨酯吸附剂具有优异的高浓度汞离子吸附性能，和优异的微/痕量汞离子吸收性能。（2）该方法制备的聚氨酯吸附剂，不但保持了水性聚氨酯材料对水介质有效的溶胀和接触效率，而且还通过与环硫氯丙烷单体交联反应来保证水性聚氨酯材料具有足够的力学强度和尺寸稳定性等物理与力学性能。（3）该方法制备的含巯基聚氨酯吸附剂具有组成可控，其尺寸在50～250nm之间，使得该吸附剂表面具有大比表面积，大幅增加了其与汞离子的接触机会，提高了其对汞离子的吸收能力和吸收速度。（4）最后，本发明的制备方法具有工艺简便、生产效率高、产品质量高和成本低廉等优点，是新一代高性能高效除汞产品，可应用于浓度范围更广泛的含汞等重金属工业污水的处理领域。

本发明所制备的除汞用含巯基水性聚氨酯吸附剂的损失率采用下列方法测定：将本发明中制得的吸附剂，准确称取0.5g放入100mL蒸馏水中，在30°C的恒温水浴中搅拌24h，过滤，取出样品，自然晾干后称重，根据处理前后的重量变化计算损失率。由3次以上重复实验取其平均值。

本发明所制备的含巯基水性聚氨酯吸附剂吸附汞离子的吸附容量和去除率，采用静态吸附法检测，步骤如下：

室温下，称取0.5 g样品投入100ml锥形瓶中，该锥形瓶再分别加入25mL不同浓度C_0下的汞离子溶液（0.1 g/L、0.5 g/L、1 g/L、5 g/L、10 g/L、20 g/L），调解pH值为7，在室温下搅拌吸附45分钟，过滤，用意大利DMA-80测汞仪测出稀释测定液中Hg^{2+}的浓度C_1。根据式（1）和（2）分别计算吸附剂的吸附容量Q（mg/g）和去除率q（%）。

$$Q = (C_0 - C_1) * 25 / 0.5 \qquad (1)$$

$$q = (C_0 - C_1) * 100\% / C_0 \qquad (2)$$

具体实施方式

下面结合实施例对本发明一种除汞用含巯基水性聚氨酯吸附剂的制备方法进行详细的说明。但本发明并不限于所列出的实例。

实施例1

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将异佛儿酮二异氰酸酯、己二酸聚酯多元醇、2，2'-二羟甲基丙酸、二丁基锡二月桂酸酯和丙酮以100：360：40：2：400(重量)的比例混合均匀，升温到60℃反应8小时，使反应趋于完成，即得以异氰酸酯封端的聚氨酯预聚物；再将以异氰酸酯封端的聚氨酯预聚物、1，4-丁二醇、二丁基锡二月桂酸酯以及丙酮，以100：12：1：100(重量)的比例，搅拌均匀，温度控制在60℃左右，反应持续5小时，再加入3g三乙胺，温度降低至45℃，反应30分钟。量取125ml去离子水，缓慢滴加入到上述混合物中，保持整个滴加时间为45分钟。滴加完毕后，再继续反应30分钟。35℃真空下除去丙酮后，得到一种水性聚氨酯分散体涂料，其固含量35%。

采用100 mL水和100 mL二氧六环为混合溶剂，其中水：二氧六环 = 1：1（体积比）。称取20 g上述水性聚氨酯分散体涂料，用水-二氧六环混合溶剂浸泡12小时，加入20 mL环硫氯丙烷，其中环硫氯丙烷浓度保持在10%以下。75 ℃下反应2小时后，加入2%氢氧化钠溶液调节pH值至11，再继续反应14小时。最后制得一种含巯基水性聚氨酯涂料，其固含量30%，由返银量滴定法测定聚氨酯涂料中巯基的含量为9.7×10^{-4}mmol/g。采用溶液共混法将活性碳和上述含巯基聚氨酯涂料以重量比1:8混合均匀，再经过过滤和烘干处理得到一种含巯基水性聚氨酯吸附剂，烘干温度为90℃，烘干时间为3.5小时，活性碳表面的聚氨酯涂覆层厚度为22μm。

经损失率试验，该含巯基水性聚氨酯吸附剂的损失率为0.3%。经静态吸附法检测，该吸附剂对25mL初始浓度为0.1 g/L的硝酸汞吸附45分钟，测得其残余汞离子浓度为0.76 mg/L，其吸附容量为4.96 mgHg/g吸附剂，汞去除率为99.2%。经静态吸附法检测，该吸附剂对25mL初始浓度为20 g/L的硝酸汞吸附45分钟，测得其残余汞离子浓度为102.5 mg/L，其吸附容量为994.9 mgHg/g吸附剂，汞去除率为99.5%。

实施例2

与实施例1相同，但是环硫氯丙烷的用量由20mL变为30mL，由返银量滴定法测定吸附剂中巯基的含量为1.28×10^{-3}mmol/g。

实施例3

与实施例1相同，但是环硫氯丙烷的用量由20mL变为10mL，由返银量滴定法测定吸附剂中巯基的含量为4.24×10^{-4}mmol/g。

实施例4

与实施例1相同，但是异佛儿酮二异氰酸酯、己二酸聚酯多元醇、2，2'-二羟甲基丙酸、二丁基锡二月桂酸酯和丙酮的重量比由100：360：40：2：400变为100：360：40：6：400。

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实施例 5

与实施例 1 相同，但是异佛儿酮二异氰酸酯、己二酸聚酯多元醇、2，2'-二羟甲基丙酸、二丁基锡二月桂酸酯和丙酮的重量比由 100：360：40：2：400 变为 100：360：40：10：400。

实施例 6

与实施例 1 相同，但是采用 50 mL 水和 100 mL 二氧六环为混合溶剂，水：二氧六环 = 1：2。

实施例 7

与实施例 1 相同，但是采用 100 mL 水和 50 mL 二氧六环为混合溶剂，水：二氧六环 = 2：1。

实施例 8

与实施例 1 相同，但是采用溶液共混法将活性碳和上述含巯基聚氨酯涂料以重量比 1:4 混合均匀。

实施例 9

与实施例 1 相同，但是基体由活性炭变为硅胶。

实施例 10

与实施例 1 相同，但是基体由活性炭变为玻璃纤维布。

实施例 11

与实施例 1 相同，但是基体由活性炭变为棉花。

实施例 12

与实施例 1 相同，但是基体由活性炭变为尼龙布。

实施例 2~12 中获得的一种除汞用含巯基水性聚氨酯吸附剂与实施例 1 的吸附剂具有类似的性能。

由以上所述可见，本发明制备的一种除汞用含巯基水性聚氨酯吸附剂，它在高浓度汞离子环境下对汞离子的吸附率可高达 99.5%，在微/痕量汞离子环境下对汞离子的吸收率也可高达 99.2%。该吸附剂的力学机械性能良好，多次使用后其破损率可低于 0.5%以下。该发明具有制备工艺简单方便、生产效率高、产品质量高和成本低廉等优点，是新一代高性能高效除汞产品，可应用于浓度范围更广泛的含汞等重金属工业污水的处理领域。

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Chemically modified chitosan mercury-removing adsorbent and preparation process thereof

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Abstract of CN101816922 (A)

The invention discloses an adsorbent used for removing mercury (Hg0) in coal smoke and a preparation process thereof. The adsorbent comprises chitosan and halogen elements of bromine and iodine; as improvement, sulfuric acid is added, wherein the mass ratio of the chitosan to an iodine (bromine) compound to the sulfuric acid is (1-15):1:(0.5-5). The adsorbent is prepared by utilizing the reaction of the kali salt of the halogen elements of bromine and iodine and the sulfuric acid and better characteristics of the chitosan to the active iodine and the bromine under an acidy condition. The adsorbent has high Hg0 removal efficiency, lower cost, industrialized application and no secondary pollution of products.

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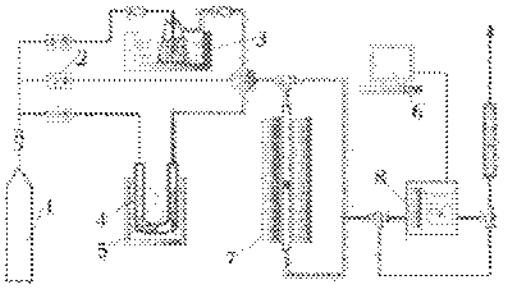
权利要求书 1 页 说明书 3 页 附图 1 页

(54)发明名称

化学改性壳聚糖吸附脱汞剂及其制备工艺

(57)摘要

本发明公开了一种用于脱除燃煤烟气中元素汞(Hg^0)的吸附剂及其制备工艺，包括壳聚糖和卤族元素(溴和碘)，作为改进，还添加了硫酸，其中壳聚糖、碘(溴)的化合物、硫酸的质量比为(1～15)：1：(0.5～5)。本工艺利用卤族元素(溴和碘)的钾盐与硫酸反应和在酸性情况下壳聚糖对活性碘和溴有较好吸附特性而制得。本发明吸附剂脱除Hg^0效率高，成本较低廉，产物不产生二次污染，可达到工业化应用要求。



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1. 一种用于脱除燃煤烟气中 Hg^0 的吸附剂，包括壳聚糖、硫酸、以及碘化钾或溴化钾，其中所述壳聚糖、硫酸与碘化钾或溴化钾的质量比为（1 ～ 15）：1：（0.5 ～ 5）。

2. 一种用于脱除燃煤烟气中 Hg^0 的吸附剂的制备工艺，包括如下步骤：

首先，称取 4-15 重量份的壳聚糖，加入 0.42-4 重量份的浓硫酸和适量的去离子水，搅拌 1 ～ 3h 后，再加入 1 重量份的碘化钾或溴化钾，不断搅拌 4 ～ 6h，静置 10 ～ 15h 后抽滤，烘箱中 80 ～ 100℃烘干，即制得所述的吸附剂。

3. 根据权利要求 2 所述的制备工艺，其特征在于，所述的浓硫酸浓度为 98%。

4. 根据权利要求 2 和 3 所述的制备工艺，其特征在于，在加入上述去离子水的同时还加入适量的无水乙醇。

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化学改性壳聚糖吸附脱汞剂及其制备工艺

技术领域

[0001] 本发明涉及一种脱除燃煤电站烟气中 Hg^0 的吸附剂及其制备工艺。

背景技术

[0002] 电力工业污染物的排放已使环境日趋恶化。煤炭大量燃烧所释放的重金属、CO_2 和酸雨等问题正严重危害着人类的健康生活。重金属汞（Hg^0、Hg^+ 和 Hg^{2+}）的污染尤为严重，据报道，全世界每年向大气中排放的总汞量为 4400 ～ 7500 吨，其中很大一部分是由煤燃烧所排放的。存在于环境或生产中的汞及其化合物可经呼吸面由肺、经溶解面由皮肤、经饮食面由消化道等途径进入人体，还可由母体胎盘进入胎儿体内。汞中毒引起肾功能衰竭，并损害神经系统，是人体运动失调，听觉损害，语言障碍等，对其研究已成为环境问题的前沿问题。

[0003] 目前研究的脱 Hg^0 吸附剂主要为活性炭、飞灰和其他矿石类（沸石、蛭石和膨润土）物质，但脱除效率不高；而这些吸附剂经 $ZnCl_2$、$CuCl_2$、KBr、KI 和渗 S 等改性后能够大幅度提高其对汞的吸附量，但经济成本偏高。开发成本廉价且能有效脱除单质汞的吸附剂是目前研究的热点和难题。

[0004] 壳聚糖（Chitosan，CTS）是一种储量极为丰富的天然碱性高分子多糖，多为虾、蟹甲壳提取物，是由甲壳素部分脱乙酰化衍生物。它无毒、无味、耐热、耐碱、耐腐蚀，兼容性宽，具有优良的生物亲和性，它由生物合成也可以被生物降解，是一种高科技绿色新材料，其分子中含有大量的 $-NH_2$ 和 $-OH$ 官能团，是重金属离子的良好吸附剂，被广泛的应用环保领域，尤其是水处理领域；另外壳聚糖还可以吸附硫酸、盐酸、I_2/KI 溶液中的碘和 Br_2/KBr 溶液中溴离子。本发明中研制的碘（溴）和硫酸改性的壳聚糖吸附剂，脱 Hg^0 能力强，价格低廉，是一种新型的环保型吸附剂。

发明内容

[0005] 本发明的目的是提供一种用于脱除燃煤烟气中 Hg^0 的吸附剂，脱汞效率高，成本低廉，产物不产生二次污染，达到工业化应用要求。

[0006] 一种用于脱除燃煤烟气中 Hg^0 的吸附剂，包括壳聚糖、硫酸、以及碘化钾或溴化钾，其中壳聚糖、硫酸与碘化钾或溴化钾的质量比为（1 ～ 15）：1：（0.5 ～ 5）。

[0007] 一种用于脱除燃煤烟气中 Hg^0 的吸附剂的制备工艺，包括如下步骤：

[0008] 首先，称取 4-15 重量份的壳聚糖，加入 0.42-4 重量份的浓硫酸和适量的去离子水，搅拌 1 ～ 3h 后，再加入 1 重量份的碘化钾或溴化钾，不断搅拌 4 ～ 6h，静置 10 ～ 15h 后抽滤，烘箱中 80 ～ 100℃烘干，即制得所述的吸附剂。

[0009] 本发明所述的浓硫酸浓度为 98%。

[0010] 本发明在加入上述去离子水的同时还加入适量的无水乙醇。

[0011] 本发明以改性膨润土和高分子化合物壳聚糖及其复合物为吸附剂，在模拟烟气（N_2+Hg^0）氛围下研究对 Hg^0 的吸附能力。实验结果显示，本发明吸附剂是一种高效、经济的脱汞吸附剂，具体体现在：

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[0012] 1. 原料易购买，吸附剂易制备，成本低、性价比高；

[0013] 2. 吸附剂比表面面积小，但是其脱汞效率较高，说明进行的是一种化学反应；

[0014] 3. 脱汞吸附剂稳定性好；

[0015] 4. 脱汞吸附剂脱汞效率高，其中实施例中 CTS-I-S-412 型吸附剂最大脱汞效率可达到 100%；

[0016] 5. 脱汞吸附剂为干态粉末，不使用水溶液，无二次污染。

发明内容

[0017] 图 1 为 N_2 氛围汞吸附实验台架示意图；

[0018] 图 2 为不同含量硫酸的溴改性 CTS 吸附剂的 Hg^0 脱汞效率；

[0019] 图 3 为不同含量硫酸的碘改性 CTS 吸附剂的 Hg^0 脱汞效率。

具体实施方式

[0020] 以下结合附图和具体实施例对本发明做进一步说明。

[0021] 实施例 1

[0022] CTS-Br-S 系列吸附剂制备：称取 4g 壳聚糖，放入 100mL 的烧杯中，再加入 30mL 去离子水（适量的无水乙醇）和 0.42g 浓硫酸（浓度为 98%），搅拌 1 ～ 3h 后，加入 1gKBr，不断搅拌 4 ～ 6h，静置 10 ～ 15h 后抽滤，烘箱中 80 ～ 100℃烘干，置于干燥皿中备用，记为 CTS-Br-S-410。用 2g 硫酸代替 CTS-Br-S-410 制备中硫酸的用量，制备出吸附剂 CTS-Br-S-412（其中 S 表示吸附剂制备过程中有硫酸添加，410 和 412 分别表示壳聚糖、改性剂和硫酸按以上制备方法的质量比）。

[0023] CTS-I-S 系列吸附剂制备：称取 4g 壳聚糖，放入 100mL 的烧杯中，再加入 30mL 去离子水（适量的无水乙醇）和 0.59g 浓硫酸（浓度为 98%），搅拌 1 ～ 3h 后，加入 1gKI，不断搅拌 4 ～ 6h，静置 10 ～ 15h 后抽滤，烘箱中 80 ～ 100℃烘干，置于干燥皿中备用，记为 CTS-I-S-410。用 2g 硫酸代替 CTS-Br-S-410 制备中硫酸的用量，制备出吸附剂 CTS-I-S-412。

[0024] 实施例 2

[0025] CTS-Br-S-813 吸附剂：称取 8g 壳聚糖，放入 100mL 的烧杯中，再加入 30mL 去离子水（适量的无水乙醇）和 3g 硫酸（浓度为 98%），搅拌 1 ～ 3h 后，加入 1gKBr，不断搅拌 4 ～ 6h，静置 10 ～ 15h 后抽滤，烘箱中 80 ～ 100℃烘干，置于干燥皿中备用，记为 CTS-Br-S-813。

[0026] CTS-I-S-813 附剂：称取 8g 壳聚糖，放入 100mL 的烧杯中，再加入 30mL 去离子水（适量的无水乙醇）和 3g 硫酸（浓度为 98%），搅拌 1 ～ 3h 后，加入 1gKI，不断搅拌 4 ～ 6h，静置 10 ～ 15h 后抽滤，烘箱中 80 ～ 100℃烘干，置于干燥皿中备用，记为 CTS-I-S-813。

[0027] 实施例 3

[0028] CTS-Br-S-1514 吸附剂：称取 15g 壳聚糖，放入 600mL 的烧杯中，再加入 100mL 去离子水（适量的无水乙醇）和 4g 浓硫酸（浓度为 98%），搅拌 1 ～ 3h 后，加入 1gKBr，不断搅拌 4h，静置 10h 后抽滤，烘箱中 80 ～ 100℃烘干，置于干燥皿中备用，记为 CTS-Br-S-1513。

[0029] CTS-I-S-1514 吸附剂：称取 15g 壳聚糖，放入 600mL 的烧杯中，再加入 100mL 去离子水（适量的无水乙醇）和 4g 浓硫酸（浓度为 98%），搅拌 1 ～ 3h 后，加入 1gKI，不断搅

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拌 4h，静置 10h 后抽滤，烘箱中 80 ~ 100℃烘干，置于干燥皿中备用，记为 CTS-I-S-1513。

[0030] 为了解本发明吸附剂的性能，特在氮气 (N_2) 氛围下研究其对 Hg^0 的吸附能力。汞吸附实验台架如图 1 所示，它由气源 1（如 N_2）、流量计 2、水蒸气发生器 3、U 形管 4、汞发生器 5、数据自动采集仪 6、立式管式炉 7、汞浓度测试仪 8 组成。其中吸附床为立式固定床，其内径为 7mm，为避免吸附剂流化，采用烟气向下流动式。温控炉为吸附床提供恒定的床温。实验中吸附剂用量为 30mg；进入汞在线的气体总流量为 1000mL/min，其中通过汞渗透管的气流为 200mL/min，氮气为平衡气；汞蒸气由高纯氮气通过恒温水浴锅加热汞渗透管提供，图中虚线为装有加热带的保温管路；实验中汞液度为 30 μg/m³，汞浓度检测采用德国 Mercury Instruments 公司的 VM3000 汞在线分析仪，它基于冷原子吸收测量采样气体中的单质汞，可实时方便的了解吸附剂对汞 (Hg^0) 的脱除效果。

[0031] 对实施例 1 中两种化学改性壳聚糖吸附剂吸附实验表明，壳聚糖经溴、碘和硫酸改性后相对于壳聚糖原样来说可以提高吸附剂的脱汞效率（如图 2 和 3 所示）。壳聚糖吸附除汞的反应是化学反应占主导，可以高效的脱除单质汞，且 CTS-I-S-412 可以长时间具有 100％的脱汞效率。采用本系列吸附除汞剂，能够达到工业应用的要求。

[0032] 利用图 1 的台架对实施 2 和 3 的吸附剂进行脱汞实验，结果表明：该吸附剂脱除 Hg^0 的反应是化学反应占主导，可以高效的脱除单质汞；在相同的制备条件下，适量硫酸的加入，可以极大的提高壳聚糖吸附剂脱汞效率。壳聚糖类型吸附剂的制备中，硫酸含量增加，可以大幅地提高其脱汞效率，但硫酸的加入量并不是越多越好。因含有硫酸根、碘（溴）和氨基等官能团，水蒸气的加入可以提高吸附剂表面的酸性氛围，更有利于 Hg^0 的脱除。

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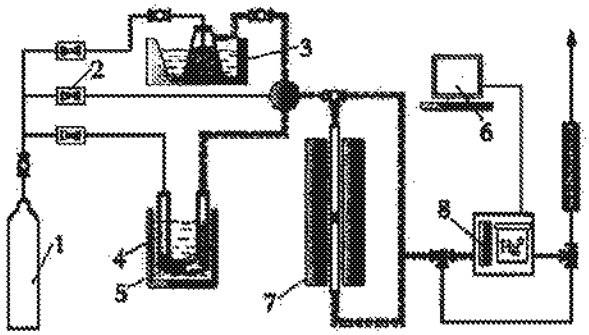


图 1

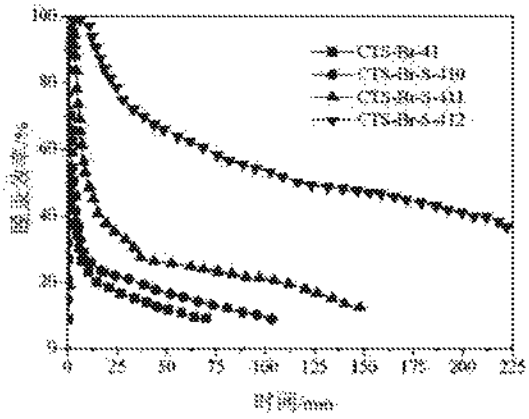


图 2

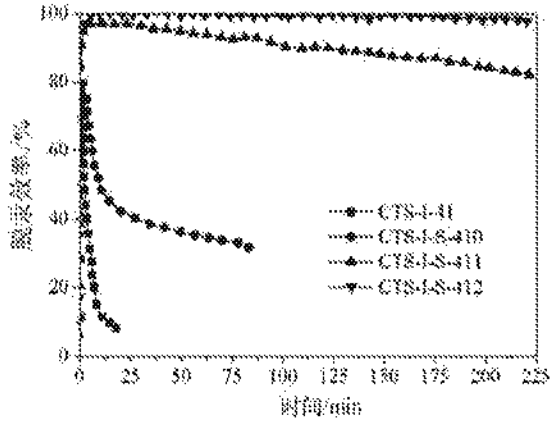


图 3

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Sorbents for the oxidation and removal of mercury

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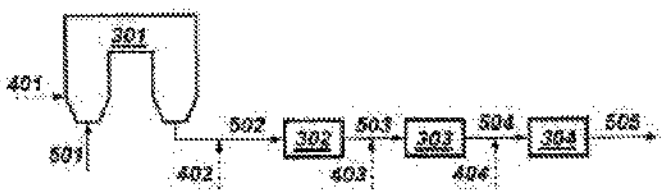
Classification: - international: ***B01D53/02; B01D53/64; F23J15/00***
- cooperative: **B01D53/10**; **B01D53/64**; **B01J20/0262**; **B01J20/027**; **B01J20/04**; **B01J20/041**; **B01J20/043**; **B01J20/10**; **B01J20/106**; **B01J20/12**; **B01J20/20**; **B01J20/223**; **B01J20/28004**; **B01J20/3416**; B01D2253/102; B01D2257/602; B01J2220/42

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Abstract of CN102413899 (A)



A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non-carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can

be regenerated and reused. Base sorbent treatment and preparation methods are also described. New methods for in not flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

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权利要求书 2 页 说明书 17 页 附图 4 页
按照条约第19条修改的权利要求书 2 页

(54)发明名称

用于汞的氧化和移除的吸附剂

(57)摘要

本发明描述了一种促进的碳/非碳基础吸附剂，它们对除去烟道气流中的汞高度有效。促进的吸附剂包括已与卤素/卤化物反应并含有某种形态的卤素/卤化物的碳和/或非碳基础吸附剂。可以添加可选组分以增加和/或保持反应性和汞的捕捉能力。这些可以直接与基础吸附剂一起添加，或者在飞行中添加在在气流(空气、烟道气等)内，以提高基础吸附剂的性能和/或汞的捕捉能力。所获得的除汞效率超过传统的方法。促进的吸附剂可以再生和再使用。还描述了基础吸附剂的处理和制备方法。描述了在飞行中制备、把活性的基础吸附剂引入到含汞的气流中并控制的新方法。

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1. 一种从含汞气体中分离汞的方法，所述方法包括：

(a) 提供吸附剂材料；

(b) 提供卤素或卤化物促进剂；

(c) 通过使所述吸附剂材料与所述卤素或卤化物促进剂发生化学反应而形成促进的卤化吸附剂，从而促进所述吸附剂材料的至少一部分；

(d) 使所述含汞气体中的原子汞与所述促进的卤化吸附剂发生化学反应以形成汞 / 吸附剂化学合成物；以及

(e) 从所述含汞气体中分离颗粒以形成清洁的气体，所述颗粒包括灰分和第一汞 / 吸附剂化学合成物。

2. 权利要求 1 所述的方法，所述方法还包括向所述含汞气体中注入所述吸附剂材料和所述卤素或卤化物促进剂的步骤。

3. 权利要求 2 所述的方法，其中所述卤素或卤化物促进剂和所述吸附剂材料在同一位置注入到所述含汞气体中。

4. 权利要求 2 所述的方法，其中所述卤素或卤化物促进剂和所述吸附剂材料在分开的位置注入到所述含汞气体中。

5. 权利要求 4 所述的方法，其中所述卤素或卤化物促进剂在所述吸附剂的注入的上游注入到所述含汞气体中。

6. 权利要求 5 所述的方法，其中所述卤素或卤化物促进剂被注入到产生含汞气体的燃烧室内，并且所述吸附剂在所述燃烧室的下游注入。

7. 权利要求 6 所述的方法，其中所述卤素或卤化物促进剂另外从所述燃烧室的下游注入。

8. 权利要求 6 所述的方法，其中所述燃烧室为锅炉，而所述含汞气体为烟道气。

9. 权利要求 3 所述的方法，其中所述卤素或卤化物促进剂和吸附剂从产生含汞气体的室的下游注入。

10. 权利要求 9 所述的方法，其中所述室为锅炉，而所述含汞气体为烟道气。

11. 权利要求 2 所述的方法，其中所述吸附剂被注入的速率、所述促进剂被注入的速率或它们的组合是根据所监测到的清洁的气体中的汞含量进行调整的，以便所述清洁的气体中的汞含量基本上保持在期望的水平。

12. 权利要求 1 所述的方法，其中所述吸附剂包括碳基材料。

13. 权利要求 12 所述的方法，其中所述吸附剂包括活性炭。

14. 权利要求 1 所述的方法，其中所述吸附剂选自非碳基材料，包括多孔长英矿物材料、泡状长英矿物材料，多孔玄武岩材料、泡状玄武岩材料、粘土基化合物、碱性化合物、氧氧化钙化合物、酷酸钠化合物、碳酸氢盐化合物以及它们的组合。

15. 权利要求 13 所述的方法，其中所述吸附剂为活性碳基础材料，所述活性碳基础材料与所述含汞气体中的氧化的汞反应以形成第二汞 / 吸附剂化学合成物。

16. 权利要求 14 所述的方法，其中所述吸附剂为非碳基础材料，所述非碳基础材料与所述含汞气体中的氧化的汞反应以形成第二汞 / 吸附剂化学合成物。

17. 权利要求 1 所述的方法，其中所述吸附剂为含有路易斯碱基团的非碳材料。

18. 权利要求 1 所述的方法，其中所述吸附剂为含有路易斯酸基团的碳材料。

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19. 权利要求 1 所述的方法，其中所述吸附剂包括碳材料和非碳材料两者。

20. 权利要求 14 所述的方法，其中所述非碳材料包括无定形形式的网硅酸盐，所述网硅酸盐包含排列有与碱土金属结合的路易斯碱氧的纳米尺度腔。

21. 权利要求 20 所述的方法，其中所述的碱土金属包括第 I 和第 II 族的碱土金属。

22. 权利要求 13 所述的方法，其中所述非碳材料包括无定形形式的页硅酸盐，所述页硅酸盐包含排列有路易斯碱氧的纳米尺度腔。

23. 权利要求 1 所述的方法，其中所述促进的吸附剂包括在所述促进剂与在非碳吸附剂上的无机物种之间形成的介稳配合物。

24. 权利要求 23 所述的方法，其中所述无机物种选自如下各项：钠化合物、钙化合物、镁化合物、铝化合物、铁化合物以及它们的组合。

25. 权利要求 1 所述的方法，其中所述促进的吸附剂包括在所述促进剂与在非碳吸附剂上的金属 - 氧 - 金属结构之间形成的介稳配合物。

26. 权利要求 25 所述的方法，其中在与所述的金属 - 氧 - 金属结构配合之后的所述促进剂处于选自如下各项的形式：双卤素基团、卤素原子、氢卤化物基团、第 V 族的卤化物、第 VI 族的卤化物以及它们的组合。

27. 权利要求 1 所述的方法，其中所述促进的吸附剂包含活化的路易斯碱基团、活化的路易斯酸基团或它们的组合。

28. 权利要求 1 所述的方法，其中促进的吸附剂与所述含汞气流之间的所述相互作用包括：

汞从气相扩散到所述促进的吸附剂表面上；以及

与活化的路易斯碱基团、活化的路易斯酸基团或它们的组合反应以引起在所述吸附剂表面上的化学吸附。

29. 权利要求 1 所述的方法，所述方法还包括对所述的吸附剂进行预处理以增加在所述吸附剂上的路易斯碱基团、路易斯酸基团或它们的组合的数量。

30. 权利要求 29 所述的方法，其中对所述吸附剂进行预处理包括化学处理、热处理、真空处理以及它们的组合。

31. 权利要求 30 所述的方法，其中所述的化学处理包括酸处理和碱处理。

32. 权利要求 1 所述的方法，所述方法还包括向所述含汞气体中引入碱性组分。

33. 权利要求 1 所述的方法，其中碳吸附剂与所述促进剂反应以制备促进的碳吸附剂。

34. 权利要求 33 所述的方法，其中所述碳吸附剂、所述促进剂或它们的组合在一个或多个位置被引入到所述含汞气体中。

35. 权利要求 34 所述的方法，其中所述碳吸附剂被引入的速率、所述促进剂被引入的速率或它们的组合是根据所监测到的清洁的气体中的汞含量进行调整的，以便所述清洁的气体中的汞含量基本上保持在期望的水平。

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用于汞的氧化和移除的吸附剂

[0001] 相关申请的交叉引用

[0002] 本申请作为 PCT 国际专利申请在 2010 年 2 月 2 日提交，对于除美国之外的所有国家的指定的申请人为 Energy & Environmental Research Center Foundation，一个美国国营公司，而仅对于美国的指定的申请人为 Edwin S. Olson（美国公民），Michael J. Holmes（美国公民）和 John H. Pavlish（美国公民），并且要求 2009 年 4 月 23 日提交的美国部分继续专利申请系列 12/429,058 的优先权。

[0003] 发明所属技术领域

[0004] 本发明涉及从烟道气或气化系统所产生的气体中除去污染物的方法和材料。具体地，通过高活性的可再生的吸附剂除去化石燃料燃烧或气化所产生的气体流中所含的汞。

[0005] 发明背景

[0006] 如煤这样的化石燃料燃烧和气化所产生的烟道气中含有源自燃料的汞和其它痕量元素。汞（和其它污染物）向环境的排放必须通过使用吸附剂、洗涤剂、过滤剂、沉降剂以及其它除去技术来得到控制。在燃烧和气化过程中，汞开始是以元素形式存在。在下游的操作段，例如燃烧系统的导管和烟囱中，一些原子汞被氧化。所氧化的量依赖于烟道气中存在的酸气量及其它因素。汞的量随燃料变化，但典型的煤燃烧所产生的烟道气流中汞的浓度小于十亿分之五 (5ppb)。大的煤燃烧工厂（例如发电厂）每天会释放一磅或更多的汞。汞的除去技术适用范围包括但不限于煤（或其它化石燃料）燃烧所产生的烟道气、废弃物的燃烧、气化过程中的放出气体，以及来自其它矿石加工、金属冶炼、干馏、水泥生产、氯碱工厂、牙齿工厂和焚尸炉的废气。

[0007] 汞吸附剂技术

[0008] 已经在研究的控制烟道气中的汞的方法有几种，包括向烟道气导管注入细的吸附剂颗粒以及使烟道气通过吸附剂床。细颗粒注射吸附剂包括活性炭、金属氧化物吸附剂、硫化钠颗粒和碱性硅酸盐或氧化物吸附剂。当应用颗粒注射技术时，吸附剂颗粒上捕获的汞在颗粒控制器 - 例如袋式除尘器或静电除尘器 (ESP)- 中从气流中除去并和灰分颗粒一起收集。硫化物、碱性硅酸盐和氧化物颗粒只对氧化的汞有效，而金属氧化物吸附剂比碳颗粒表现出更慢的捕捉动力学。此外，向烟道气流中注入细的碳颗粒对移除汞特别是原子汞仅取得了部分的成功，对一些采用 FF（织物过滤器）收集碳和灰分的应用而言有效除去的只有约 60%。当使用 ESP 收集碳时，由于碳与气体的接触时间很短，观察到的除去效率甚至更低。

[0009] 现有的碳注射系统的一个主要问题是吸附剂对汞是相对非活性的。因而，为了有效捕捉汞，这些吸附剂必须大量使用，吸附剂与汞的比例很高。这些吸附剂常常相对昂贵，也不能很容易地从灰分中分离以便再生和使用。收集灰分中的碳也会产生固体废弃物的问题，已用过的吸附剂可能污染收集的灰分，从而妨碍其在各种应用中的使用。

[0010] 一个方案是加入氧化的吸附剂，它包含活性炭和浸渍了非常大剂量的一种或多种氧化的金属卤化物的铝硅酸盐材料。例子可参见 Varma 等人的工作 (20070140940)。然而，用于汞氧化的金属盐的量通常较大且昂贵。此外，可用于这一工艺的几种盐是高毒性的。尽

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管这种工艺中含有用于氧化的金属盐，但是为了得到汞的吸附，活性炭仍是必需的。这样，铝硅酸盐并没有显示出协同效应，因为它们看起来只是作为用于氧化的盐的载体。

[0011] 另一个途径是注入铝硅酸盐颗粒，例如膨润土，它既不含有氧化的盐，也不含有与路易斯碱部位配位的卤素，因而缺少在本发明中所描述的配合物的强大氧化能力。这样的例子可参加美国专利7,413,719。此外，人们已经知道注入含有次氯酸钙的铝硅酸盐（高岭土或偏高岭土），次氯酸钙遇热分解产生卤素。例子可参见美国专利申请20030103882。为了生成氧化部位，这些和类似的浸渍的铝硅酸盐技术需要在适当高温下的飞行时间以加热一种或多种浸渍的盐。与本专利中所描述的在合适的路易斯碱吸附剂的表面上发生的路易斯酸的极快的配合反应相比，这显然表现出对活化的动力学障碍。这种动力学障碍仅针对加热次氯酸钙以将其分解为氯原子或分子的情形。卤素（双分子或原子）会在任意更低的温度下与碳或非碳配合而形成反应性的氧化部位。此外，卤化物需要非常高的温度或强酸以形成反应性的卤素或卤素配合物。

[0012] 另一方法是注入膨润土加上金属硫化物和金属盐，它们都不能氧化原子汞，因而需要慢的热活化步骤。例子可见美国专利申请20070119300。

[0013] 本领域中熟知的另一技术是向加加热区内注入卤素或卤素的前体，然后与碱性材料在湿或干的洗涤器中接触。据称以这种方法原子汞被卤素氧化成Hg(II)，Hg(II)被洗涤器中的碱性材料收集。例子可见美国专利6,808,692(Ochr)、美国专利3,849,627(Hilgen)、美国专利5,435,980(Felsvang)、美国专利6,375,909(Dangtran)、美国专利申请20020114749(Cole)、美国专利6,638,485(Iida)、美国专利申请20030185718(Sellakumar)、美国专利申请20030147793(Breen)和美国专利6,878,358(Vosteen)。然而，尽管已经知道在燃烧过程的某些阶段注入卤素形式，这一工艺没有利用在吸附剂表面上的配合方法来进行氧化和捕捉。此外，碱性材料的表面迅速被高浓度的酸气所覆盖，降低了其对Hg(II)的吸附能力。也已经认识到最初引入或产生的卤素形式对烟道气中的更大浓度的SO_2和湿气有远更高的反应性，所以卤素与汞的气相反应受到阻碍。相比之下，本发明利用了在吸附剂表面上迅速形成的路易斯酸配合物来实施汞的氧化，而不依赖于气相反应来进行氧化。这样HCl、HBr、SO_2Br及其它气相产物都在表面上结起了花彩，通过与吸附剂形成配合物而形成被促进的吸附剂，从而促进了吸附剂的活性。

[0014] 因此，仍需要更经济和有效的除汞技术。本发明为低成本的除去污染物－包括汞而提供，它使用吸附剂增强添加剂和/或高反应性的吸附剂，只需数秒（或更少）的接触时间，而且可以再生和重复使用。

[0015] 概述

[0016] 本发明的各实施方案克服了现有技术在各个方面的不足，提供了从使用化石燃料而产生的气体中除去汞的新的经济方法。

[0017] 所述的卤素/卤化物促进的吸附剂对于从烟道气流中除汞是高度有效的。吸附剂包括任意的活性炭和/或非碳化合物，例如多孔的或泡状的长英矿物材料或玄武岩材料、粘土基化合物、碱性化合物、氧化钙化合物、醋酸钠化合物和/或碳酸氢盐化合物以及它们的组合。可以加入的可选第二组分和强碱进一步增加反应性和汞的捕捉量(capacity)。所获得的除汞效率胜过或达到传统的方法，并且具有额外的优点，例如降低的成本。可选地，促进的吸附剂可以再生和重新使用。也描述了吸附剂的处理和/或制备方法。描述了

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吸附剂、促进剂和促进的吸附剂的在飞行中的制备（in-flight preparation）、引入及控制到汞污染的气流中的方法。

[0018] 当促进的或非促进的基础吸附剂与原子态或氧化态的汞反应时，就形成了汞/吸附剂的化学合成物，并且在原子汞与促进的基础吸附剂反应的情况下，汞就被氧化。如在说明书的其它部分的进一步详细论述的那样，基础吸附剂可以是碳或非碳材料或它们的组合物。此外，汞/吸附剂化学合成物可以由在促进的或非促进的基础吸附剂与氧化的汞之间的共价键、离子键和/或化学配合构成。非促进的基础吸附剂上的路易斯酸基团，或者促进的基础吸附剂上的未促进的部分，可以用于与含汞气体中已经存在的氧化的汞上的路易斯酸基团反应。这样，通过甚至在同一过程中的多种不同的汞/吸附剂化学合成物的形成，汞就可以从含汞的气流中被除去。例如，当基础吸附剂颗粒上的反应点具有一部分被促进时，在吸附剂颗粒上的多个反应点可以形成多种不同的汞/吸附剂化学合成物。

[0019] 在一些实施方案中，公开了碳和/或非碳的促进吸附剂和/或它们的组合，其包括与选自卤化物、卤素和它们的组合中的促进剂反应的吸附剂结构，以使得反应产物对于除去气流中的汞是有效的。碳吸附剂含有反应性路易斯酸基团/部位，而非碳吸附剂包含反应性路易斯碱基团/部位。

[0020] 在一个实施方案中，提供了一种促进的碳和/或非碳吸附剂，其中基础吸附剂选自碳、活性炭、多孔的或泡状的长英矿物材料和玄武岩材料、粘土基化合物、碱性化合物、氢氧化钙化合物、醋酸钠化合物和/或碳酸氢盐化合物或它们的组合，其中平均粒径与热过程（燃烧或气化）产生的飞灰的粒径相近或者比所产生的飞灰的粒径大以便能用物理方法分离，或上述情况的组合，并且促进剂选自分子卤素、第V族元素（在整篇文档中均使用CAS命名）的卤化物、第VI族元素的卤化物、氢卤化物以及它们的组合物。在一个实施方案中，促进的吸附剂（碳、非碳或者它们的组合）可以具有大的质量平均粒径，以便其可以通过物理方式基本上从将要移除其中的汞的气流中所夹带的灰分中分离。在一个实施方案中，基础吸附剂（碳、非碳或它们的组合）的质量平均粒径可能大于约40微米。

[0021] 在另一实施方案中，促进的吸附剂包括约1至约30克促进剂/100克基础吸附剂。另一实施方案还包含可选的第二组分，所述可选的第二组分包含卤素或卤化氢，以便促进的吸附剂的反应性和对汞的捕捉能力得到增强。

[0022] 在另一个实施方案中，可选的第二组分在吸附剂成品上的浓度为促进剂在吸附剂成品上的浓度的约1至约15重量%。

[0023] 在另一实施方案中，可以优选地加入可选的碱性组分，以通过这种碱与基础吸附剂的结合而形成协同效应。

[0024] 在另一实施方案中，可选的第二组分选自第V族元素的卤化物、第VI族元素的卤化物、HI、HBr、HCl及它们的组合。在另一实施方案中，当与基础吸附剂结合时，促进剂实质上处于气态。在另一实施方案中，促进剂在与基础吸附剂反应之前先与有机溶剂结合。在另一实施方案中，促进剂和可选的第二组分与基础吸附剂基本上同时结合。另一实施方案中还包括加入汞的稳定试剂，这些试剂选自S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5及它们的组合。另一实施方案中还包括加入可选的碱性组分。

[0025] 在一实施方案中，提供包括如下过程的方法：提供颗粒基础吸附剂并将该基础吸附剂与促进剂反应，所述促进剂选自卤素、卤化物及它们的组合，以便反应产物包含对除去

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气流中的汞有效的被促进的吸附剂。在进一步的实施方案中，反应产物包含约 1 至约 30 克促进剂 /100 克基础吸附剂。在另一实施方案中，反应产物的平均粒径分布比要除去汞的气流中夹带的灰分粒子的平均粒径尺寸大，这样反应产物可以通过物理方式从夹带的灰分粒子上基本上除去。在另一实施方案中，反应产物的质量平均粒径大于约 40 微米。

[0026] 在另一实施方案中，促进剂选自分子卤素、氢卤化物、第 V 族元素的卤化物、第 VI 族元素的卤化物及它们的组合。在另一实施方案中，当与基础吸附剂（碳、非碳及其组合）接触时，促进剂处于气相。在另一实施方案中，当与基础吸附剂接触（碳、非碳及其组合）时，促进剂在有机溶剂中。

[0027] 在另一实施方案中，促进剂选自 Br_2，第 V 族元素的溴化物、第 VI 族元素的溴化物及它们的组合物。

[0028] 在另一实施方案中，方法还包括将颗粒的非碳吸附剂与可选的第二组分反应，以提升促进的吸附剂的反应性和对汞的捕捉能力，所述第二组分包含卤素或氢卤化物。在另一实施方案中，促进剂和可选的第二组分同时与非碳的基础吸附剂结合。另一实施方案中，所述方法还包括加入汞的稳定试剂，这些试剂选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 及它们的组合。在一个实施方案中，提供了控制烟道气中汞的方法，并且该方法显著降低了对吸附剂的需求。通过提升吸附剂的反应性，每克吸附剂的除汞量增加，这样就通过降低吸附剂的需求量来减少了资金和运行的成本。

[0029] 在一个实施方案中，促进的吸附剂通过直接引入到烟道气流中而被引入。在另一个实施方案中，基础吸附剂在烟道气流内被促进。

[0030] 在一个实施方案中，提供了减少烟道气中汞的方法，所述方法包括通过向含汞烟道气流中注射或原位产生而提供吸附剂，在促进的吸附剂上收集超过 70 重量％的汞，以得到清洁的烟道气，然后从清洁的烟道气中基本回收促进的吸附剂。在期望除汞不超过 70 重量％的实施方案中，可使用比所需要的标准的基础吸附剂更少的基础吸附剂来实现。在进一步的实施方案中，还包括监测清洁烟道气中的汞含量、对回收的促进吸附剂进行再生并使用监测到的清洁的烟道气中的汞含量来控制基础吸附剂和促进剂的速率。在另一实施方案中，注入的促进的吸附剂是在通过基础吸附剂（碳、非碳及其组合）与促进剂在气动输送管线内反应而在飞行中制得的，反应产物通过气动输送管线注入到含汞烟道气流中。

[0031] 在另一实施方案中，促进剂选自分子卤素、卤化物及它们的组合。在另一实施方案中，促进剂在气相或作为气体发生反应。在另一实施方案中，相对于 100 克基础吸附剂（碳、非碳或它们的组合）加入约 1 至约 30 克促进剂。

[0032] 在另一实施方案中，注入的促进吸附剂是通过如下过程而在飞行中制得的：通过基础吸附剂（碳、非碳及它们的组合）、促进剂和可选的第二组分在气动运输管线内反应，以提高促进的吸附剂的反应性和捕捉能力，反应产物通过气动输送管线注入到含汞烟道气流中。

[0033] 在另一实施方案中，可选的第二组分选自碘、氢卤化物、第 V 族的卤化物、第 VI 族的卤化物及它们的组合。在另一实施方案中，可选的第二组分按促进剂含量的约 1 至约 15 重量％添加。在另一实施方案中，还包括向促进的吸附剂中加入汞的稳定试剂，所述汞的稳定试剂选自 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 及它们的组合。

[0034] 在一个实施方案中，所述方法还包括共同注入可选的碱性材料，包括但不限于碱

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性的和碱土的成分，以通过捕捉氧化的汞和/或捕捉那些可以以其它方式降低促进的吸附剂的能力的气体成分来改善捕汞的效率。在另一实施方案中，可选的碱性材料可以优选包括本技术领域已知的氧化钙、碳酸钠及类似物。

[0035] 在另一实施方案中，所述方法还包括通过监测清洁后的烟道气中的汞含量来控制促进的吸附剂的成分。在另一实施方案中，促进的吸附剂是通过基础吸附剂（碳、非碳或它们的组合）与促进剂在烟道气流中或在输送管线里的反应而在飞行中制得的，反应产物通过输送管线注入到含汞的烟道气流中，其中此处的促进剂选自卤素分子、卤化物及它们的组合，其中促进剂是在气相或作为气体反应的，其中促进剂是按照每 100 克基础吸附剂（碳、非碳或它们的组合）加入约 1 至约 30 克的量添加的，其中促进剂的加入速度和促进的吸附剂的注入速度是至少部分根据监测到的清洁后的烟道气的汞含量由数字电脑确定的。

[0036] 在一个实施方案中，提供了一种用于降低含汞和灰分的气流中汞含量的方法，其中质量平均尺寸大于 40 微米的颗粒碳和/或非碳的促进的吸附剂被注入到气流中，汞被促进的吸附剂颗粒从气体中除去，促进的吸附剂颗粒与灰分颗粒按照尺寸大小来分离，然后促进的吸附剂颗粒被重新注入到气流中。在另一实施方案中，对含汞的促进吸附剂进行再生以除去部分或者基本上全部的汞。在另一实施方案中，碱性组分被注入到气流中。在另一实施方案中，促进的吸附剂还可以含有促进剂。促进剂可以优选包括卤化物、卤素或二者。

[0037] 在一个实施方案中，公开了一种将含汞气体中的汞降至期望水平的方法。此方法包括将碳基础吸附剂与至少一种选自分子卤素、卤化物和它们的组合中的促进剂反应，得到促进的碳吸附剂；使上述的促进碳吸附剂与含汞气体作用以在促进的吸附剂上捕捉含汞气体中的汞，从而得到清洁的气体；并监测清洁的气体中的汞含量。在有些实施方案中，碳基础吸附剂和促进剂在相同或不同的位置被引入到含汞气体中。在有些实施方案中，碳基础吸附剂或促进剂或它们的组合在一个或多个位置被引入到含汞气体中。在一个实施方案中，根据清洁的气体中的监测的汞含量来调整碳基础吸附剂的引入速度或者促进剂的引入速度或者二者的引入速度，以便以最小的操作成本使清洁的气体的汞含量基本上保持在期望的水平。

[0038] 在进一步的实施方案中，所述方法包括将非碳基础吸附剂与至少一种选自分子卤素、卤化物和它们的组合中的促进剂反应，得到促进的非碳基础吸附剂；使所述的促进的非碳基础吸附剂与含汞气体作用以在促进的吸附剂上捕捉含汞气体中的汞，从而得到清洁的气体；以及监测清洁的气体中的汞含量。在有些实施方案中，非碳基础吸附剂和促进剂在相同或不同的位置引入到含汞气体中。在有些实施方案中，非碳基础吸附剂或促进剂或它们的组合在一个或多个位置引入到含汞气体中。在一个实施方案中，根据监测的清洁的气体的汞含量来调整非碳基础吸附剂的引入速度或者促进剂的引注入速度或者二者的引入速度，以便以最小的操作成本使清洁的气体的汞含量基本上保持在期望的水平。

[0039] 在进一步的实施方案中，给出了将含汞气体中的汞含量降至期望水平的方法，所述方法包括将基础吸附剂与至少一种选自分子卤素、卤化物和它们的组合中的促进剂反应，得到促进的吸附剂，其中基础吸附剂选自非碳材料、碳材料和它们的组合；使所述的促进的吸附剂与含汞气体作用以在促进的吸附剂上捕捉含汞气体中的汞，从而得到清洁的气体；以及监测清洁的气体中的汞含量。

[0040] 在有些实施方案中，基础吸附剂和促进剂在相同或不同的位置引入到含汞气体

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中。在有些实施方案中，基础吸附剂或促进剂或它们的组合在一个或多个位置引入到含汞气体中。在有些实施方案中，引入基础吸附剂和促进剂包括：将基础吸附剂和促进剂注射到含汞气体中。在有些实施方案中，促进剂在基础吸附剂的引入的上游被引入到含汞气体中。在有些实施方案中，促进剂在锅炉或燃烧室的上游引入。在一个实施方案中，根据监测的清洁的气体的汞含量来调整基础吸附剂的引入速度或者促进剂的引入速度或者二者的引入速度，以便以最小的操作成本使清洁的气体的汞含量基本上保持在期望的水平。

[0041] 在一个实施方案中，用于促进的吸附剂的基础吸附剂选自由如下各项组成的组中：碳、活性炭、多孔的长英矿物材料、泡状的长英矿物材料、多孔玄武岩材料、泡状玄武岩材料、粘土基化合物、碱性化合物、氢氧化钙化合物、醋酸钠化合物、碳酸氢盐化合物以及它们的组合。在有些实施方案中，非碳材料含有路易斯碱基团，而碳材料含有路易斯酸基团。在有些情形下，非碳材料包括无定形形式的网硅酸盐（tectosilicate），所述网硅酸盐包括排列有与碱土金属结合的路易斯碱氧的纳米尺度腔。碱土金属包括第 I 族的元素和第 II 族的碱土金属。在有些其它情形下，非碳材料包括无定形形式的页硅酸盐，页硅酸盐包含排列有路易斯碱氧的纳米尺度腔。

[0042] 在一个实施方案中，促进的吸附剂包括本公开的促进剂与在非碳基础吸附剂上的无机物种之间形成的介稳配合物。在有些实施方案中，所述的无机物种选自钠化合物、钙化合物、镁化合物、铝化合物、铁化合物以及它们的组合。在一个实施方案中，所述的促进的吸附剂由本公开的促进剂与在非碳基础吸附剂上的金属－氧－金属结构之间形成的介稳配合。在有些实施方案中，与金属－氧－金属结构配合之后的促进剂处于选自如下各项的形式：双卤素基团、卤素原子、氢卤化基团、第 V 族元素的卤化物、第 VI 族元素的卤化物以及它们的组合。在一个实施方案中，促进的吸附剂包括活化的路易斯碱基团或活化的路易斯酸基团或它们的组合。在有些实施方案中，促进的吸附剂与所述含汞的气流之间的相互作用包括：汞从气相扩散到所述的促进的吸附剂表面上；以及与活化的路易斯碱基团或活化的路易斯酸基团或它们的组合反应，从而导致在促进的吸附剂表面上的化学吸附。

[0043] 在一个实施方案中，用于将含汞气体中的汞减少至期望水平的方法还包括对基础吸附剂进行预处理以增加路易斯酸基团或路易斯碱基团或它们的组合的数量。在一些情形下，预处理方法包括化学处理、热处理、真空处理和它们的组合。在有些实施方案中，化学处理包括酸处理和碱处理。在一个实施方案中，用于将含汞气体中的汞减少至期望水平的方法还包括：将碱性组分引入到含汞气体中。

[0044] 如下文将要更详尽描述的那样，本发明与已有的已知技术相比表现出几个方面的优点，包括用于废气的更为显著有效及经济的汞吸收剂以及有利地可应用于处理来自燃烧和气化系统的气体流。

[0045] 为了可以更好理解下文的对本发明的详细描述，前面已经相当广泛地列出了本发明的特征和技术优势。本发明的另外的特点和优势将在下文中描述，形成本发明的权利要求书的内容。本领域技术人员应当认识到，所公开的概念和特定实施方案可以很容易地用作用于改变或设计其它结构以完成与本发明相同的目标的基础。本领域技术人员也应意识到，这样的等价构建并没有超出后附权利要求书所述的本发明的精神和范围。

[0046] 附图的简述

[0047] 为了更详细描述本发明的优选实施方案，现参考附图。

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[0048] 图 1 示意示出了依据本发明的用于制备促进的碳和 / 或非碳吸附剂的方法。

[0049] 图 2 示出了所提出的导致汞的氧化和捕捉的化学反应机理模型。

[0050] 图 3 示意示出了依据本发明的促进的碳和 / 或非碳吸附剂的制备以及用于将烟道气和 / 或由气化系统的产物气体中的烟道气体汞减少的方法，包括促进的碳和 / 或非碳吸附剂的在飞行中制备。

[0051] 图 4 给出了通过反应性卤素配合吸附剂的形成而促进金属氧化物基础吸附剂以及随后在促进的吸附剂上捕捉原子汞的机理。

[0052] 图 5A 示意性给出了促进的碳和 / 或非碳吸附剂的飞行中制备的示例性工艺流程图。

[0053] 图 5B 示意性给出了促进的碳和 / 或非碳吸附剂的飞行中制备的示例性工艺流程图。

[0054] 详细说明

[0055] 在此将详细描述本发明的特定优选实施方案，需要理解的是，此处公开的内容应被视作本发明原理的一个例证，而非将本发明局限于本文所示出和描述的内容。本发明易受不同形式或次序的优选实施方案的理解，但不应解释为本发明被限制为本文包含的特定表达方法或组成。特别地，本发明的各种优选实施方案提供了很多发明方法、组成及其用途的不同配置及应用。

[0056] 本发明提供了一种低成本的利用极高反应性的卤素 / 卤化物促进的吸附剂来捕捉污染物的方法，其使用溴化物（或其它卤素 / 卤化物）处理促进的吸附剂，通过汞 - 吸附剂的表面反应，在几秒以下的非常短的接触时间内捕捉汞。促进的吸附剂对污染物（即汞）的反应性被极大提高，并且吸附能力可以再生；也就是说，促进的吸附剂可以再生、再循环和 / 或再使用。

[0057] 本文论述的处理过的基础吸附剂（碳、非碳及它们的组合）、处理技术和可选的添加剂除了适用于来自燃烧系统的烟道气外，还适用于来自气化系统、合成气发生器的一种或多种产物气或废气及其它含汞气流的汞控制。因而应理解，本说明书全文中使用的术语燃烧系统和烟道气可以同等地应于气化系统和合成气或者燃料气，这点会为本领域的技术人员所理解。

[0058] 此后本公开可以有时会进一步详细论述碳基础吸附剂的使用，但非碳的基础吸附剂及碳与非碳的基础吸附剂的组合至少应与碳基础吸附剂受到同等程度的考虑。

[0059] 现参见图 1，它给出了一个方框流程图，示出了本发明的制备用于在含汞气体中 - 例如烟道气或来自气化系统气流的产物气中 - 捕捉汞的促进的吸附剂的方法的一些优选实施方案。在一个以路径 10-20 表示的优选实施方案中，方框 10 示出了提供基础吸附剂，而方框 20 示出了加入与基础吸附剂反应以产生促进的吸附剂产物的卤素或卤化物促进剂。例如在卤素或卤化物以气体形式加入的实施方案中，可以不再需要更多的步骤。在卤素或卤化物以在溶剂中的形式加入的实施方案中，可以适宜地使用由方框 20A 所示的溶剂移除，以产生适合于注射的促进的吸附剂产物。

[0060] 仍然参见图 1，本发明的方法的另一优选实施方案以路径 10-20-30 表示，包括：方框 10 所显示的提供基础吸附剂，方框 20 所表示的加入与基础吸附剂反应的卤素或卤化物促进剂，以及方框 30 表示的加入与方框 20 的结果反应形成促进的吸附剂产物的第二组分。

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当在一些实施方案中，卤素或卤化物促进剂及第二组分均以气体形式加入时，可以不再需要另外的步骤。当在一些实施方案中，卤素或卤化物促进剂和/或第二组分以例如在溶剂中加入时，可以适宜地使用方框 30A 表示的溶剂移除，从而对产生适合用于注射的促进的吸附剂产物。

[0061] 仍参见图 1，本发明的方法的另一优选实施方案以路径 10-40 表示，包括方框 10 表示的提供基础吸附剂，以及向基础吸附剂中一起加入卤素或卤化物促进剂及第二组分，它们间发生反应得到以方框 40 表示的促进的吸附剂产物。同样地，当在有些实施方案中，向基础吸附剂加入气态添加物时，可以不再需要更多的步骤。当在有的实施方案中，一种或多种组分被加入在溶剂中时，可以提供方框 40A 表示的溶剂移除步骤，从而产生适合用于注射的促进的吸附剂产物。

[0062] 仍参见图 1，以路径 10-50 与路径 20-50 相结合说明本发明的方法的另一优选实施方案。在此实施方案中，以方框 10 所表示的基础吸附剂被引入到以方框 50 所表示的含汞气体中，同时以方框 20 所表示的卤素或卤化物促进剂被引入到含汞气流中。这样基础吸附剂与促进剂在方框 50 反应，得到促进的吸附剂产物。以类似的方式，方框 30 所表示的第二组分可加入到以方框 20 所表示的卤素或卤化物促进剂并引入到由方框 50 表示的含汞气体中。当在有些实施方案中，卤素或卤化物促进剂与第二组分以蒸气形式加入时，不需要更多的步骤。当在有些实施方案中，卤素或卤化物与/或第二成分被加入在溶剂中时，可以适宜地使用以方框 20A 和/或方框 30A 所表示的溶剂除移除。

[0063] 仍参见图 1，也示出了一些优选的实施方案，其中如方框 50 所表示的那样，用如上所述制备的产品促进的吸附剂处理含汞气流。

[0064] 在有些优选的实施方案中，所提供的碳基础吸附剂可以优选是几种类型中的任意一种，这点可被本领域的技术人员所理解。例如，碳基础吸附剂可包括粉状的活性炭、颗粒状的活性炭、碳黑、未燃烧的碳、碳纤维、蜂窝炭或盘状结构的炭 (plate structure)、气凝胶炭薄膜、热解焦炭，由产物促进的碳吸附剂再生的活性炭，或本领域中已知的其它类型。

[0065] 在有些优选的实施方案中，所提供的碳基础吸附剂优选比要处理的含汞气体例如烟道气流中的飞灰有更大的质量平均粒径。

[0066] 在有些优选的实施方案中，所提供的碳基础吸附剂的质量平均粒径可以优选大于 40 微米，更优选大于 60 微米，或者其粒径分布比要处理的烟道气流或者其它要处理的含汞气体中的飞灰或夹带的灰分的粒径分布更大，以便可以通过物理方式分离活性炭和灰分。

[0067] 在有些实施方案中，加入了卤素或卤化物促进剂并与之反应的碳基础吸附剂可以优选包括（仅作为说明并不是限制性的）在蒸气或气体形式的分子卤素、在有机溶剂中的分子卤素、第 V 或第 VI 族元素的卤化物，例如分别在气相、液相或溶液形式（尽管并非在水溶剂中）的 PBr_3 或 SCl_2。

[0068] 所提供的有些实施方案中，有机溶剂可以优选包括氯化烃（例如二氯甲烷）、烃溶剂（包括例如石油醚、粗汽油、戊烷、己烷、甲苯和苯）、二硫化碳、废溶剂、醚、回收溶剂、超临界溶剂（例如超临界 CO_2）、水（不适用于第 V 族元素或第 VI 族元素的卤化物的情况）及其它对本领域技术人员显而易见的溶剂。

[0069] 现参见图 4，以图解说明了有科学证据的理论，以揭示促进的化合物的本质。例如，如图 4 所示，分子溴分子与包含大表面积形式的金属氧化物的基础吸附剂表面形成配合

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物。通过与沿间隙腔排列的路易斯碱氧原子的结合及表面上的碱作用，与溴的配合可发生在表面上及玻璃状的无定形网硅酸盐表面上的缺陷部位。分子溴化氧或亲电的或路易斯酸溴化合物的反应形成类似的结构。在 Stark 和 Klabunde 的显示了向 MgO 表面添加酸、HCl、SO_3 和 NO 以形成表面配合物的一篇文章 (Klabunde K. J., Chem. Mater. 1996, 8, 1913-1918) 中描述了与酸性物种的金属氧化物表面配合物的这种促进的优先次序。在 Koper 等的美国专利 6,517,423 中，所述的表面配合物对破坏生物试剂和毒素有活性。如图 4 所示，向金属氧化物表面 (A) 上加入卤素可以形成可被描述为溴化物 - 溴氧化合物物种 (B) 的配合物，其中归因于正电荷在表面上的形成而保持了亲电活性。在金属氧化物基础吸附剂上形成的亲电配合物包含用于原子汞的氧化的活性部位。向配合物加入汞导致汞氧键的形成，同时，图 4 中的配合物 C 也显示出汞溴键的形成。这样，最后的结构是可描述为溴化金属氧化汞 (metaloxymercuric bromide) 的稳定的氧化的汞形式 (D)。

[0070] 总之，现已发现，新的与金属氧化物表面的溴化物配合物的形成增加了对汞和其它污染物的表面活性。此外，所形成的溴化物化合物特别适合于促进汞的氧化。显然地，氧化的有效性来自卤化物的促进效果，卤化物在汞的氧化过程中影响正电荷的形成，这作为一种特定的催化效应在化学领域中是已知的。这样当汞的电子被拉向正的表面氧时，卤化物阴离子上的电子从另一侧推入，对汞上显现的正电荷起到了稳定作用并且降低了氧化过程所需的能量。溴的活性特别高，这是由于在离子的外层 4p 轨道上有高度极化的电子。因而向适当的金属氧化物加入 HBr 或 Br_2 而形成了类似的表面溴化合物配合物，其中正的氧在溴化物离子的帮助下对汞进行氧化。

[0071] 在有些实施方案中，带有含金属 - 氧 - 金属结构的路易斯碱部位 / 基团的非碳基础吸附剂被本公开的促进剂所活化，从而形成促进的吸附剂。促进剂与具有金属 - 氧 - 金属结构的非碳基础吸附剂形成介稳的配合物，这种配合物通过化学吸附捕捉汞。例如，介稳配合物可在卤素促进剂与非碳基础促进剂上的无机物种之间形成，其中无机物种包括钠 (Na)、钙 (Ca)、镁 (Mg)、铝 (Al)、铁 (Fe) 化合物及它们的组合。在有些实施方案中，介稳配合物包括与基础吸附剂的金属 - 氧 - 金属结构配合的双卤素基团，比如 Br-Cl、Br-Br。在有些实施方案中，介稳配合物包括与基础吸附剂的金属 - 氧 - 金属结构配合的卤素原子。在有些实施方案中，介稳配合物包括与基础吸附剂的金属 - 氧 - 金属结构配合的卤化氢基团。在有些实施方案中，介稳配合物包括与基础吸附剂的金属 - 氧 - 金属结构配合的第 V 族元素或第 VI 族元素的卤化物。在有些实施方案中，基础吸附剂的金属 - 氧 - 金属结构与本文披露的官能团的组合进行配合。不希望局限于理论的情况下，据信经由化学吸附的对汞的捕捉通过由这些介稳配合物所提供的汞氧化的作用而发生。

[0072] 在有些实施方案中，由石墨烯片层构成的含路易斯酸部位 / 基团的碳基础吸附剂被本公开的促进剂所活化，从而形成促进的吸附剂。促进剂与碳基础吸附剂的石墨烯片层形成稳定的化合物，它负责通过化学吸附捕捉汞。在不希望受限于理论的情况下，据信经由化学吸附的汞捕获通过由这些稳定的化合物所提供的汞氧化的行为而发生。在这一领域的技术人员会意识到与本公开的基础吸附剂（碳、非碳和它们的组合）和促进剂相关的化学多样性能够使得用于捕捉汞的促进的吸附剂系统具有多样化的应用。由于每天、每次操作和每个工厂的烟道气中的汞含量都会变化，这一点具有特别的益处。

[0073] 非碳基础吸附剂的例子是无定形形式的网硅酸盐，所述网硅酸盐包含排列有与第

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I 族的碱金属元素和第 II 族的碱土金属结合的路易斯碱氧的纳米尺度腔。这种网硅酸盐可以在自然界出现的矿物中找到，包括但不限于珍珠岩和浮岩。非碳基础吸附剂的例子还包括无定形形式的页硅酸盐。也可使用其它矿物，而且还经化学和热处理以增加基础吸附剂材料（如无定形形式的页硅酸盐）的活性。

[0074] 在有些实施方案中，使用膨润土作为非碳基础吸附剂，包括钠膨润土和钙膨润土。也可考虑使用其它类型的膨润土，因为这对本领域的技术人员来说是已知的。使用膨润土基础吸附剂时，是将它们在汞捕捉系统的温度低于 800℃的某一位置引入到烟道气中。

[0075] 在有些实施方案中，对基础的吸附剂进行化学和 / 或热处理以增加它们的活性。例如，作为基础吸附剂的珍珠岩可先经真空处理后经热处理以减少它们含有的水分、增加其活性并可选地改变其形貌。其它处理过程包括化学处理，例如酸处理和碱处理。也可将这些处理方法组合以达到期望的效果，本领域的技术人员熟知这一点。一种期待的效果是增加碳基础吸附剂中可用的路易斯酸部位 / 基团和 / 或非碳基础吸附剂中可用的路易斯碱部位 / 基团的数量，这些部位 / 基团用于随后的经由与本文公开的促进剂的反应的活化。

[0076] 现参见图 3，提供了汞控制系统 100 的示意性流程图，它包括根据本发明的优选实施方案的促进的基础吸附剂的制备和烟道气中汞的减少。在给出的示例性实施例中，提供了基础吸附剂储存器 110，卤素 / 卤化物促进剂储存器 120，第三组分储存器 130 和碱性组分储存器 180，它们中的每一个都分别具有对应的一个或多个流量控制器 201、202、203 和 208/209。与碱性组分储存器 180 相结合的情况下，流量控制器 208 和 209 可以独立使用、一起使用或者不用。此外，储存器 110、120、130 和 180 是可选的，并且可以任意组合使用或者完全不用，由此其它的储存成分可以通过共同或独立的其它方式引入到系统中。此外，碱性和第三组分在系统中可以完全不使用，如果希望如此的话。

[0077] 如所示的，储存器 110、120、130 和 180 通过它们各自的流量控制器和经由相关的管道系统与输送管线 115 相连。碱性组分储存器 180 也可通过相应的流量控制器及经由相关的管线与输送管线 118 相连。为了夹带从储存器 110、120、130 和 180 流出的材料以及将这些材料通过注射点 116 注入到污染的烟道气流 15 中，空气、氮气或其它载气的源通过气源 170 提供至输送管线 115。为了夹带从储存器 180 流出的材料以及将这些材料通过注射点 119 注入到烟道气流 15 中，空气、氮或一种或多种其它输送气体可以通过气源 171 提供给输送管线 118。根据需要，气源 170 和 171 可以相同或不同。另一种选择是，通过气源 170 同时向输送管线 115 和 118 提供一种或多种输送气体（源 170 与管线 118 的连接未显示）。尽管图 3 中显示的气源 170 和 171 为压缩机或鼓风机，但是本领域的技术人员会想到，本领域中已知的输送能量中的任一种源也是可以接受的。

[0078] 为清晰起见，图 3 显示了单一注射点 116 或 119，尽管本领域的技术人员会理解多重注射点和 / 或位置是包括在本发明的范围内的。在所示的实施方案中，输送管线 15 包括多条管线，这使得基础吸附剂 110 和促进剂 120 和 / 或 130 的多重注射和分开的和 / 或组合的注射成为可能。例如，一种操作模式包括在共用管线中提供基础吸附剂 110，它在“飞行中”被促进剂 120 和 / 或 130 在管线内促进并且在点 116 处被注入。另一种操作模式例如包括：在单独的管线中的基础吸附剂 110 被注入到在促进剂 120 和 / 或 130 在管线中在点 116 注入的下游的点，点 116 在基础吸附剂 110 的注入的上游，由此导致在流 15 内促进的吸附剂的在飞行过程制备。

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[0079] 在所示的示例性实施例中，一个或多个可选的光密度测量器 204 与输送管线 115 和 / 或 118 相连接，以提供代表输送管线 115 和 / 或 118 内光密度随时间变化的信号。

[0080] 在注入点 116 和 119 的下游提供有粒子分离器 140。作为说明而不是限制性的，粒子分离器 140 可以包括一个或多个织物过滤器、一个或多个 ESP 或其它本领域已知的粒子除去装置。还应注意到可存在超过一个的串行或并行的粒子分离器 140，而当并行、串行或串并混连时，注射点 116 和 119 可以在 140 上游和 / 或下游的多个位置。粒子分离器 140 至少会产生主要的气态流（清洁的）142 和含有分离的固体材料的流 141。吸附剂 / 灰分分离器 150 将流 141 分离为基本为灰分的流 152 和基本为吸附剂的流 151。然后优选将流 151 通过可选的吸附剂再生器 160，得到再生的吸附剂流 161 和废气流 162。

[0081] 在废气流 35 中提供一种可选的用于汞的连续排放监测器（以下表示为“CEM”）205，以提供表示废气流 35 中汞浓度随时间的变化的电信号。可选的汞 CEM 205 与流量控制器 201、202、203、208 和 209 的经由可选的线 207（或者通过无线）电连接至可选的数字计算机（或控制器）206，所述数字计算机（或控制器）206 接收和处理信号并优选控制促进的碳吸附剂的制备及向污染的烟道气流 15 的注入。

[0082] 在运行中，作为实例，促进的吸附剂和 / 或可选的碱性组分被注入到污染的烟道气流 15 中。注入的材料经过与污染的烟道气流 15 接触后，注入的材料降低了汞的浓度，将污染的烟道气转变为降低汞的烟道气 25。注入的材料分别通过分离器 140 从烟道气 25 中除去，抛弃掉或进一步通过可选的分离器 150 分离，然后抛弃掉或通过可选的再生器 160 再生。然后通过可选的 CEM 205 监测降低汞的清洁烟道气流 142 的汞含量，CEM205 向可选的计算机 / 控制器 206 提供相应的信号。然后来自 206 的逻辑和优化的信号根据本领域熟知的控制算法调节流量控制器 201、202、203、208 和 209 以保持废气流 35 中汞的浓度在期望的限值内。流量控制器 201、202、203、208 和 209 也可以通过人工或通过一些其它自动化的方式根据本领域熟知的控制算法调节，以保持废气流 35 中汞的浓度在期望的限值内。

[0083] 仍参见图 3，图解说明了根据本发明制备和注射促进的吸附剂和 / 或碱性组分的几个实施方案。流 111 提供从储存器 110 引入基础吸附剂，由流量控制器 201 手动或根据计算机 206 的指令计量。卤素 / 卤化物可以按照几种提供的方法中的任一种与基础吸附剂结合并反应。卤素 / 卤化物可以优选通过管线 121 直接结合到输送管线 115，在 115 内它与基础吸附剂接触并反应，这发生在注射点 116 之前或点 116 的下游。这导致按照本发明的促进的吸附剂的飞行中制备。此外，在进入输送管线 115 之前，卤素 / 卤化物可通过管线 121b 与基础吸附剂结合。还另外地，卤素 / 卤化物可通过经由管线 121c 引入储存器 110 与基础吸附剂接触并反应。例如当储存器 110 中包含基础吸附剂的沸腾床或流化床时，优选使用这种可选的方式，这样卤素 / 卤化物以气态或作为蒸汽流动通过沸腾床或流化床。当然，如前面讨论的，也可能优选卤素 / 卤化物与液态或在溶剂中的基础吸附剂接触，如果需要，可以如参考图 1 论述的实施方案所提及的，提供溶剂移除（未在图 3 中显示）。

[0084] 类似地，可选的第二组分可以经由管线 131，或可选地如上面关于卤素 / 卤化物所述，经由管线 131b 和 131c，在输送管线 115 中直接进行接触与反应。

[0085] 类似地，来自 180 的可选碱性组分可以直接加入到输送管线 115，或可以通过输送管线 118 单独注射，在下游的烟道气 15 中结合，以实现与基础吸附剂、促进的吸附剂或可选的第二组分的协同效应。能够在现场调节可选的碱性组分相对于基础吸附剂、促进吸附剂

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或可选的第二组分的量对于克服和优选现场特定的操作和烟道气条件是关键性特征。

[0086] 在有些优选的实施方案中，各组分的接触和反应是在液态或在溶剂中进行的情况下，可以提供这些液体和/或淤浆混合物的搅拌。在另外的有些实施方案中，卤素/卤化物促进剂和一种或多种可选的第二组分最好以溶液形式喷洒到基础吸附剂内或喷洒到基础吸附剂上。在一些这样的实施方案中，然后可以增加本领域熟知的干燥、过滤、离心、沉淀、倾析或其它溶剂移除方法。

[0087] 在有些实施方案中，卤素/卤化物促进剂处于气态或蒸汽形式，这时可能需要以空气、氮气或其它气体适当地稀释。卤素/卤化物气体，例如气态的 HBr 和 Br_2，可以通过颗粒或纤维状的基础吸附剂的沸腾床或流化床，其中通过用于注射的气体夹带，所产生的促进的吸附剂从床的顶部被除去。

[0088] 在有些实施方案中，一种或多种第二组分可以优选包括碘或其它卤素、卤化氢（包括但不限于 HI、HBr 和 HCl）、第 V 族或第 VI 族元素与的分子卤素，如 SCl_2 及其它。在有些优选的实施方案中，促进的吸附剂可以包括按每 100 克基础吸附剂计的约 1 至约 30 克卤素/卤化物。在有些优选的实施方案中，促进促进剂可以包含第二组分并且第二组分的浓度为卤素/卤化物组分的浓度的约 1 至约 15 重量%。

[0089] 在再其它的实施方案中，促进的吸附剂产物会可以施加到基底上。在其它实施方案中，可以使这样制备的一种或多种基底与污染的烟道气或气化系统产物气体流接触，以实现降低汞的目标。这样的基底可以是单斜的、旋转的或以其它本领域技术人员熟知的任何数量的方式暴露于气流中。

[0090] 在有些实施方案中，提供了向促进的吸附剂加入汞稳定试剂以形成双官能吸附剂的方法。这样的一种或多种稳定试剂可以在卤素/卤化物添加和反应之前或之后顺序添加。在有些实施方案中，卤素/卤化物优选包括 Br 或 HBr，并且汞稳定试剂可以包括 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 及它们的组合。

[0091] 捕捉汞的卤素

[0092] 以卤素处理烟道气的方法一直存在难点，原因在于它们与其它气体和金属的反应能力，从而会导致腐蚀和健康问题。“卤素”被定义为包括元素周期表中第 VIIA 族元素（全文使用 CAS 命名：第 VIIA 族 (CAS) 相当于第 VIIB 族 (IUPAC)）在内的非常活泼的元素的成员。分子形式的卤素中，包括 F_2、Cl_2、Br_2 和 I_2，它们会与热烟道气中的成分反应，而与原子汞的反应部分极少。包括氟、氯、溴和碘原子在内的原子形式的元素卤素与汞的反应活性要高一百万倍以上，但以原子形式存在的浓度一般是极低的。对于大部分烧煤的电力设施而言，这么低的浓度不足以氧化相当大量的汞。

[0093] 本文使用的“卤化物”被定义为卤素与其它原子或自由基反应而形成的化合物。卤化物化合物通常的反应性比卤素分子弱很多，具有低的化学势。卤化物被视为还原态，它们不单独氧化其它化合物。因此在传统的观念中，卤化物盐处理的吸附剂不会有效氧化并捕捉原子汞。

[0094] 卤素促进的吸附剂的特点

[0095] 本文所述的促进吸附剂对氧化汞具有非常高的初始活性，因而以非常少的量使用就可实现很高的捕捉效率，从而降低运行成本并减少废物处理的问题。此外，可以通过使用本发明的技术所得到的促进的吸附剂的再生和再使用来进一步减少处理问题。汞与本发明

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的促进的吸附剂在烟道气导管内成功相互作用及此后对促进的吸附剂上的汞和灰分的收集所需的时间间隔很短－不超过数秒钟。显然，这样的收集时间需要促进的吸附剂对汞具有高的捕捉能力和高的反应性。可以使用非常细的粉末态的促进的吸附剂，以尽量减小传质的限制。然而，同样地，反应性应该很高以捕捉细的粒子遇到的所有汞。此外，这些增强技术的使用使得对于更大的吸附剂粒也可有效捕捉，这也使促进的吸附剂与灰分分离，以使得此后的再生及灰分利用成为可能。此发明的一个特征是制备在基础吸附剂结构上和/或内含有卤化物成分的促进的吸附剂的方法，这提供了一种与汞污染的气流初始接触时具有高活性的吸附剂，这允许非常有效地捕捉汞。

[0096] 所发明的吸附剂利用基础吸附剂上的路易斯酸/碱部位化学结合溴物种。例如，X 射线光电子能谱已经确认加入的溴、氯、溴化氢或氯化氢在碳结构上形成了化合物。这样由卤素和基础吸附剂得到的促进的吸附剂不能表示为分子卤素的形式，而是一种新的发生化学变化的结构。对于反应性较低的碘或许不会出现这一现象，而是 I_2 分子配合物可存在于碳基面上。在溴的情况下，改性的碳正离子对汞的氧化而言有足够高的化学势。因而在图 2 中给出了表示溴处理的碳对汞的反应性的全新模型。反应性的碳形式可以优选通过加入溴、溴化氢或溴与其它元素的组合而产生，这如本文中所述。卤素处理形成更高反应性的碳，这是由于卤化物阴离子（特别是溴化物和碘化物）对促进氧化是有效的，这是通过对处于过渡的氧化态的汞上显现的正电荷的稳定化来促进的。基于这一模型，已经开发了几种新颖的低成本的反应性增强特征。

[0097] 可选的第二组分

[0098] 已经确定加入除溴以外的可选的第二组分会改善促进的吸附剂的反应性和吸附能力，典型地超过未处理的基础吸附剂和溴化的碳这二者的情况。第二组分包括第二卤素或由第二卤素衍生的化合物，例如 IBr。这样除了已有的反应性碳形式外，第二组分产生对于稳定在汞上显现的正电荷具有更大能力的路易斯碱。因而第二组分为拥有多个可极化电子 (4p 和 5p) 的元素。

[0099] 可选的碱性组分

[0100] 已经证实向基础的或促进的活性炭加入可选的碱性组分会增加汞的捕捉，效果一般超过未处理的碳和促进的碳这二者的情形。测试数据表明，烟道气污染物、烟道气组分 (SO_2、NO_x、HCl 等)、运行温度、汞的形式及汞的浓度都会影响碱性组分加入的效果。为了克服和优化给定的现场条件组，这建议需要能够调整和调节在现场的碱与活性炭的比例。

[0101] 对共同注入两种材料获得的协同效应可作如下解释。首先，测试显示活性炭（此后以“AC”表示）上的结合部位可以被氯物种、硫物种（即硫酸盐）及其它烟道气污染物（砷酸盐、硒酸盐等）消耗。加入可选的碱性材料会与这些物种/污染物作用和反应，这样使它们对 AC 汞结合部位的消耗降至最低。其次，测试也显示即使结合部位被完全消耗之后，标准的 AC 仍会继续对汞进行氧化。因而，这种氧化的汞可与碱性材料反应，并且随后被粒子控制器捕捉。因而，加入的可选的碱性组分起到保护汞结合部位及捕捉氧化的汞的作用，从而以更低的成本改进汞的减少。碱的成本通常比 AC 更低（约低一个数量级），这样碱性组分使用的越多，整体成本就会降低越多。

[0102] 在飞行中的吸附剂制备

[0103] 如前所述，卤素促进的吸附剂可以容易地在飞行中制备。例如，这可通过卤素和可

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选的第二组分的任一组合的蒸气与基础吸附剂粒子在飞行中的接触而实现。这些粒子可分散在输送空气的气流（或其它气体，例如烟道气自身）中，此气流也将卤素/卤化物促进的吸附剂粒子输送到烟道气导管，或者分散在其它污染的气流中，然后将其中的汞移除。对于这种接触，没有特别的温度要求。这一技术的操作显然非常简单，并且使用此种用于汞捕捉的技术的设施的费用大为节省。

[0104] 参见图5A和5B，工艺流程图被表示为从含汞气体中（例如烟道气）除去汞的工艺的一个例子。在图5A所示的一个实施方案中，气体入口流501通过腔室301，然后作为流502进入空气加热器302，然后作为流503离开空气加热器302并通过粒子控制器303，并作为流504进入洗涤器304；最后它作为流505离开洗涤器304。如图所示，腔室301为锅炉，然而，本领域的技术人员应当理解到腔室301也可为烧煤锅炉的燃烧室、独立的燃烧室或任何其它的其中产生或通过含汞气体的燃烧室。除了流501外，注射流401、402、403和404为多个可以引入促进剂、基础吸附剂或促进剂与基础吸附剂的组合的位置。

[0105] 图5B显示了与图A类似的一个实施方案，但洗涤器和粒子控制器的位置互换了。具体地，气体入口流501'通过腔室301'，然后作为流502'进入空气加热器302'，然后作为流503'离开气体加热器302'，并且通过洗涤器304'，然后作为流504'进入粒子控制器303'；最后它作为流505'离开粒子控制器303'。如图所示，腔室301为锅炉，然而，本领域的技术人员应当理解到腔室301也可为烧煤锅炉的燃烧室、独立的燃烧室或任何其它的其中产生或通过含汞气体的燃烧室。除了流501'外，注射流位置401'、402'、403'和404'为多个其中可以引入促进剂、基础吸附剂或促进剂与基础吸附剂的组合的位置。

[0106] 对于每个前面提到的注射流位置401、401'、402、402'、403、403'、404和404'，都会考虑多重注射点501、501'，以便促进剂和基础吸附剂可作为单一注射流或作为分开的注射流注射，这还会在下面的示例性实施方案中说明。

[0107] 在一个实施方案中，促进剂在位置401处引入到腔室301中。基础吸附剂（碳、非碳及它们的组合）在空气加热器302的上游的位置402处被引入。在另外的实施方案中，促进剂在空气加热器302的上游的位置402处被引入。基础吸附剂（碳、非碳及它们的组合）也在位置402处作为分开的气流或作为与促进剂混合的单流被引入。在另外的实施方案中，促进剂在位置401和402被引入。基础吸附剂（碳、非碳或它们的组合）在位置402作为分开的流引入或作为与促进剂的混合单流引入。

[0108] 借助于本公开内容，本领域的普通技术人员将能够组合出许多不同方式的用于使用促进的吸附剂除汞的方法。所有这些组合都被认为是所披露的方法的等价物，因此也包含在所要求保护的发明的范围内。

[0109] 现场制备的优点

[0110] 卤素/卤化物促进的吸附剂在一定位置（on location）的飞行中制备有一定的优点。例如，处理系统可以与基础吸附剂注入系统在使用终端现场相结合。使用此技术，卤素/卤化物被引入到在输送管线中（或基础吸附剂储存和注入系统的烟道气导管部分）的基础吸附剂空气（或其它气体，包括烟道气或其它含汞气体）中。与不在现场处理吸附剂的当前的传统概念相比，这提供了如下的好处：

[0111] ●省去了处理设施的资金设备成本。

[0112] ●省去了运行处理设施的成本。

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[0113] ●省去了向处理设施输送碳和添加剂的成本。

[0114] ●本发明工艺使用现有的硬件和操作程序。

[0115] ●本发明技术确保吸附剂总是是新制的，这样会有更高的反应性。

[0116] ●不会带来新的处理问题。

[0117] ●从处理系统中移走碳不需要成本。

[0118] ●本发明工艺允许在现场对添加剂－吸附剂的比例进行调整，以配合烟道气变化的需要，例如当更换燃料或减小负荷时就会有这种需要，从而进一步优化成本。

[0119] ●本发明技术减少了用过的吸附剂的丢弃量。

[0120] 鉴于前述的及其它的特性，根据本发明提供的实施方案中包括制备和再生卤素／卤化物促进的吸附剂，通过向基础吸附剂结构中加入卤素（例如溴）而提升它们对汞的捕捉能力。

[0121] 吸附剂注入位置

[0122] 有些优选的实施方案使用粉末形态的卤素增强的吸附剂，它在灰分粒子除去之前或之后被注入到烟道气流中。其它的实施方案中，发明的卤素促进的吸附剂的组成包括通过添加 Br_2 或 HBr 与第二可选组分而制备的改性的粉末状 AC。其它的实施方案中，允许可选的碱性组分与基础的 AC 的结合添加和／或基于卤素的吸附剂的使用，以及本专利提供的吸附剂技术的任何其它组合的使用。其它的实施方案中，通过促进剂和基础吸附剂的使用及结合，容许在飞行中制备促进的吸附剂。此外，有些实施方案包括这样的方法：其中基础吸附剂处在移动的接触器上，其由含有一种或多种上面列出的组分的粒子或纤维组成。

[0123] 吸附剂的再生

[0124] 上述卤素／卤化物促进的碳和／或非碳吸附剂的任一实施方案都可以容易再生；烟道气中的毒性污染物被优先除去，并且加入低价的促进试剂，从而恢复对汞的吸附能力。这种提升碳和／或非碳自身能力的工艺与早期向基础吸收剂加入试剂（例如过氧化物、金、三碘化物等）的更昂贵的传统方法形成了对照。本发明的以溴和／或可选的组分处理的卤素／卤化物促进的碳吸附剂不具有腐蚀性。吸附剂再生技术的具体例子在共同悬而未决的共有的 PCT 专利申请 PCT/US04/12828 中有描述，该 PCT 专利申请的名称为“已用吸附剂的再生过程(process for regenerating a spent sorbent)”，该PCT专利申请通过引用将其全部内容结合到此。

[0125] 吸附剂注射控制方案

[0126] 本发明的另一优势体现在使用反馈系统以便能更有效地利用本发明的某些方面。当可能与期望的情况下，本发明的汞控制技术可优选利用汞排放的连续测量作为反馈以帮助控制吸附剂的注射速率。以这种方法可实现对吸附剂和一种或多种可选的组分水平的更严密控制，这将确保以最少的材料消耗达到除汞的要求，从而使相关成本最小化。在一个实施方案中，在注射位置的下游，优选是在烟囱的废气里，连续测量汞的排放。

实施例

[0127] 为了更清楚地对本发明进行解释，下面给出实施例。这个实施例是说明性的，不能依据此实施例得到或推论出对本发明的任何限制。

[0128] 实施例 1----- 在工业装置中对非碳的促进的吸附剂的测试

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[0129] 在几家装配了 ESP 的烧煤设施进行了工业化的商业测试，其中三种类型的前体于 325° F 注入在 ESP 的上游。通过改变基础吸附材料、基础吸附剂材料的注入速度和促进剂的注入速度，总共进行了超过二十项的测试。促进剂为卤素基的材料。基础吸附剂为粘土基的材料，例如珍珠岩和浮岩 (pumacite)，它们是泡状形式的网硅酸盐，包括其中碱金属处于间隙 (interstitial) 空间内的硅酸盐和铝四面体。每种基础吸附剂都在 ESP 的上游注入。

[0130] 所测试的烟道气流速近似为 2300 万 $dsft^3$/ 小时，对应的汞流速为 0.0097 磅的汞 / 小时。在引入基础吸附剂或促进的吸附剂之前，烟道气中的初始汞浓度近似为 0.000417 磅汞 / 百万 $dsft^3$。

[0131] 如表 1 所示，每种基础吸附剂以三种不同的测试速度注入：约 100 磅 / 小时 (“低”)、约 150 磅 / 小时 (“平均”) 和约 200 磅 / 小时 (“高”)。在每种测试速度，都测量使用和未使用促进剂的除汞速度，以展示向烟道气流中引入促进剂的相对益处。对于向烟道气流中注入促进剂的测试，对“低”、“平均”和“高”的测试，促进剂的注入速度分别为约 20 磅 / 小时、约 25 磅 / 小时和约 30 至约 50 磅 / 小时。每次测试的除汞百分比都是基于对入口烟道气和出口烟道气的测定值而计算的。表 1 给出的结果清楚显示出，与只注入基础吸附剂时的情况相比，促进剂和基础吸附剂均被注入时在汞捕捉方面有显著的改善。

[0132] 表 1 对非碳的促进的吸附剂的测试数据

[0133]

基础吸附材料	基础吸附剂注入速度（磅/小时）			促进剂注入速度（磅/小时）			除汞百分比（%）		
	低	平均	高	低	平均	高	低	平均	高
珍珠岩	100	150	200	0	0	0	37	40	43
	100	150	200	20	25	35	55	72	74
浮岩	100	150	200	0	0	0	25	25	25
	100	150	200	20	25	50	52	60	65
二氧化硅和铝的粘土基混合物	100	150	200	0	0	0	50	52	54
	100	150	200	20	25	30	58	65	74

[0134] 尽管已经给出和描述了本发明的优选实施方案，但是本领域的技术人员可以在不脱离本发明的精神和教导的情形下对其进行改动。本文描述的实施方案仅是示例性的而非意在限制性的。对本文公开的发明的很多变动和改变都是可能的，并且在本发明的范围之内。因此，保护的范围并不限于以上描述的内容，而仅是由后附的权利要求书限制，保护范围包括等价于所有权利要求的主题的内容。

[0135] 在此公开中提供的实施例只是出于阐述和解释的目的而给出，而非意在限制本发明的权利要求或实施方案。尽管本发明的优选实施方案已经给出和描述，但是本领域的技术人员可以在不脱离本发明的精神和教导的情形下对其进行改动。对于本领域的技术人员而言，根据本文公开的内容，很容易确定实施本发明所需的工艺标准、设备等条件。本文公开的实施方案只是示例性的而非没有限制的意图。对在本文公开的发明的很多变化和变动是可能的，并且包括在本发明的范围之内。与本发明任一要素相关的术语“可选的”的使用意味着这种主题要素是需要的，或者备选地，是不需要的。它的替代选项也包括在本发明的范围内。

[0136] 在发明背景中的参考文献的论述并非是承认其是本发明的现有技术，尤其是出版日期在本申请的优先日期之后的任何参考文献。对所有在本文中引用的专利、专利申请和

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出版物的公开内容都通过引用将它们的全部内容结合在此，在某种程度上它们为本专利的内容提供了例证、程序或其它细节补充。

[0137] 尽管本发明作为促进的吸附剂材料以及相关的对其制备及使用在本文中进行了描述，然而并不意在局限于所述的细节，因为在不脱离本发明的精神的情况下以及在权利要求的等价内容的范围内，可以在其中进行各种改变和结构变化。

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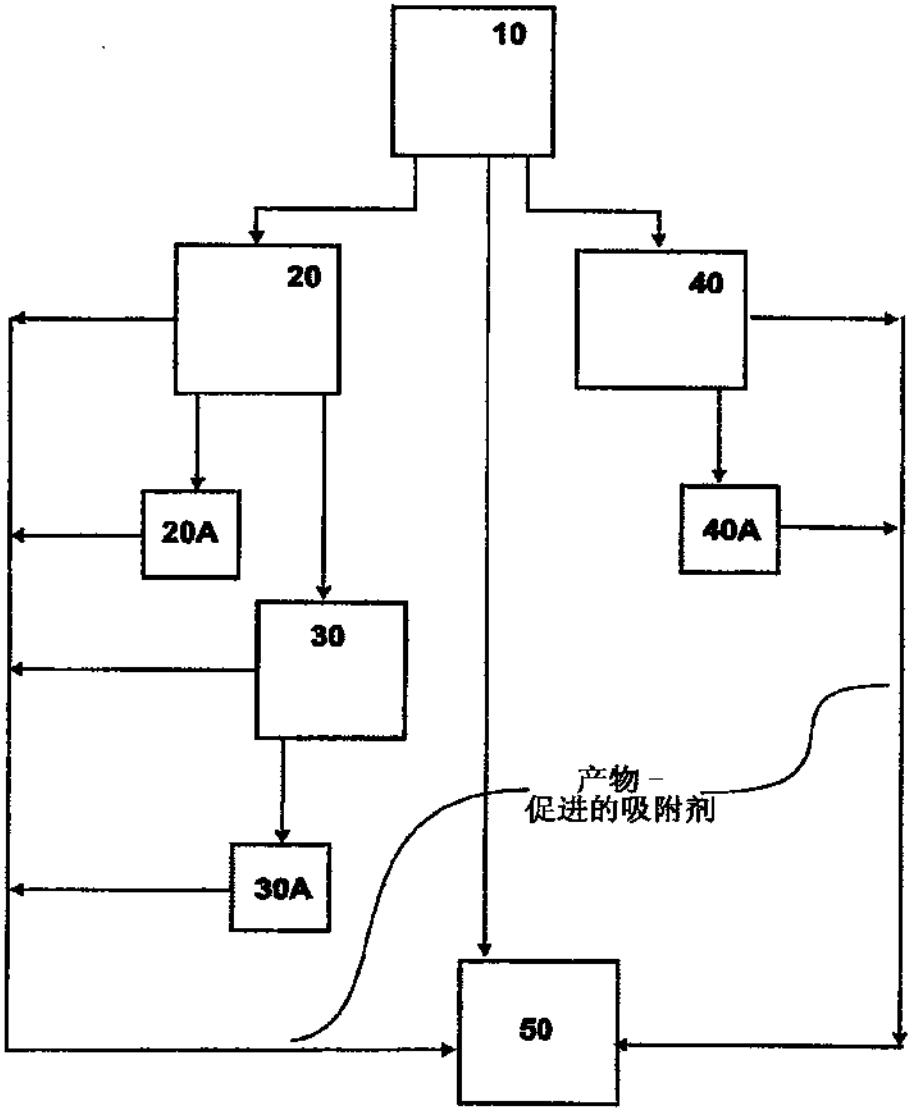


图 1

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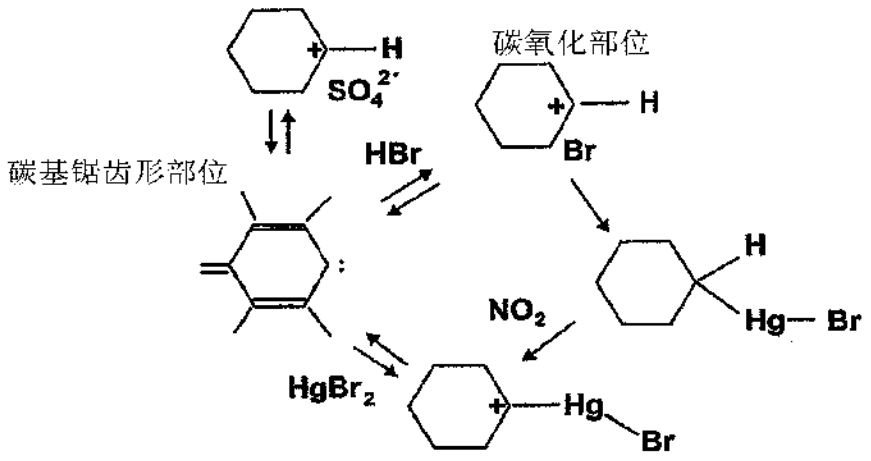


FIG. 2

图 2

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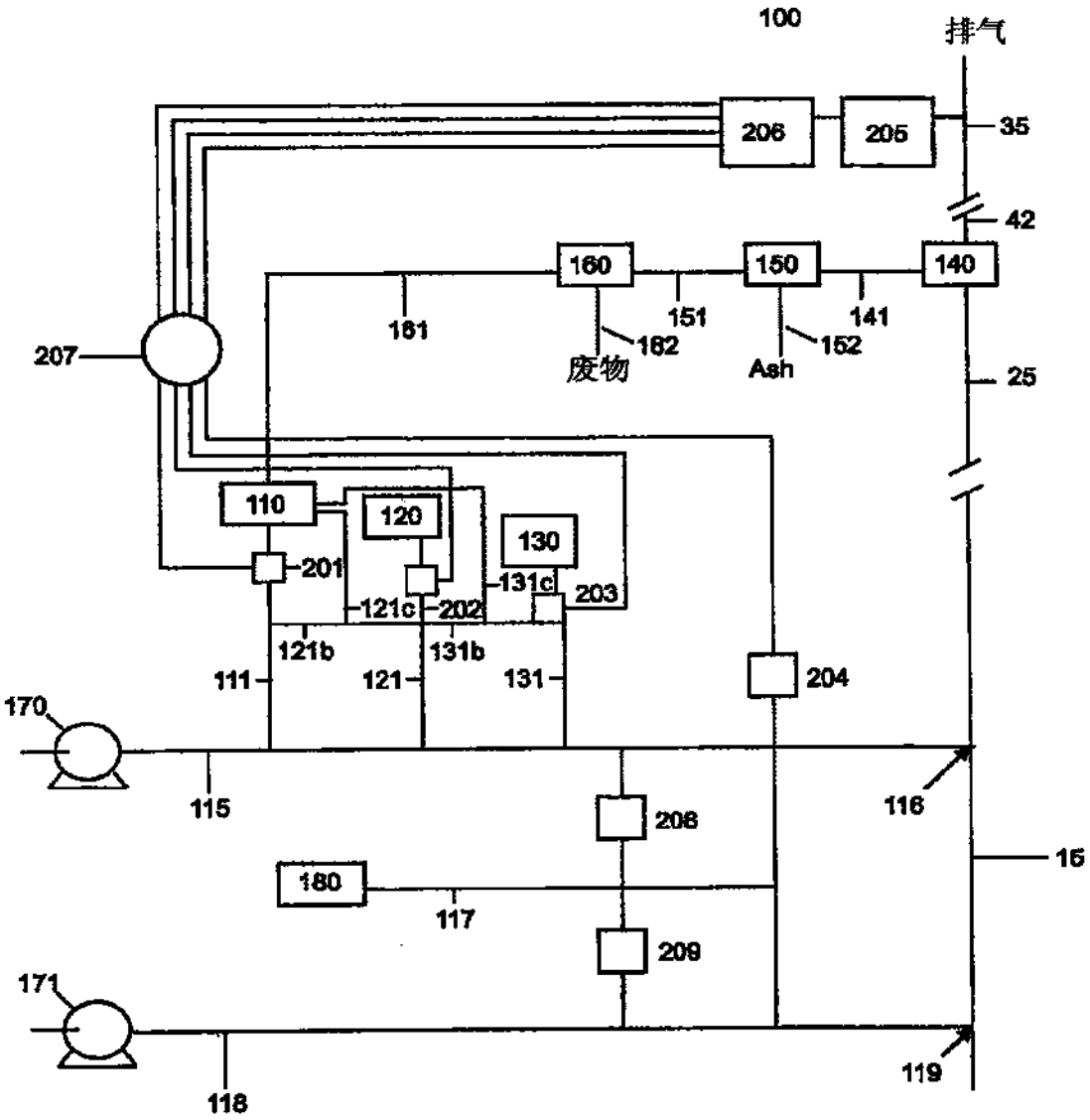


图 3

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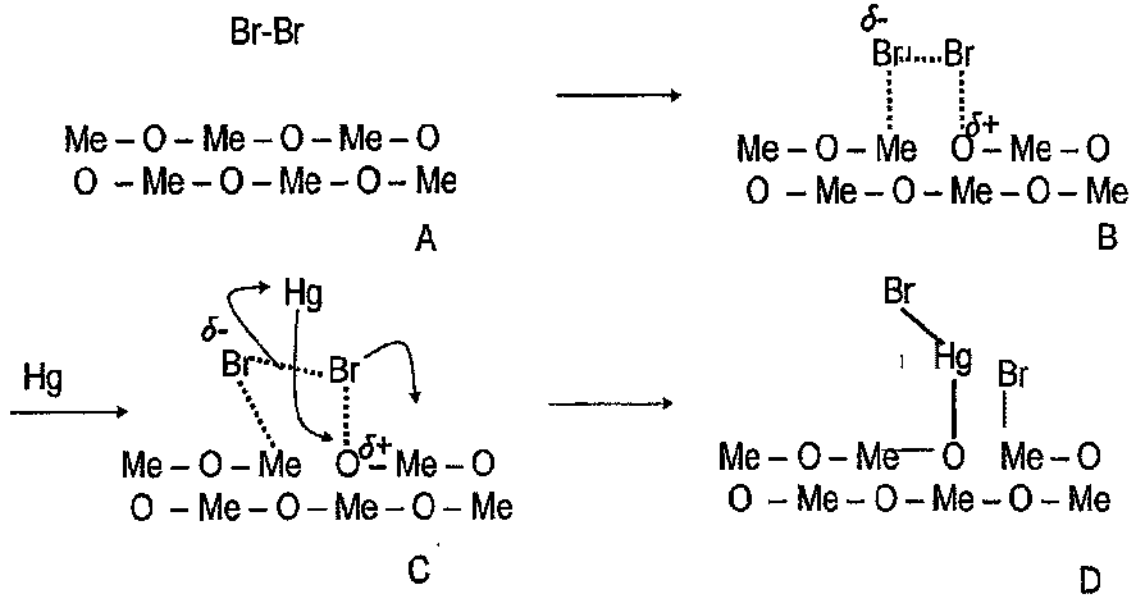


图 1

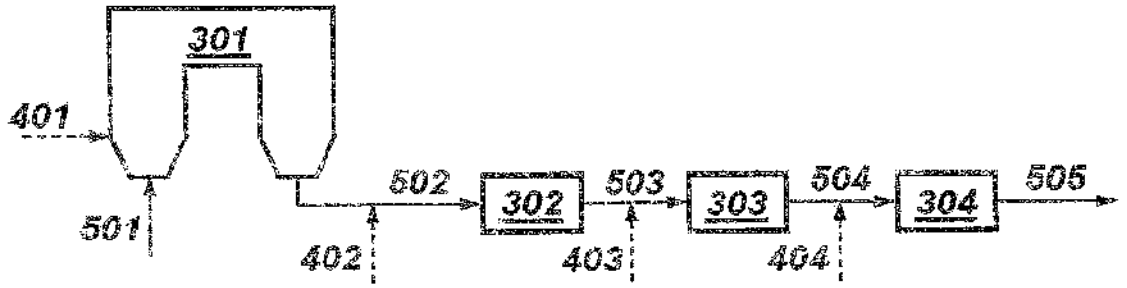


图 5A

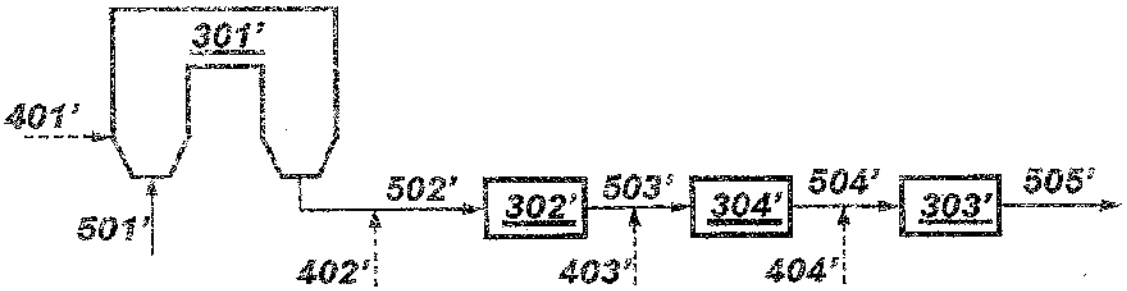


图 5B

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1. 一种从含汞气体中分离汞的方法，所述方法包括：

(a) 提供非碳吸附剂材料；

(b) 提供卤素或卤化物促进剂；

(c) 通过使所述非碳吸附剂材料与所述卤素或卤化物促进剂发生化学反应而形成促进的卤化吸附剂，从而促进所述非碳吸附剂材料的至少一部分；

(d) 使所述含汞气体中的原子汞与所述促进的卤化吸附剂发生化学反应形成汞/吸附剂化学合成物；以及

(e) 从所述含汞气体中分离颗粒以形成清洁的气体，所述颗粒包括灰分和第一汞/吸附剂化学合成物。

2. 权利要求 1 所述的方法，所述方法还包括向所述含汞气体中注入所述非碳吸附剂材料和所述卤素或卤化物促进剂的步骤。

3. 权利要求 2 所述的方法，其中所述卤素或卤化物促进剂和所述非碳吸附剂材料在同一位置注入到所述含汞气体中。

4. 权利要求 2 所述的方法，其中所述卤素或卤化物促进剂和所述非碳吸附剂材料在分开的位置注入到所述含汞气体中。

5. 权利要求 4 所述的方法，其中所述卤素或卤化物促进剂在所述非碳吸附剂材料的注入的上游注入到所述含汞气体中。

6. 权利要求 5 所述的方法，其中所述卤素或卤化物促进剂被注入到产生含汞气体的燃烧室内，而非碳吸附剂材料在所述燃烧室的下游注入。

7. 权利要求 6 所述的方法，其中所述卤素或卤化物促进剂另外在所述燃烧室的下游注入。

8. 权利要求 6 所述的方法，其中所述燃烧室为锅炉，而所述含汞气体为烟道气。

9. 权利要求 3 所述的方法，其中所述卤素或卤化物促进剂和所述非碳吸附剂材料在产生含汞气体的室的下游注入。

10. 权利要求 9 所述的方法，其中所述室为锅炉，而所述含汞气体为烟道气。

11. 权利要求 2 所述的方法，其中所述非碳吸附剂材料被注入的速率、所述促进剂被注入的速率或它们的组合是根据所监测到的清洁的气体中的汞含量进行调整的，以便所述清洁的气体中的汞含量基本上保持在期望的水平。

12. 权利要求 1 所述的方法，其中所述非碳吸附剂材料选自如下各项：多孔长英矿物材料、泡状长英矿物材料，多孔玄武岩材料、泡状玄武岩材料、粘土基化合物、碱性化合物、氢氧化钙化合物、酷酸钠化合物、碳酸氢盐化合物以及它们的组合。

13. 权利要求 12 所述的方法，其中所述非碳吸附剂材料是与所述含汞气体中的氧化的汞反应形成第二汞/吸附剂化学合成物的材料。

14. 权利要求 1 所述的方法，其中所述非碳吸附剂材料含有路易斯碱基团。

15. 权利要求 1 所述的方法，其中所述非碳吸附剂材料包括无定形形式的网硅酸盐，所述网硅酸盐包含排列有与碱土金属结合的路易斯碱氧的纳米尺度腔。

16. 权利要求 15 所述的方法，其中所述的碱土金属包括第 I 族和第 II 族的碱土金属。

17. 权利要求 1 所述的方法，其中所述非碳吸附剂材料包括无定形形式的页硅酸盐，所述页硅酸盐包含排列有路易斯碱氧的纳米尺度腔。

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18. 权利要求 1 所述的方法，其中所述促进的吸附剂包括在所述的促进剂与在所述非碳吸附剂上的无机物种之间形成的介稳配合物。

19. 权利要求 18 所述的方法，其中所述无机物种选自如下各项：钠化合物、钙化合物、镁化合物、铝化合物、铁化合物以及它们的组合。

20. 权利要求 1 所述的方法，其中所述促进的吸附剂包括在所述促进剂与在所述非碳吸附剂上的金属 - 氧 - 金属结构之间形成的介稳配合物。

21. 权利要求 20 所述的方法，其中与所述金属 - 氧 - 金属结构配合之后的所述促进剂处于选自如下各项的形式：双卤素基团、卤素原子、氢卤化物基团、第 V 族的卤化物、第 VI 族的卤化物以及它们的组合。

22. 权利要求 1 所述的方法，其中所述促进的吸附剂包含活化的路易斯碱基团、活化的路易斯酸基团或它们的组合。

23. 权利要求 1 所述的方法，其中促进的吸附剂与所述含汞气流之间的相互作用包括：

汞从所述气相扩散到所述促进的吸附剂表面上；以及

与活化的路易斯碱基团、活化的路易斯酸基团或它们的组合反应以引起在所述吸附剂表面上的化学吸附。

24. 权利要求 1 所述的方法，所述方法还包括对所述吸附剂进行预处理以增加所述吸附剂上的路易斯碱基团、路易斯酸基团或它们的组合的数量。

25. 权利要求 24 所述的方法，其中对所述吸附剂进行预处理包括化学处理、热处理、真空处理以及它们的组合。

26. 权利要求 25 所述的方法，其中所述化学处理包括酸处理和碱处理。

27. 权利要求 1 所述的方法，所述方法还包括向含汞气体中引入碱性组分。

28. 权利要求 1 所述的方法，其中使碳吸附剂与所述促进剂反应以制备促进的碳吸附剂。

29. 权利要求 28 所述的方法，其中所述碳吸附剂、所述促进剂或它们的组合在一个或多个位置引入到所述含汞气体中。

30. 权利要求 29 所述的方法，其中所述碳吸附剂被引入的速率、所述促进剂被引入的速率或它们的组合是根据所监测到的清洁的气体中的汞含量进行调整的，以便所述清洁的气体中的汞含量基本上保持在期望的水平。

31. 权利要求 28 所述的方法，其中所述碳吸附剂包括活性炭。

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Carbon nanocomposite sorbent and methods of using the same for separation of one or more materials from a gas stream

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Abstract of CN104619410 (A)

The present invention relates to carbon nanocomposite sorbents. The present invention provides carbon nanocomposite sorbents, methods for making the same, and methods for separation of a pollutant from a gas that includes that pollutant. Various embodiments provide a method for reducing the mercury content of a mercury-containing gas.

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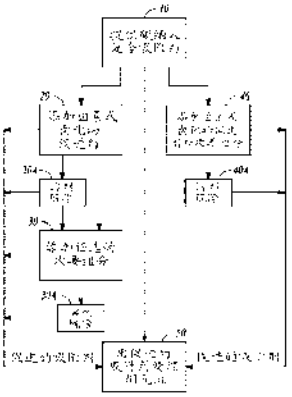
权利要求书3页 说明书24页 附图7页

(54)发明名称

碳纳米复合吸附剂及其用于从气流中分离一种或多种材料的方法

(57)摘要

本发明涉及碳纳米复合吸附剂。本发明提供碳纳米复合吸附剂、其制造方法和从包括污染物的气体中分离该污染物的方法。各种实施方案提供了降低含汞气体的汞含量的方法。



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1. 从包含一种材料的气体中分离所述材料的方法，所述方法包括：

提供或获得碳纳米复合吸附剂；

使至少一部分所述材料与所述吸附剂接触以形成材料－吸附剂组合物；和

从含所述材料的气体中分离至少一部分所述材料－吸附剂组合物以产生分离的气体。

2. 权利要求 1 的方法，其中所述材料是污染物。

3. 权利要求 2 的方法，其中所述污染物是汞。

4. 权利要求 2-3 任一项的方法，进一步包括

提供促进剂；和

通过使至少一部分吸附剂材料与所述促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；

其中与至少一部分污染物接触的吸附剂包含所述促进的吸附剂。

5. 权利要求 4 的方法，其中所述促进剂是卤素或卤化物促进剂。

6. 降低含污染物的气体的污染物含量的方法，其包括：

提供或获得碳纳米复合吸附剂材料；提供或获得卤素或卤化物促进剂；

通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；

使至少一部分促进的吸附剂与含污染物的气体中的污染物接触以形成污染物－吸附剂组合物；和

从所述含污染物的气体中分离颗粒物，所述颗粒物包含至少一部分所述污染物－吸附剂组合物，以产生净化气体。

7. 权利要求 6 的方法，其中所述污染物是汞。

8. 权利要求 6-7 任一项的方法，其中获得或提供碳纳米复合吸附剂包括

提供或获得碳前体；

提供或获得基底材料；

使碳前体和基底材料接触以提供纳米复合原材料；和

加热所述纳米复合原材料以提供碳纳米复合吸附剂。

9. 权利要求 8 的方法，进一步包括使加热的纳米复合原材料与酸或碱反应以提供碳纳米复合吸附剂。

10. 权利要求 8-9 任一项的方法，其中所述碳前体包含碳水化合物。

11. 权利要求 8-10 任一项的方法，其中所述碳前体包含红糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜或糖废品。

12. 权利要求 8-11 任一项的方法，其中所述基底材料包含硅藻土、粘土、沸石或矿物。

13. 权利要求 8-12 任一项的方法，其中所述加热包括加热至超过大约 100℃。

14. 权利要求 6-13 任一项的方法，其中所述吸附剂材料包含与含污染物的气体中的污染物结合的结合位点。

15. 权利要求 6-14 任一项的方法，其中所述吸附剂材料包含已与卤素、卤化氢和第 V 族和第 VI 族卤化物反应或被卤素、卤化氢和第 V 族和第 VI 族卤化物浸渍的碳以形成所述促进的吸附剂中的污染物结合位点。

16. 权利要求 15 的方法，其中促进的 AC 中的结合位点与含污染物的气体中的污染物结

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合以形成污染物 - 吸附剂组合物。

17. 权利要求 15-16 任一项的方法，其中促进的 AC 中的结合位点与含污染物的气体中的污染物反应以形成污染物 - 吸附剂组合物。

18. 权利要求 15-17 任一项的方法，其中 AC 的至少一部分结合位点与含污染物的气体中的氧化污染物反应以形成另一污染物 - 吸附剂化学组合物。

19. 权利要求 6-18 任一项的方法，其中从含污染物的气体中分离颗粒物的步骤包括在包含一个或多个 ESP 的颗粒物分离器中分离。

20. 权利要求 7-19 任一项的方法，其中所述含汞气体中的汞包含元素汞。

21. 权利要求 7-20 任一项的方法，其中所述汞 - 吸附剂组合物中的汞是氧化汞。

22. 权利要求 7-21 任一项的方法，其中所述促进的吸附剂与所述含汞气体中存在的至少大约 70 重量％的汞结合。

23. 权利要求 6-22 任一项的方法，其中所述卤素或卤化物促进剂是包含蒸气形式、固体形式、在溶剂中或其组合的形式。

24. 权利要求 6-23 任一项的方法，其中所述卤素或卤化物促进剂包含第 V 族卤化物和第 VI 族卤化物中的至少一种。

25. 权利要求 6-24 任一项的方法，其中所述吸附剂上的或随所述吸附剂注入的促进剂前体转化成与所述吸附剂反应的卤素或卤化物促进剂。

26. 权利要求 6-25 任一项的方法，其中所述卤素或卤化物促进剂是 NH_4Br、NaBr、HBr、NaCl、$CaCl_2$或 HCl。

27. 权利要求 6-26 任一项的方法，进一步包括将碱性组分注入含污染物的气体中。

28. 权利要求 27 的方法，其中所述碱性组分包含碱金属或碱土金属元素的氧化物、氢氧化物、碳酸盐和磷酸盐中的至少一种。

29. 权利要求 6-28 任一项的方法，进一步包括将附加的卤素或卤化物促进剂添加到所述促进的吸附剂中。

30. 权利要求 29 的方法，其中所述附加的卤素或卤化物促进剂包含 HI、HBr、HCl、与卤素结合的第 V 族元素和与卤素结合的第 VI 族元素中的至少一种。

31. 权利要求 6-30 任一项的方法，进一步包括将稳定剂添加到所述促进的吸附剂中。

32. 权利要求 31 的方法，其中所述稳定剂包含 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2和 P_2S_5中的至少一种。

33. 权利要求 6-32 任一项的方法，其中促进至少一部分吸附剂材料的步骤至少部分在含污染物的气体与促进的吸附剂接触之前进行。

34. 权利要求 6-33 任一项的方法，进一步包括向气流中以一定注射速率注入碳纳米复合吸附剂和以一定注射速率单独注入至少一种促进剂，由此飞行中的反应产生促进的吸附剂，其中所述促进剂选自分子卤素、卤化物及其组合，其中所述促进剂在气相中或作为蒸气反应，其中每大约 100 克碳纳米复合吸附剂材料加入大约 1 至大约 30 克促进剂。

35. 权利要求 34 的方法，其中所述气流是含污染物的气体。

36. 根据权利要求 35 的方法，其中所述气流是输运气体。

37. 权利要求 34-36 任一项的方法，其中注入气体中的促进剂注射速率和吸附剂注射速率至少部分由所述净化气体的监测污染物含量确定。

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38. 权利要求 6-37 任一项的方法，进一步包括由所述污染物 - 吸附剂化学组合物再生所述促进的吸附剂的步骤。

39. 权利要求 38 的方法，进一步包括使用再生的促进的吸附剂从含污染物的气体中除去污染物。

40. 权利要求 6-39 任一项的方法，其中所述促进、所述接触和所述分离中的至少一项在水洗涤器中进行。

41. 权利要求 40 的方法，其中所述促进在洗涤器中进行，其中所述洗涤器包括包含所述促进剂的水性浆料。

42. 权利要求 40-41 任一项的方法，其中所述接触在洗涤器中进行，其中所述洗涤器包括包含活性炭纳米复合吸附剂的水性浆料。

43. 降低含汞气体的汞含量的方法，所述方法包括：

提供或获得碳纳米复合吸附剂，通过下列步骤制造所述碳纳米复合吸附剂：

提供或获得碳前体；

提供或获得基底材料；

使碳前体和基底材料接触以提供纳米复合原材料；和

加热所述纳米复合原材料以提供碳纳米复合吸附剂；

提供或获得卤素或卤化物促进剂；

通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；

使至少一部分促进的吸附剂与汞接触以形成汞 - 吸附剂组合物；和

从含汞气体中分离至少部分所述汞 - 吸附剂组合物。

44. 制造碳纳米复合吸附剂的方法，所述方法包括：

提供或获得碳前体；

提供或获得基底材料；

使碳前体和基底材料接触以提供纳米复合原材料；

加热所述纳米复合原材料以提供碳纳米复合吸附剂。

45. 通过权利要求 44 的方法制成的碳纳米复合吸附剂。

46. 通过一种方法制成的促进的碳纳米复合吸附剂，所述方法包括通过使至少一部分权利要求 45 的吸附剂材料与卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。

47. 通过使权利要求 45-46 任一项的碳纳米复合吸附剂与含汞气体接触制成的汞 - 吸附剂组合物。

48. 与汞或氧化汞接触的权利要求 45-47 任一项的碳纳米复合吸附剂。

49. 通过一种方法制成的促进的碳纳米复合吸附剂，所述方法包括通过使至少一部分碳纳米复合吸附剂材料与卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。

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碳纳米复合吸附剂及其用于从气流中分离一种或多种材料的方法

[0001] 优先权声明

本专利申请要求2012年4月23日提交的美国专利申请序号13/453,274的优先权，其全文并入本文作为参考。

[0002] 政府资助声明

本发明在U.S. Department of Energy (DOE)依据名为"EERC-DOE Joint Program on Research and Development for Fossil Energy-Related Resources"的DOE Cooperative Agreement Number DE-FC26-08NT43291；名为"Fate and Control of Mercury and Trace Elements"的Subtask 4.8；EERC Fund Number 14990给予的政府资助下完成。美国政府在本发明中拥有某些权利。

[0003] 发明背景

汞(Hg)排放由于它们的毒性和生物积累能力而成为健康和环境问题。美国环境保护署(EPA)已经颁发了用于控制来自垃圾能源化(waste-to-energy)、水泥生产和燃煤发电厂的Hg排放的规章。可以通过注入吸附剂，如活性炭捕获来自工业来源(例如发电厂)的烟气中的汞，然后可通过微粒收集装置除去。市场所需的标准吸附剂(例如活性炭)的量很大。标准吸附剂并非总是有效并随着注射速率提高而变得更昂贵。

[0004] 纳米复合材料是一种多相固体材料，其中一个相具有至少一个小于大约1000纳米的尺寸或其中小于大约1000纳米的重复距离将构成该材料的相隔开。纳米复合材料——其中一个或多个相是本体基质且一种或多种其它材料是纳米尺寸的相——具有独特的性质，该纳米复合材料的机械、电、热、光学、化学或催化性质明显不同于各组成材料。

[0005] 碳纳米复合材料的最初实例是通过将单体插入粘土中的层间间隙、使单体聚合并将该聚合物碳化制成。碳层的最小厚度为1.1纳米(Kyotani-1988)。在接下来的二十年，各种单体与几种粘土和其它多孔载体材料一起使用。在一些情况下，除去该复合材料的无机部分以研究类石墨的碳结构。在2004年，Bakandritsas等人使用蔗糖作为碳源生产碳-粘土纳米复合材料(Bakandritsas-2004)。对于粘土和石墨烯层，各层的厚度分别为大约1纳米和0.4纳米。稍后，这一团队描述了这些用于吸附水溶液中的气体(CO_2、CH_4、N_2)和有机溶质的用途(Bakandritsas-2005)。由于它们容易成型、具有高表面积并导电，使用源自蔗糖的碳-粘土纳米复合材料制造电极和传感器(Darder-2005, Gomez-Aviles-2007, Fernandez-Saavedra-2008, Gomez-Aviles-2010)。源自蔗糖的多孔碳-粘土纳米复合材料也已用于催化剂载体(Nguyen-Thanh-2006a, Nguyen-Thanh-2006b, Ikeue-2008)。

[0006] 在文献中已经描述了复合材料用于吸附金属离子，如Hg^{2+}的几个用途。这些包括下列材料：壳聚糖涂覆的陶瓷(Boddu-2002)、在粘土上的聚吡咯膜(Eisazadeh-2007)、在硅藻上的巯基官能化聚硅氧烷膜(Wang-2007)、在灰分上的聚苯胺膜(Ghorbani-2011)和聚苯胺与腐殖酸的复合材料(Zhang)。这些无一是碳纳米复合材料；相反，它们通常是沉积在载体上的聚合物膜并受限于稳定性以及再循环和加工困难。

[0007] 已用由非碳材料制成的几种类型的纳米复合材料从气流中分离元素或氧化汞。

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SiO_2-TiO_2纳米复合材料在紫外辐射下用于 Hg 捕获(Li-2008)。这种技术受困于必须有效照射含有细粒的燃烧流出物的困难。描述了磁铁矿 - 和 Ag- 浸渍的沸石纳米复合材料(Dong-2009)。Ag 纳米复合材料被质疑本身代表重大的环境风险以及是高成分吸附剂。报道了用 CeO_2-WO_3/TiO_2纳米复合材料捕获烟气中的 Hg(Wan-2011)。这些非碳吸附剂具有不合期望的更高成本和更慢动力学。

[0008] 发明概述

在各种实施方案中,本发明提供从包括一种材料的气体中分离所述材料的方法。在一些实施方案中,该材料可以是污染物或所述气体的不想要的成分。该方法包括提供或获得碳纳米复合吸附剂。该方法还包括使至少一部分所述材料与所述吸附剂接触以形成材料 - 吸附剂组合物 (composition)。该方法还包括从含所述材料的气体中分离至少一部分所述材料 - 吸附剂组合物。该分离产生分离的或部分分离的气体。

[0009] 在各种实施方案中,本发明提供降低含污染物的气体的污染物含量的方法。该方法包括提供或获得碳纳米复合吸附剂。该方法包括提供或获得卤素或卤化物促进剂 (promoter)。该方法包括促进至少一部分吸附剂材料。吸附剂材料的促进包括使吸附剂材料的所述部分与所述卤素或卤化物促进剂化学反应。吸附剂材料的促进产生促进的吸附剂。该方法包括使至少一部分促进的吸附剂与污染物接触。在一些实施方案中,该方法还可包括使所述污染物与未促进的吸附剂接触。促进的吸附剂与污染物的接触形成污染物 - 吸附剂组合物。该方法还包括分离至少一部分所述污染物 - 吸附剂组合物。该分离产生具有比原材料(例如未净化的)含污染物的气体低的污染物含量的净化气体。在各种实施方案中,该污染物可以是汞。

[0010] 在各种实施方案中,本发明提供形成碳纳米复合材料的方法。该方法包括获得或提供碳前体材料。该方法包括提供或获得基底材料。该方法包括使碳前体和基底材料接触以提供纳米复合原材料。该方法还包括加热所述纳米复合原材料以提供碳纳米复合吸附剂。在各种实施方案中,本发明提供由该方法生成的碳纳米复合材料。在一些实例中,本发明提供与所述纳米复合材料在所述方法的运行过程中遇到的各种材料结合的纳米复合材料,如与汞、与氧化汞或与含汞气体结合的纳米复合材料。在一些实施方案中,该方法可包括添加卤素或卤化物促进剂并使所述促进剂与所述吸附剂反应以形成促进的碳纳米复合吸附剂。

[0011] 令人惊讶地,尽管活性炭常规用于捕获烟气流中的污染物,但碳纳米复合材料以前尚未用于气相汞捕获。传统意见在于,碳纳米复合材料中的过量无机载体,如粘土阻碍污染物吸附在碳上。但是,令人惊讶地,根据本发明的一些实施方案,该非碳部分可增强污染物吸附在邻近的碳石墨烯层上。该纳米复合材料的碳部分的基面在碳纳米复合结构内确实严重受阻。但是,在该结构中非常充分暴露出碳边缘结构,而这些是有效用于污染物捕获(例如汞、硒、砷等)的碳部分。如本文所述,可通过与卤素、卤化氢或卤化铵的反应促进石墨烯边缘结构以产生对污染物,如汞的氧化和捕获具有高度反应性的碳正离子边缘结构。

[0012] 由于载体材料,如粘土本身是惰性的,某些载体材料促进污染物被碳层氧化也是出乎意料的。但是,根据本发明的一些实施方案,聚阴离子铝硅酸盐层(例如来自粘土)可以稳定邻近的石墨烯碳结构上的阳离子位点(这对污染物,如汞的氧化是必不可少的)的开发。对于由石墨烯层和极性无机结构构成的碳 - 硅藻(硅酸盐)纳米复合材料或其它纳米复

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合材料可发生相同的稳定效应。

[0013] 在包括通过由相应卤化铵的降解或反应获得的卤化氢化合物促进纳米复合材料的实施方案中，无机部分的另一有利作用是为铵盐的分解或反应释放的氨提供结合位点。结合的氨形成具有碱性特征的络合物，其与烟气中的 SO_3 反应并防止它们干扰污染物，如汞捕获在边缘结构上。

[0014] 在包括粘土作为载体的实施方案中无机载体的另一优点在于，该粘土稳定地分散在水性介质中。粘土通常难从水性介质中过滤或分离，但在与碳的纳米复合材料的形式下，该材料容易通过过滤从水性介质中分离。因此，该纳米复合材料可方便地用于捕获水环境中的汞。

[0015] 本发明可以有利地比其它方法更有效地从包括一种材料的气体中分离所述材料(例如污染物)。本发明与用于从含汞气体中除汞的其它方法和材料相比提供某些优点。本发明的各种实施方案的方法和材料可以比其它除汞方法更有效地从气体中捕获和脱除汞。本发明的各种实施方案的方法和材料可以比其它除汞方法更有效地运行。例如，各种实施方案的方法和材料与其它方法相比可以以更小的财政支出量除去给定量的汞。例如，各种实施方案的方法和材料与其它除汞方法相比，包括与包含碳吸附剂的其它除汞方法相比可以在给定的碳质量下除去更大量的汞。因此，各种实施方案的方法和材料与其它除汞方法相比能够使用更少的吸附剂材料(例如总体上更少的碳)以及处置更少的用过的吸附剂材料。

[0016] 在各种实施方案中，本发明提供降低含汞气体的汞含量的方法。该方法包括提供或获得碳纳米复合吸附剂。通过包括提供或获得碳前体和提供或获得基底材料的步骤制造所述碳纳米复合吸附剂。步骤还包括使碳前体和基底材料接触。该接触提供纳米复合原材料。步骤还包括加热所述纳米复合原材料。该加热提供所述碳纳米复合吸附剂。用于降低含汞气体的汞含量的方法还包括提供或获得卤素或卤化物促进剂。该方法包括促进至少一部分吸附剂材料。吸附剂材料的促进包括使吸附剂材料的所述部分与所述卤素或卤化物促进剂化学反应。吸附剂材料的促进产生促进的吸附剂。该方法包括使至少一部分促进的吸附剂与汞接触。促进的吸附剂与汞的接触形成汞-吸附剂组合物。该方法还包括从所述气体中分离至少一部分所述汞-吸附剂组合物。该分离产生具有比未净化气体低的汞含量的净化气体。

[0017] 在各种实施方案中，本发明提供制造碳纳米复合吸附剂的方法。该方法包括提供或获得碳前体。该方法包括提供或获得基底材料。该方法包括使碳前体和基底材料接触。碳前体和基底材料的接触提供了纳米复合原材料。该方法还包括加热所述纳米复合原材料。所述纳米复合原材料的加热提供了所述碳纳米复合吸附剂。

[0018] 附图简述

在不一定按比例绘制的附图中，几个视图中的类似数字描述基本类似的部件。具有不同字母后缀的类似数字代表基本类似的部件的不同情况。附图通常示例，例如但不作为限制，本文中论述的各种实施方案。

[0019] 图 1 示意性示例根据各种实施方案制备促进的碳吸附剂的方法。

[0020] 图 2 示例根据各种实施方案导致汞氧化和捕获的化学反应的提出的机械模型。

[0021] 图 3A 和 3B 示意性示例根据各种实施方案制备促进的碳吸附剂和烟气(例如来自

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燃烧）和/或来自气化系统的产物气体中的烟气除汞方法。

[0022] 图4示例根据各种实施方案的NanoG-CM测试的微粒试验燃烧器（particulate test combustor）（PTC）结果。

[0023] 图5示例根据各种实施方案的NanoG-CM测试的PTC结果。

[0024] 图6示例根据各种实施方案，在高硫烟气中用复合吸附剂捕获飞行中的汞的模型结果。

[0025] 发明详述

现在详细提到所公开的主题的某些权利要求，在附图中示例其实例。尽管将联系枚举的权利要求描述所公开的主题，但要理解的是，它们无意将所公开的主题限于这些权利要求。相反，所公开的主题意在涵盖可包括在如权利要求规定的本公开的主题的范围内的所有替代物、修改和等同物。

[0026] 在本说明书中提到“一个实施方案”、“一种实施方案”“一个实施例实施方案”等是指所述实施方案可包括特定要素、结构或特征，但不一定每一实施方案都包括该特定要素、结构或特征。此外，此类术语不一定是指同一实施方案。此外，当联系一个实施方案描述特定要素、结构或特征时，其意味着联系其它实施方案应用此类要素、结构或特征在本领域技术人员的知识范围内，无论是否明确描述。

[0027] 以范围格式表示的值应以灵活方式解释以不仅包括作为该范围的界限明确列举的数值，还包括该范围内包含的所有单个数值或子范围，就像明确列举各数值和子范围那样。例如，“大约0.1%至大约5%”的浓度范围应被解释为不仅包括大约0.1重量%至大约5重量%的明确列举的浓度，还包括所述范围内的各浓度（例如1%、2%、3%和4%）和子范围（例如0.1%至0.5%，1.1%至2.2%，3.3%至4.4%）。

[0028] 在本文中，除非上下文清楚地另有规定，术语“一种”、“一个”或“该”用于包括一种（个）或多于一种（个）。除非另有说明，术语“或”用于表示非排他的“或”。此外，要理解的是，本文所用的并且没有另行定义的用词或术语仅用于说明而非限制。章节标题的任何使用意在有助于阅读本文而非解释为限制；与章节标题相关的信息可能出现在该特定章节内或外。此外，本文中提到的所有出版物、专利和专利文献全文并入本文作为参考，就像逐一并入作为参考一样。在本文和并入本文作为参考的那些文献之间的用法不一致的情况下，并入的参考文献中的用法应被视为补充本文的用法；对于不可调和的矛盾，以本文中的用法为准。

[0029] 在本文所述的制造方法中，步骤可以以任何次序进行而不背离本发明的原理，除非明确地列举时间或操作上的次序。

[0030] 此外，指定的步骤可以同时进行，除非明确的权利要求用语提到它们单独进行。例如，要求保护的实施X的步骤和要求保护的实施Y的步骤可以在单个操作内同时进行，所产生的方法落在要求保护的方法的字面范围内。

[0031] 定义

术语“大约”允许数值或范围的一定程度的可变性，例如在指定的数值或指定的范围界限的10%内、5%内或1%内。当给出一个范围或一连串数值的名单时，除非另有规定，也公开了该范围内的任何数值或给定的一连串数值之间的任何数值。

[0032] 本文所用的术语“烃”是指包括碳和氢原子的官能团或分子。该术语还是指通常

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包括碳和氢原子但其中所有氢原子被其它官能团取代的官能团或分子。

[0033] 本文所用的术语“孔隙”是指固体物中的任何尺寸或形状的凹陷、狭缝或空穴。孔隙可以贯穿物体或部分穿过物体。一个孔隙可与其它孔隙相交。

[0034] 本文所用的术语“溶剂”是指可以溶解固体、液体或气体的液体。溶剂的非限制性实例是硅酮、有机化合物、水、醇、离子液体和超临界流体。

[0035] 本文所用的术语“空气”是指具有与通常在地平面取自大气的气体的天然组成大致相同的组成的气体混合物。在一些实例中，空气取自周围环境。空气的组成包括大约 78% 氮气、21% 氧气、1% 氩气和 0.04% 二氧化碳，以及少量的其它气体。

[0036] 本文所用的术语“室温”是指环境温度，其可以为例如大约 15℃ 至大约 28℃。

[0037] 本文所用的“基本”是指大多数或大部分，例如至少大约 50%、60%、70%、80%、90%、95%、96%、97%、98%、99%、99.5%、99.9%、99.99% 或至少大约 99.999% 或更大。

[0038] 本文所用的“纳米复合材料”是指一种多相固体材料，其中一个相具有至少一个小于大约 1000 纳米的尺寸或其中小于大约 1000 纳米的重复距离将构成该材料的至少一些相隔开。在一些实施方案中，一个相具有至少一个大约 1 纳米 -1000 纳米的尺寸或大约 1-1000 纳米的的重复距离将构成该材料的至少一些相隔开；在另一些实施方案中，该范围的下限可以小于大约 1 纳米。

[0039] 本文所用的“相”是指一个空间区域，其中材料的所有物理性质基本均匀，如物理状态、结构和化学。例如，液态和气态可以是两个不同的相。例如，分布在基底上的碳材料可以是两个不同的相。例如，分布在多孔基底上的碳材料可以是两个不同的相。

[0040] 本文所用的“矿物”是指通过生物地球化学过程形成的天然存在的固体化学物质，其具有例如特有的化学组成、高度有序的原子结构和特定的物理性质。

[0041] 描述

本发明的各种实施方案提供用于从气体中分离材料的方法和材料。在一些实施方案中，该材料可以是污染物或不想要的成分。在另一些实施方案中，该材料可以是任何合适的材料。该气体包括该材料；例如，该材料可以溶解或悬浮在该气体中。该材料包括碳纳米复合吸附剂。该方法包括提供或获得碳纳米复合吸附剂。该方法包括使气体中的至少一部分所述材料与所述吸附剂接触以形成材料 - 吸附剂组合物。该方法还包括从该气体中分离颗粒物。颗粒物包括至少一部分所述材料 - 吸附剂组合物。该分离产生分离的气体——其中所述材料的量低于原材料气体。在本文中给出实施方案的许多具体实例，其中被分离的材料是汞，其中用卤化物或卤素处理（例如促进）碳纳米复合吸附剂，或其中用其它材料处理碳纳米复合吸附剂。但是，本领域普通技术人员会由这些实例类推并且会认识到实施方案包括使用任何合适的碳纳米复合材料从气体中分离任何合适的材料（例如任何合适的污染物，例如砷、硒等）。

[0042] 在各种实施方案中，从气体中分离的材料是污染物（例如不想要或不合意的成分）并且希望从气体中除去该材料以净化气体。污染物可包括汞。污染物可包括元素汞。污染物可包括氧化汞。在各种实施方案中，该方法可包括提供促进剂。可以使该促进剂与至少一部分吸附剂材料化学反应，以形成促进的吸附剂。与污染物接触的吸附剂可包括促进的吸附剂。在各种实施方案中，该促进剂可以是卤素或卤化物促进剂。

[0043] 降低含汞气体的汞含量

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在各种实施方案中，本发明提供用于降低含汞气体的汞含量的方法和材料。该方法包括提供或获得碳纳米复合吸附剂。该方法可包括提供或获得卤素或卤化物促进剂。该方法可包括通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。该方法包括使至少一部分促进的吸附剂与汞接触以形成汞－吸附剂组合物。在各种实施方案中，与汞接触的吸附剂也可包括未促进的吸附剂。该方法还包括从含汞气体中分离至少一部分汞－吸附剂组合物。该分离产生具有比原材料气体低的汞含量的净化气体。该含汞气体中的汞可以是汞的任何合适的形式，例如元素汞。汞可以悬浮或溶解在该气体中。在一些实施方案中，促进剂可以是 HBr 或 NH_4Br，在一些实例中，可通过溴化铵 NH_4Br 的降解或反应提供 HBr。在一些实施方案中，促进剂（例如 HBr）或促进剂前体（例如 NH_4Br）可以与碳纳米复合吸附剂分开或与碳纳米复合吸附剂一起以一定注射速率注入烟气中（例如可以在注射前施加到吸附剂中）。

[0044] 碳纳米复合吸附剂

本发明实施方案提供的方法使用碳纳米复合吸附剂从气体中除去材料，例如从含汞气体中除汞。纳米复合材料由两个或更多个相构成，以使这些相在纳米级尺寸（例如 1000 纳米或更小）下互相密切连接。当这些纳米复合材料高度多孔，尤其是微米多孔或纳米多孔时，两种纳米复合材料的密切连接可产生该高表面积以及相应高的催化活性。当催化活性的材料，如某些形式的碳分散在具有高表面积的本体（bulk）基底上时，情况尤其如此。碳纳米复合材料可包括涂布在无机载体上或插入无机载体中的石墨烯片的薄层。

[0045] 在一些实施方案中，该碳纳米复合吸附剂可以含有大约 50% 或更少的碳，或大约 3 重量％至大约 50 重量％碳，或大约 5 重量％至大约 10 重量％碳。在一些实施方案中，该碳纳米复合吸附剂可以含有大约 1 重量％至大约 99.5 重量％的本体基底，或大约 50 重量％至大约 97 重量％的本体基底，或大约 90 重量％至大约 95 重量％的本体基底（例如硅藻土、蒙脱石粘土等）。

[0046] 本发明的纳米复合材料可以是任何合适的碳纳米复合材料。在一些实例中，该纳米复合材料可以是分布在适当多孔或适当高表面积的基底上的适当形式的碳。该纳米复合材料可以制造或可以由商业途径获得。在一些实施方案中，由商业途径获得该纳米复合材料，并可能需要进一步加工步骤以适当活化碳以使用于分离材料，如分离汞。适当活化该纳米复合材料的进一步加工步骤可包括用热处理（例如煅烧）、用碱处理、用卤化物或卤素处理（例如促进）或它们的组合。例如，在一些实施方案中，用卤化物或卤素处理纳米复合材料可促进纳米复合材料以在纳米复合材料中形成可将汞从元素汞转化成氧化汞（例如汞氧化物）的活性位点。在一些实施方案中，不促进该纳米复合材料。例如，在一些实施方案中，用酸或碱处理纳米复合材料可以使纳米复合材料准备好用卤化物或卤素促进，或可以使纳米复合材料获得合适的反应性。在另一些实施方案中，在使用卤化物或卤素促进之前或在使用吸附剂从气体中除去汞或其它材料之前不用酸或碱处理。

[0047] 该方法可包括使至少一部分纳米复合吸附剂与气体中的材料，如汞接触以形成组合物，如汞－吸附剂组合物。本发明不依赖于任何特定的作用机制；只要使用碳纳米复合吸附剂从气体中除去该材料，作为本发明的一个实施方案包含该方法。在一些实施方案中，汞以其元素形式被该吸附剂吸收；汞－吸附剂组合物可包括吸附剂和汞的元素形式。在一些实施方案中，汞被该吸附剂通过化学反应（如氧化）转化，以使来自该气体的汞转化成汞的

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氧化物(例如 HgO);汞 - 吸附剂组合物可包括吸附剂和汞的转化形式,如氧化汞。在一些实施方案中,汞 - 吸附剂组合物可包括元素汞和转化汞,如氧化汞的组合。在一些实例中,元素汞的吸收或汞的转化可改变该吸附剂,以使吸附剂在形成该组合物后至少略微不同;例如在特定形式的汞原子转化成氧化汞后,造成转化的吸附剂的活性位置可能变得无反应性或反应性较低。

[0048] 在一些实例中,元素汞或转化的汞可保持吸收在吸附剂上直至在稍后的分离步骤中除去该汞 - 吸附剂组合物。例如,元素汞或转化的汞可以被吸收到,或反应并吸收到吸附剂组合物中或上,以使含汞气流中至少大约 1 重量%、3 重量%、5 重量%、10 重量%、20 重量%、30 重量%、40 重量%、50 重量%、60 重量%、70 重量%、80 重量%、90 重量%、95 重量%、96 重量%、97 重量%、98 重量%、99 重量%、99.9 重量%、99.99 重量%或大约 99.999 重量%或更多的汞被吸收到,或反应并吸收到吸附剂组合物中或上。在一些实施方案中,在从气体中分离汞 - 吸附剂组合物之前,可以从该汞 - 吸附剂组合物中释放元素汞或转化的汞;例如,可以从该汞 - 吸附剂组合物中释放少于大约 1 重量%、3 重量%、5 重量%、10 重量%、20 重量%、30 重量%、40 重量%、50 重量%、60 重量%、70 重量%、80 重量%、90 重量%、95 重量%或少于大约 99 重量%的汞。在一些实例中,大部分被吸收的元素汞或转化的汞可保持为汞 - 吸附剂组合物的一部分直至在稍后的分离步骤中除去该汞 - 吸附剂组合物。在一些实例中,从汞 - 吸附剂组合物中释放的转化汞可稍后通过分离步骤从该气体中除去。在一些实例中,已从汞 - 吸附剂组合物中释放的元素汞或转化的汞可以接触碳纳米复合吸附剂以形成稍后通过分离步骤除去的汞 - 吸附剂组合物。

[0049] 在各种实施方案中,该碳纳米复合吸附剂包括与含汞气体中的汞结合的结合位点。在一些实例中,该吸附剂材料包括与卤素或卤化物反应或用卤素或卤化物浸渍的碳以形成促进的吸附剂中的汞结合位点。在一些实例中,该吸附剂材料可包括至少部分通过用碱处理活化的碳,其中该碱活化碳可以与卤素、卤化氢和第 V 或 VI 族卤化物反应或被卤素、卤化氢和第 V 或 VI 族卤化物浸渍以形成促进的吸附剂中的汞结合位点。在一些实例中,该碳中的结合位点与含汞气体中的汞反应以形成汞 - 吸附剂组合物。在一些实例中,该碳的至少一部分结合位点与含汞气体中的氧化汞反应以形成汞 - 吸附剂组合物。

[0050] 在一些实施方案中,该碳纳米复合材料中的至少一部分碳是石墨烯形式的碳。石墨烯形式的碳在一些实施方案中可包括较高浓度的适合作为纳米复合材料的活性位点的位置。在一些实例中,石墨烯碳的某些部分可具有适合作为纳米复合材料的活性位点的位置的最高浓度;在一些实施方案中在边缘,在一些实施方案中在非边缘位置。适合作为活性位点的此类位置可通过如本文所述用卤化物或卤素处理活化。在各种实施方案中,该碳纳米复合材料中的碳可具有至少大约 1 重量%、2 重量%、3 重量%、4 重量%、5 重量%、10 重量%、20 重量%、30 重量%、40 重量%、50 重量%、60 重量%、70 重量%、80 重量%、90 重量%、95 重量%、96 重量%、97 重量%、98 重量%、99 重量%、99.9 重量%、99.99 重量%或大于大约 99.999 重量%的石墨烯形式的碳。

[0051] 在一些实施方案中,该碳纳米复合吸附剂具有大于 40 微米或大于 60 微米的平均粒径或大于要处理的烟气流中的飞灰或夹带灰分的粒度分布,以使碳纳米复合吸附剂和灰分可以在分离步骤中通过物理手段分离。

[0052] 在一个实例中,该纳米复合材料可以是当该多孔结构中所含的卤化物盐在注入加

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热管道的过程中分解时被促进的(针对气相 Hg 氧化)碳纳米复合材料。在一些实例中,该卤化物盐可以是溴化铵。在一些实例中,该碳纳米复合材料可包括石墨烯。在一些实例中,该纳米复合材料的非碳部分包括高表面积的多孔无机基质。

[0053] 形成碳纳米复合吸附剂的方法

该碳纳米复合吸附剂可以获得、可以合成或它们的任何组合。例如,获得的碳纳米复合材料在适用于本发明的方法的实施方案之前可能需要进一步处理。各种实施方案提供形成碳纳米复合吸附剂的方法、由此形成的碳纳米复合吸附剂或碳纳米复合吸附剂与含汞气体的组合。例如,制造碳纳米复合吸附剂的方法可包括提供或获得碳前体,其中该碳前体提供碳纳米复合吸附剂中的碳。该方法可包括提供或获得基底材料,其中该基底材料提供碳纳米复合吸附剂中的本体基底。该方法可包括使碳前体和基底材料接触以提供纳米复合原材料。该方法可包括加热该纳米复合原材料。纳米复合原材料的加热提供了纳米复合吸附剂。在使用前,可任选对该纳米复合吸附剂施以加工步骤,如用碱处理,如用卤素或卤化物处理,这能在碳纳米复合材料上形成可与元素汞反应以将汞例如转化成氧化汞(例如汞氧化物)的活性位点。

[0054] 在一些实例中,使用基底,如粘土(例如提供开放和多孔的下部结构的基底),可以使碳水化合物(例如碳前体)与该基底接触。可以加热所得混合物,这产生具有低碳密度的碳层,其覆盖该基底材料的开放多孔结构。在一些实施方案中,在加热该混合物时,基底可以溶胀。可以通过由加热步骤造成的碳前体的化学反应,包括分解反应,包括例如热解、脱水或脱羧反应制造碳层。在一些实施方案中,制成的碳层包括石墨烯形式的碳,例如作为石墨烯带。石墨烯形式的碳,尤其在其边缘,在一些实施方案中可包括较高浓度的适合作为纳米复合材料的活性位点的位置。该碳涂布在高度多孔基质中无规堆叠的粘土粒子的表面。在实例中,可以将卤化物或卤素引入吸附剂,促进碳并增强吸附剂对汞的反应性。卤化物或卤素可以以各种形式引入。

[0055] 在一些实施方案中,可以"在飞行中"产生促进的吸附剂。这可以通过例如使卤素的任何组合的蒸气在飞行中与碳纳米复合吸附剂接触实现。可以通过在输运空气流或含汞的污染气流(要从中除汞)中使卤素的任何组合的蒸气与碳纳米复合吸附剂接触实现碳纳米复合吸附剂在飞行中的促进。可以将粒子分散在输运空气(或其它气体)流中,其将该卤素-/卤化物促进的碳吸附剂粒子送往烟道或其它污染气流,然后从中除汞。在一些实施方案中,可以将粒子直接分散在烟气流中。

[0056] 在飞行中促进的简单性和所带来的成本节省是有利的。可以消除处理设施的资本设备成本、运行成本和运输成本。在飞行中的制备可以利用现有硬件和运行程序并有助于确保促进的吸附剂始终新鲜并因此更有反应性。在飞行中的制备能够快速现场调节吸附剂的促进程度以确保反应性足以匹配烟气变化的要求(如改变燃料或降低负荷时可能需要的那样),因此进一步优化汞捕获的经济性和效率。

[0057] 碳前体

制造碳纳米复合吸附剂的方法可包括提供或获得碳前体,其中该碳前体提供碳纳米复合吸附剂中的碳。可以通过由加热步骤造成的碳前体的化学反应,包括分解反应,包括例如热解、脱水或脱羧反应制造该纳米复合材料中的碳层。

[0058] 碳前体可包括任何合适的碳前体,以使加热步骤将碳前体和基底转化成合适的碳

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纳米复合吸附剂。例如，碳前体可以是任何糖源，如碳水化合物(糖类)，包括例如红糖、麦芽糖、焦糖、蔗糖、玉米糖浆、糖蜜、糖或糖加工废品，如甜菜糖废品、蔗糖废品等。碳前体可以是任何合适的淀粉或淀粉源。

[0059] 在一些实例中，碳前体可以以碳纳米复合吸附剂的原材料的大约 1 重量％至大约 99 重量％，大约 20 重量％至大约 80 重量％，或大约 40 重量％至大约 60 重量％存在。在一些实例中，碳前体可以以碳纳米复合吸附剂的原材料的大约 50％或更少碳、或大约 3 重量％至大约 50 重量％碳、或大约 5 重量％至大约 10 重量％碳存在。这一段中的重量％是指基于碳前体和基底材料的总重量的重量百分比。

[0060] 基底材料

制造碳纳米复合吸附剂的方法可包括提供或获得基底材料，其中该基底材料提供碳纳米复合吸附剂中的本体基底。

[0061] 该基底材料可包括任何合适的基底材料，以使加热步骤将碳前体和基底材料转化成合适的碳纳米复合吸附剂。该基底可包括任何合适的多孔材料。例如，该基底材料可以是硅藻土、沸石、多孔矿物(例如粘土)，包括例如蒙脱石(例如蒙脱土、膨润土、绿脱石、皂石)、高岭土、伊利石、绿泥石、海泡石或绿坡缕石。在一些实例中，该基底可包括聚合物、非金属、金属、类金属、陶瓷或混合物和共混物，以及它们的复合材料和合金。该材料可以是合成的或天然存在的或天然衍生的材料。合成聚合物的实例包括任何常见的热塑性材料和热固性材料。金属的实例包括铝、钛、铜、钢和不锈钢。陶瓷的实例包括任何形式的氧化铝、氧化锆、二氧化钛和二氧化硅。天然存在或天然衍生的材料的实例包括木材、木复合材料、纸、乙酸纤维素和地质地层，如花岗岩或石灰石。非金属的实例包括各种形式的碳，如石墨或碳。类金属的实例包括硅或锗。多孔材料可以是建筑材料，如混凝土或沥青。

[0062] 在一些实例中，基底材料可以以碳纳米复合吸附剂的原材料的大约 1 重量％至大约 99 重量％，大约 20 重量％至大约 80 重量％，或大约 40 重量％至大约 60 重量％存在。这一段中的重量％是指基于碳前体和基底材料的总重量的重量百分比。

[0063] 接触和加热

制造碳纳米复合吸附剂的方法可包括使碳前体和基底材料接触以提供纳米复合原材料。该方法可包括加热(例如提供能量给)纳米复合原材料，加热(或以其它手段提供能量给)纳米复合原材料提供了纳米复合吸附剂。

[0064] 该接触可以以任何合适的方式进行。该接触将碳前体和基底材料混合，以便在加热该凝聚体(conglomeration)时(或施以任何其它合适的能量源)时，形成碳纳米复合吸附剂。可以进行该接触以使碳水化合物大致均匀分布在基底上。在一些实例中，可以添加水或另一溶剂以助于碳前体分布在基底上。在碳前体和基底的混合物中包括水的实例中，该凝聚体可以在加热之前干燥。干燥可以以任何传统方式进行(例如对流、传导、微波等)，包括在溶剂的沸点附近或以上(在水的情况下为例如 50℃ -120℃或更高)、在大气压下、在压力下或在真空下加热。

[0065] 然后可以加热碳前体和基底的接触组合物以形成碳纳米复合吸附剂。该加热足以造成将碳前体转化成碳纳米复合材料中存在的碳形式的化学反应(例如分解反应)，包括例如热解、脱水或脱羧反应。该加热可以在任何合适的温度下进行以充分形成碳纳米复合材料，例如大约 50℃、100℃、200℃、300℃、400℃、500℃、600℃、700℃、800℃、900℃、1000℃、

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1100℃或大约 1200℃。该加热可以进行任何合适的时间以充分形成碳纳米复合材料，例如超过大约 1 分钟、2 分钟、5 分钟、10 分钟、30 分钟、1 小时、1.5 小时、2 小时、3 小时、4 小时、5 小时、10 小时或超过大约 24 小时。该加热可以在任何合适的装置中进行，例如能使加热的空气在被加热的混合物周围流动的装置或炉。可以根据装置和纳米复合材料加速或延长该加热。

[0066] 卤素或卤化物促进剂

"卤素"被定义为周期表第 VIIA 族中包括的元素成员（第 VIIA 族 [CAS] 相当于第 VIIB 族 [IUPAC]）。卤素的分子元素形式，包括 F_2、Cl_2、Br_2和 I_2相对不与热烟气中的元素汞反应。任何卤素离子、气体或化合物可以是促进剂。

[0067] 降低含汞气体的汞含量的方法的实施方案包括提供或获得卤素或卤化物促进剂。该方法包括促进至少一部分吸附剂材料。吸附剂材料的促进包括使一部分吸附剂材料与卤素或卤化物促进剂化学反应或用卤素或卤化物促进剂浸渍一部分吸附剂材料。该卤素或卤化物促进剂可衍生自另一化合物（例如促进剂前体）的反应或降解。吸附剂材料的促进产生促进的吸附剂。吸附剂材料的促进可以在注入气流中之前、在注入气流中的过程中、在注入气流中后进行，或它们的组合，其中该气流可以是含汞气流、输运气流或其组合。在一些实例中，可以在促进剂和吸附剂反应之前将促进剂添加到吸附剂中，以使该促进剂添加至的气流的热造成吸附剂的促进。例如，该促进剂可以作为气体、作为溶解在液体中的气体或作为固体，如盐，或溶解在液体（例如水）中的其它物质（例如酸）添加。在促进剂在液体，如水中加入的实例中，可以使水干燥，这可以使促进剂附着到纳米复合吸附剂上、浸渍纳米复合吸附剂或与纳米复合吸附剂反应，或它们的组合。在一些实例中，预添加的促进剂可以是铵盐，如氯化铵、溴化铵或碘化铵，包括例如单－、二－、三－或四烷基卤化铵，或 NH_4^+卤化物盐。在一些实例中，可以在接近促进时或在促进时将促进剂添加到吸附剂中；例如，促进剂可以与吸附剂一起添加到气流中或其在加热的气流，如含汞气流或进料气流内接触吸附剂。在一些实例中，该促进剂可以是 NH_4Br。

[0068] 在一些实施方案中，该促进剂可以是 HBr，在一些实例中，可通过促进剂前体，如溴化铵、溴化钠或溴化钙的降解或反应提供 HBr。该促进剂可以是 HCl，在一些实例中，可通过促进剂前体，如氯化铵、氯化钠或氯化钙的降解或反应提供 HCl。该促进剂可以是 HF，在一些实例中，可通过促进剂前体，如氟化铵、氟化钠或氟化钙的降解或反应提供 HF。在一些实例中，促进剂（例如 HBr 或 HCl）或促进剂前体（例如 NH_4Br、NaBr、$CaBr_2$、NH_4Cl、NaCl、$CaCl_2$）可以与碳纳米复合吸附剂分开或与碳纳米复合吸附剂一起注射到烟气中（例如可以在注射前施加到吸附剂中，在相同位置同时注射，或在不同位置同时注射）。

[0069] 无意将实施方案局限于任何特定的作用机制，在各种实施方案中，将卤素或来自卤化氢酸的质子添加到碳边缘结构上的碱性卡宾位点上形成了碳正离子，其从中性汞原子接收电子，以形成结合到吸附剂表面上的氧化汞物类。该反应性位点也可以在碳上的活性位点生成反应性卤素基团或碳基团。由此该碳纳米复合吸附剂提供可氧化汞并促进其捕获在碳纳米复合吸附剂上的高反应性含卤素试剂。在一些实施方案中，含有溴或由溴或溴试剂促进的吸附剂预计比由氯或氯试剂促进的相应吸附剂更具反应性并且比由碘或碘试剂促进的吸附剂便宜。

[0070] 卤素和酸性物类与促进的碳纳米复合吸附剂上的结合位点的反应可产生用于氧

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化汞的活性位点。其它金属离子，如硼、锡、砷、镓、Sb、Pb、Bi、Cd、Ag、Cu、Zn、Se 或其它污染物也可以与该碳上的氧化位点反应。

[0071] 在一些实施方案中，添加到碳纳米复合吸附剂中并与其反应的卤素或卤化物促进剂可包括，例如但不限于，蒸气或气态形式的分子卤素、在有机溶剂中的分子卤素、蒸气、液体或溶液形式（例如在水或非水溶剂，如醇或其它有机溶剂中）的第 V 族或第 VI 族卤化物，分别例如 PBr_3 或 SCl_2。

[0072] 还提供有机溶剂包括氯化烃，如二氯甲烷，烃溶剂，包括例如，石油醚、轻石油（ligroin）、戊烷、己烷、甲苯和苯，二硫化碳、废溶剂、醚、再循环溶剂、超临界溶剂，如超临界 CO_2，水（尽管在第 V 族或第 VI 族卤化物的情况中不行）和如本领域技术人员显而易见的其它溶剂的实施方案。

[0073] 在一些实施方案中，该方法可包括将附加的卤素或卤化物促进剂添加到所述促进的吸附剂中。该附加的卤素或卤化物可以是本文中被描述为适合作为第一卤素或卤化物的任何卤素或卤化物。例如，该附加的卤素或卤化物促进剂可包括 HI、HBr、HCl、与卤素结合的第 V 族元素或与卤素结合的第 VI 族元素。

[0074] 在各种实施方案中，促进至少一部分吸附剂材料的步骤可以至少部分在含汞气体与该吸附剂接触之前进行。在一些实例中，促进至少一部分吸附剂的步骤可以至少部分在含汞气体与该吸附剂接触的过程中进行。在一些实例中，可以将碳纳米复合吸附剂以一定注射速率注射到气流中，其中将至少一种促进剂以一定注射速率单独注射到气流中，由此飞行中的反应产生促进的吸附剂。在一些实例中，该促进剂可以在气相中或作为蒸气反应。在一些实例中，每 100 克碳纳米复合吸附剂材料加入大约 0.01 克至大约 200 克，或大约 0.1 克至大约 100 克，或大约 1 克至大约 30 克促进剂。在一些实例中，吸附剂和促进剂注入的气流之一或两者可以是输运气体、烟气流（例如含汞气体）或其组合。在一些实例中，注入气体中的促进剂注射速率和吸附剂注射速率至少部分由净化气体的监测汞含量确定。

[0075] 吸附剂和含汞气体中的汞接触

在降低含汞气体的汞含量的方法的实施方案中，该方法可包括使至少一部分促进的吸附剂与含汞气体中的汞接触。促进的吸附剂与含汞气体中的汞的接触包括使促进的吸附剂与含汞气体接触。促进的吸附剂与汞的接触形成汞－吸附剂组合物。该接触可以在任何合适的位置进行。例如，该接触可以在气体中进行。在另一实施方案中，该接触可以在水性液中进行。在另一实例中，该接触可以在气体中进行，随后也可以在水相，如洗涤器中进行接触。

[0076] 在各种实施方案中，可以使用汞排放的测量结果作为反馈以助于控制吸附剂注射速率。由此可以实现对吸附剂和任选组分水平的更严密控制，这有助于确保以最低限度的促进剂和吸附剂要求满足除汞要求，由此使相关的成本最小化。在一个实施方案中，在注射位置下游，例如在烟囱的废气中连续测量汞排放。在各种实施方案中，至少一部分促进的吸附剂与含汞气体中的汞的接触可以在颗粒物控制装置之间进行。

[0077] 从含汞气体中分离至少一部分汞－吸附剂组合物

在降低含汞气体的汞含量的方法的实施方案中，该方法包括从气体中分离至少一部分汞－吸附剂组合物。该分离产生具有比原材料含汞气体低的汞含量的净化气体。在一些实施方案中，从含汞气体中分离至少一部分汞－吸附剂组合物包括从该气体中分离颗粒物，

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其中所述颗粒物包含至少一部分汞-吸附剂组合物。

[0078] 在一些实例中，从含汞气体中分离颗粒物的步骤包括在颗粒物分离器中从该气体中分离颗粒物。该颗粒物分离器可以是任何合适的分离器。该颗粒物分离器可包括一个或多个旋风分离器、静电除尘器、织物分离器、洗涤器或如本领域中已知的其它颗粒物脱除装置。在一些实施方案中，可以使用静电除尘器，接着洗涤器。在另一些实施方案中，可以使用静电除尘器，无洗涤器，或可以使用另一颗粒物分离器。可充当颗粒物分离器的一些装置还可具有其它功能，例如洗涤器还可如下文进一步描述从气流中除去 SO_2 或 SO_3。在包括汞与吸附剂在水相中，例如在洗涤器中接触的实施方案中，通过汞与吸附剂在水相中的反应或相互作用而在水相内发生的该气体的除汞可被视为从该气体中分离汞-吸附剂组合物。

[0079] 在一些实例中，通过从含汞气体中分离颗粒物，可以从含汞气流中除去至少大约 20 重量%、30 重量%、40 重量%、50 重量%、60 重量%、70 重量%、80 重量%、90 重量%、95 重量%、96 重量%、97 重量%、98 重量%、99 重量%、99.9 重量%、99.99 重量%或大约 99.999 重量%或更多的汞。如本文中论述，汞可以以元素汞形式、转化的汞，如氧化汞(例如汞氧化物)形式除去。

[0080] 洗涤器

在降低含污染物的气体的污染物含量的方法的各种实施方案中，可以使用水洗涤器。水洗涤器能使水性液体或水性浆料接触气流。洗涤器可以将水性材料喷洒、喷雾或以其它方式分布在气流流过其中的空间内，以提高在洗涤器中接触该气体的液体的表面积。该水溶液可落到洗涤器底部，在此其可再循环回顶部，或取出以再生、净化或更换。该水洗涤器可以是任何合适的水洗涤器。在一些实例中，该水洗涤器可以从气流中除去一种或多种污染物。

[0081] 洗涤器可以从气流中除去颗粒物。例如，当包含颗粒物的气流经过洗涤器时，接触到微滴或其它形式的水溶液的颗粒物会粘在或浸渍在该水溶液中。随着水溶液落到洗涤器的底部，粒子随其落下。该水溶液可以带着其中的至少一些粒子再循环回洗涤器顶部。该水溶液可具有任何合适的稠度，如自由流动的透明液体、具有悬浮固体的液体或任何合适粘度的浆料。连续或分批地，可以净化或更换洗涤器中的水溶液，以除去例如粒子、污染物或污染物副产物。在一个实例中，可以如 US 2007/0167309 中所述分离和再生水溶液中的吸附剂。

[0082] 在各种实施方案中，该方法可包括从含污染物的气体中除去至少一些 SO_2 或 SO_3 (例如降低 SO_2 或 SO_3 的浓度)。可以以任何合适的方式进行脱除。在一些实例中，水洗涤器可以例如通过洗涤器中的水中存在的化学化合物与 SO_2 或 SO_3 的反应从气流中除去 SO_2 或 SO_3。洗涤器中的水中包括的可与 SO_2 或 SO_3 反应的化学化合物的一些实例包括在水中形成碱性溶液的盐，例如具有任何合适的抗衡离子，例如铵(NH_4^+)、钠(Na^+)、钾(K^+)、镁(Mg^{+2})或钙(Ca^{+2})的碳酸盐(CO_3^{-2})、碳酸氢盐(HCO_3^-)或氨基甲酸盐($OCONH_2^-$)。例如，该碱性盐可以是碳酸铵($(NH_4)_2CO_3$)、碳酸氢铵($(NH_4)HCO_3$)或氨基甲酸铵($(NH_4)OCONH_2$)。

[0083] 在各种实施方案中，促进剂或促进剂前体可以在洗涤器的水溶液中。在一些实施方案中，可以将促进剂(例如 HBr)直接添加到水洗涤器中的水中。在一些实例中，可以将促进剂前体(例如 NH_4Br)直接添加到水洗涤器中的水中，其可以在此分解形成促进剂(例如 HBr)。可以将促进剂前体注射到热气体(例如热载气或烟气流)中，其可以在此转化成促进

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剂，随后该气流可进入洗涤器，在此该前体吸收或溶解在洗涤器中的水中。该促进剂或促进剂前体可以以任何合适的方式进入洗涤器的任何合适的部分，例如其可以在进入洗涤器之前进入烟气流，其可以单独注射到洗涤器的气相中，或其可以注射到洗涤器的水相中。

[0084] 在一些实施方案中，洗涤器中的水溶液可包括活性炭纳米复合吸附剂。在这样的实施方案中，该洗涤器可通过使该活化的吸附剂在水相中与来自气流的一种或多种污染物反应或吸收来自气流的一种或多种污染物而从气流中除去一种或多种污染物，如汞。该纳米复合材料可以以任何合适的方式在任何合适的位置进入洗涤器，例如其可以在进入洗涤器之前进入烟气流，其可以单独注射到洗涤器的气相中，或其可以注射到洗涤器的水相中。任选地，包括活性炭纳米复合吸附剂的水溶液可包括可与该气流中的污染物反应的其它化学品，以使该洗涤器可除去多于一种类型的污染物。例如，除活性炭纳米复合吸附剂外，水洗涤器溶液还可包括可与 SO_2 反应的碱性盐。

[0085] 在一些实例中，碳纳米复合材料可以在该洗涤器中活化，如在洗涤器的水中包括促进剂的实施方案中。可以将碳纳米复合材料直接添加到洗涤器中（例如添加到气相或液相中），或在洗涤器之前添加到流入洗涤器的气流中。可以在颗粒物控制装置（例如 ESP）和洗涤器之间的任何合适的点加入碳纳米复合材料。在一些实例中，可以将碳纳米复合材料和促进剂或促进剂前体都注射到热气流（例如热载气或烟气流）中，在此在进入洗涤器之前可以形成促进的碳纳米复合吸附剂。在一些实施方案中，可以用促进剂或促进剂前体涂布碳纳米复合材料并将涂布的碳纳米复合材料注射到热气体（例如热载气或烟气流）中，其可在此转化成促进剂，随后吸收在洗涤器中的水中。

[0086] 在包括 ESP 和洗涤器的实施方案中，碳纳米复合材料可任选在 ESP 之前以及在湿洗涤器中用于污染物脱除。在这种实施方案中，ESP 可除去纳米复合材料 - 污染物。或者，该碳纳米复合材料可用在洗涤器中并且不在 ESP 之前使用。或者，该碳纳米复合材料可以仅在 ESP 之前使用并且不用在洗涤器中或不主要用在 ESP 中。

[0087] 碱性组分

在一些实例中，从含汞气流中除汞的方法可包括将碱性（alkaline）（例如碱性（basic））组分注射到含汞气体中。在一些实例中，该碱性组分包括碱金属或碱土金属元素的氧化物、氢氧化物、碳酸盐或磷酸盐。

[0088] 在各种实例中，与碳纳米复合吸附剂分开或一起添加碱性组分可改进汞捕获，在一些实例中超过促进的和未促进的碳纳米复合吸附剂。各种因素会影响碱性组分的添加效力，例如烟气污染物、烟气成分（例如 SO_3、NO_x、HCl 等）、运行温度、汞形式和汞浓度。在一些实例中，可以调节碱性组分 / 活性炭比率以针对给定的现场条件组进行优化。

[0089] 稳定剂

在一些实例中，可以将稳定剂添加到促进的吸附剂中。该稳定剂可以是汞稳定剂。在一些实施方案中，提供了将汞稳定剂添加到促进的碳吸附剂中以制造双功能吸附剂的方法。此类稳定剂可以在卤素 / 卤化物的添加和反应之前或之后依序加入。在一些实施方案中，卤素 / 卤化物包括 Br 或 HBr，且汞 - 稳定剂可包括 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 及其组合。

[0090] 吸附剂的再生

在用于从含汞气流中分离汞的方法或材料的任何实施方案中，可以再生该碳吸附剂；

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可以除去来自烟气的使吸附剂中毒的污染物；并可以将吸附剂再促进以恢复汞吸附活性。再生的吸附剂然后再用于该方法。在共同待审的共有 PCT 专利申请 No. PCT/US04/12828（名为“PROCESS FOR REGENERATING A SPENT SORBENT”，其全文并入本文作为参考）中描述了吸附剂再生技术的详细实例。

[0091] 示例性方法

在各种实施方案中，除来自燃烧系统的烟气外，本文中论述的碳纳米复合吸附剂、除汞方法和任选添加剂还可用于来自气化系统、合成气发生器的产物或排出气体和其它含汞气流的汞控制。因此，应该理解的是，本说明书通篇所用的术语燃烧系统和烟气如本领域技术人员理解的那样同样适用于气化系统和合成气或燃料气。

[0092] 现在参照图 1，显示了示例根据各种实施方案制备促进的碳吸附剂的方法的方框流程图。方框 10 示例提供碳纳米复合吸附剂，在方框 20 处示例添加卤素或卤化物促进剂，其与碳反应以产生促进的碳纳米复合吸附剂。在卤素或卤化物在例如溶剂中加入的实施方案中，可以如方框 20A 所示除去溶剂。方框 30 指示添加在方框 30 中示例的任选次要组分，其与方框 20 或 20A 的产物反应以产生促进的碳纳米复合吸附剂。在卤素或卤化物促进剂和 / 或次要组分在例如溶剂中加入的实施方案中，可以如方框 30A 所示除去溶剂。

[0093] 在图 1 中，步骤 50 之前的步骤在用促进的吸附剂处理烟气流之前产生促进的吸附剂。一种或多种促进剂的添加和与促进剂的反应或相互作用（这导致该吸附剂的促进）可以在任何合适的位置进行。在一些实例中，可以在热气流中，如在烟气流中，或如在热载气流中促进该吸附剂。在一些实施方案中，可以在将吸附剂注射到热气流中之前将促进剂添加到吸附剂中。在一些实施方案中，可以将促进剂与吸附剂一起添加到热气流中，在本文中称作吸附剂的“飞行中”促进。因此，在一些实施方案中，在步骤 50 之前，促进剂和吸附剂可以一起或分开注射到烟气流或另一热气流中。

[0094] 再参照图 1，路径 10-40 包括如方框 10 所示提供碳纳米复合吸附剂和如方框 40 所示将卤素或卤化物促进剂和次要组分一起添加到吸附剂中，它们与吸附剂反应以产生促进的碳纳米复合吸附剂。在一种或多种组分在溶剂中加入的实施方案中，可以如方框 40A 所示提供溶剂脱除步骤。

[0095] 再参照图 1，也示例了如方框 50 所示用如本文所述制备的促进的碳纳米复合吸附剂处理烟气流的实施方案。

[0096] 现在参照图 2，示例了由科学证据展开的解释促进化合物的性质的理论，其无意将本发明的实施方案限于任何具体操作理论。本发明的方法包括使用碳纳米复合材料以任何合适的方式从气体中除汞。

[0097] 例如，如图 2 中所示，溴化氢可以与碳纳米复合吸附剂的不饱和结构反应。可以由例如溴化铵提供溴化氢。仅举例而言，碳纳米复合吸附剂上的碳的反应性部分可以是该碳的石墨烯片结构的边缘上的卡宾物类。分子溴或其它溴化合物可反应形成类似结构——其具有可有效用于氧化汞（其随后被该吸附剂捕获）的正碳。

[0098] 含碳的溴化物化合物的形成提高了碳纳米复合材料对汞和其它污染物的反应性。另外，所得溴化物化合物独特地适合促进汞的氧化。该氧化的效率可来自该卤化物对氧化过程中汞上的正电荷开发的促进效应，这在化学领域中已知为特定的催化效应。因此，随着汞电子被吸引到正碳上，卤素阴离子电子可以从另一侧推入，以稳定汞上的正电荷开发和

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降低该氧化过程的能量要求。由于该离子的外 4p 轨道中的高度可极化电子，溴化物尤其具有反应性。因此，将 HBr 或 Br_2 添加到碳纳米复合材料中可形成类似的溴化碳，其中正碳可借助溴离子氧化汞。

[0099] 图 3A 显示汞控制系统 100 的示意性流程图，其包括根据本发明的实施方案制备促进的碳吸附剂和烟气除汞。提供了碳纳米复合吸附剂储器 110、任选的卤素 / 卤化物促进剂储器 120、任选的次要组分储器 130 和任选的碱组分储器 180，它们各自分别具有相应的流量控制装置 201、202、203 和 207/208/209。具有相应的流量控制器 201、202 和 203 的储器 110、120 和 130 可以与传输线路 113 和 115 一起独立地使用，一起使用或完全不使用。例如，具有控制器 201 的储器 110 可以与传输线路 113 一起使用以独立地和单独地在注射点 114 注入材料，同时，具有相应的流量控制器 202 和 / 或 203 的任选储器 120 和 / 或 130 可以与传输线路 115 一起使用以独立地和单独地在注射点 116 注入材料。与任选的碱组分储器 180 一起，任选的流量控制装置 207、208 和 209 可以独立使用，一起使用或完全不使用。

[0100] 储器 110、120、130 和 180 通过它们各自的流量控制装置并经由相应的管路连向传输线路 113 和 115。任选的碱组分储器 180 也可以通过各自的流量控制装置并经由相应的管路连向传输线路 118。由气体源 169 向传输线路 113 提供空气、氮气或其它输运气体源以携带从储器 110、120、130 和 180 排出的材料并将此类材料经注射点 114 注射到污染的烟气流 15 中。由气体源 170 向传输线路 115 提供空气、氮气或其它输运气体源以携带从储器 110、120、130 和 180 排出的材料并将此类材料经注射点 116 注射到污染的烟气流 15 中。由气体源 171 向传输线路 118 提供空气、氮气或其它输运气体源以携带从储器 180 排出的材料并将此类材料经注射点 119 注射到烟气流 15 中。气体源 169、170 和 171 可以视需要相同或不同。或者，可以通过气体源 170 向传输线路 113、115 和 118 提供输运气体（没有显示从源 170 连向传输线路 113 和 / 或 118）。尽管气体源 169、170 和 171 在图 3A 中显示为压缩机或鼓风机，如本领域普通技术人员会认识到的本领域中已知的任何传输能量源是可接受的。例如，在 120 作为液体添加的情况下，169 可以是泵。

[0101] 为清楚起见，在图 3A 中显示了单注射点 114、116 和 119，尽管本领域普通技术人员会理解，多注射点也在本发明的范围内。将光学密度测量装置 204 连向传输线路 113 或 115（或 118，未显示）以提供随时间变化的代表传输线路 113、115 或 118 内的光学密度的信号。

[0102] 在注射点 116 和 119 下游提供颗粒物分离器 140。例如但非限制地，颗粒物分离器 140 可包括一个或多个织物过滤器、一个或多个静电除尘器（下文称作“ESP”）或如本领域中已知的其它颗粒物脱除装置。应该进一步指出，可相继或并列存在多于一个颗粒物分离器 140，当并列存在、相继存在或存在它们的组合时，注射点 116 和 119 可以在 140 上游和 / 或下游的位置。颗粒物分离器 140 可至少产生主要气态（“净化”）流 42 和包括分离的固体材料的流 141。吸附剂 / 灰分分离器 150 可以将流 141 分离成主要灰分流 152 和主要吸附剂流 151。或者，未显示地，流 141 可作为废物流弃置或直接送往任选的吸附剂再生器 160。然后可将流 151 送往任选的吸附剂再生器 160，这产生再生吸附剂流 161 和废物流 162。

[0103] 在任选的 ESP 140 后提供任选的水洗涤器 190。水洗涤器 190 可以与 ESP 140 一起或不与 ESP 140 一起提供。洗涤器 190 可以从气流中除去颗粒物，可以通过与碱性水性液体的化学反应从气流中除去污染物，如 SO_2，可以通过与洗涤器中的活性炭纳米复合吸附剂反应或被其吸收从气流中除去污染物，如汞，或它们的任何合适的组合。除了或代替在单

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元 140 之前注入和促进碳纳米复合吸附剂，可以向水洗涤器 190 提供促进剂 120 或促进剂前体。可以将该促进剂或促进剂前体注射到气流 42 中，或可以直接提供到洗涤器中(没有显示 120/130 和 190 之间的传输线路)。促进剂或促进剂前体可以作为用促进剂或促进剂前体涂布或与促进剂或促进剂前体结合的碳纳米复合吸附剂在洗涤器 190 之前提供或提供到洗涤器 190 中。涂布或结合的吸附剂 / 前体的促进可以在洗涤器 190 中，在该洗涤器前的气流 42 中或在向 42 或 190 输送活化的纳米复合材料的加热载气线路(未显示)中进行。除了或代替在单元 140 之前注入和促进碳纳米复合吸附剂，可以向水洗涤器 190 提供碳纳米复合材料。可以将该碳纳米复合材料注射到气流 42 中，或可以直接提供到洗涤器中(没有显示 110 和 190 之间的传输线路)。洗涤器中的水溶液可以在分批或连续法中再生或更换，以除去吸收的颗粒物、吸收的污染物或吸收的污染物副产物。

[0104] 在废气流 35 中提供对汞的任选连续排放监测器(下文称作“CEM”)205 以提供随时间变化的代表废气流 35 中的汞浓度的电信号。任选的汞 CEM 205 和流量控制器 201、202、203、207、208 和 209 经由任选线路 227(或无线)电连接到任选的数字计算机(或控制器)206 上，其接收和加工信号并可以控制促进的碳吸附剂的制备和注射到污染的烟气流 15 中。

[0105] 在示例性运行中，可以将碳纳米复合吸附剂和 / 或任选的促进剂和 / 或任选的碱组分注射到污染的烟气流 15 中。在注入的材料与污染的烟气流 15 接触后，注入的材料降低汞浓度，以将污染的烟气转化成汞减少的烟气流 25。分别地，可以通过分离器 140 从汞减少的烟气流 25 中除去注入的材料，弃置或通过任选分离器 150 进一步分离，和弃置或通过任选再生器 160 再生。或者或另外，洗涤器 190 可以借助促进的碳纳米复合材料除去 SO_3、污染物，如汞，除去颗粒物，或它们的任何组合。然后通过任选的 CEM 205 监测汞减少的“净化”烟气流 42 和 / 或 35 的汞含量，这向任选的计算机 / 控制器 206 提供相应的信号。来自 206 的逻辑和优化信号随后可根据本领域中公知的控制算法调节流量控制器 201、202、203、207、208、209 以使废气流 35 中的汞浓度保持在所需界限内。也可以手工或通过另一些自动化手段根据本领域中公知的控制算法调节流量控制器 201、202、203、207、208、209 以使废气流 35 中的汞浓度保持在所需界限内。

[0106] 再参照图 3A，示例了用于制备和注射碳纳米复合吸附剂、促进的碳吸附剂、卤素和卤化物促进剂和 / 或碱组分的几个实施方案。流 111 用于从储器 110 引入碳纳米复合吸附剂，其手动或在计算机 206 的指导下通过流量控制器 201 计量加入。卤素 / 卤化物可以根据几个提供的方法的任一种与碳纳米复合吸附剂结合和反应。卤素 / 卤化物 (120 和 / 或 130) 可经由传输线路 121 (和 / 或 131)直接并入传输线路 115(或 113) 中，在其内在注射点 116 (或 114)之前与碳纳米复合吸附剂(例如在储器 110)接触和反应。这一选项是在本文中被称作根据本发明的促进的碳吸附剂的“飞行中”制备的一种形式。此外，卤素 / 卤化物 (120 和 / 或 130) 可通过传输线路 121 (和 / 或 131) 经由烟气流 15 并入传输线路 115 和注射点 116，其在传输线路 113 中传输并在注射点 114 注入碳纳米复合材料后与烟气流 15 中的碳纳米复合材料(例如来自储器 110)接触和反应。这一选项是在本文中被称作根据本发明的促进的碳纳米复合吸附剂的“飞行中”制备的另一形式。此外，卤素 / 卤化物可经由传输线路 121b 与进入传输线路 113 和 / 或 115 之前的碳纳米复合吸附剂合并。再进一步，卤素 / 卤化物可以通过经传输线路 121c 引入储器 110 而与碳纳米复合吸附剂接触和反应。当例如储器 110 包括碳纳米复合吸附剂的沸腾床或流化床时，可以使用这一选项，卤

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素 / 卤化物以气体形式或作为蒸气流经该床。在另一些实施方案中，卤素 / 卤化物可以如上文论述以液体形式或在溶剂中与碳纳米复合吸附剂接触，然后如果必要，如参照图 1 论述的实施方案中提到的那样，提供溶剂脱除(未显示在图 3A 中)。

[0107] 类似地，任选的次要组分可以经由传输线路 131 直接在传输线路 115(和 / 或 113)中，或任选如上文参照卤素 / 卤化物所述经由传输线路 131b 和 131c 接触和反应。

[0108] 类似地，来自储器 180 的任选的碱组分可以直接在传输线路 113 和 / 或 115 中添加，或可以由传输线路 118 单独注入，以保持独立和 / 或在烟气流 15 的下游结合以与碳纳米复合吸附剂、促进的碳或任选的次要组分协同作用。可以针对现场特有的运行条件和烟气条件优化任选碱组分的量的现场变化(相对于碳纳米复合吸附剂、促进的碳或任选的次要组分)。

[0109] 图 3B 显示汞控制系统 300 的示意性流程图，其包括根据本发明的实施方案制备促进的碳吸附剂和烟气除汞。碳吸附剂 310 可以经线路 395 注射到位置 396 或经线路 390 注射到位置 391。促进的碳吸附剂 320 可以经线路 395 注射到位置 396 或经线路 390 注射到位置 391。碳吸附剂 310 可以在飞行中促进，如通过将线路 390 和 / 或 395 将碳吸附剂 310 注射到位置 391 和 / 或 396 并经线路 380 将卤素 / 卤化物促进剂 340 注射到位置 385，或通过经线路 390 和 / 或 395 将碳吸附剂 310 注射到位置 391 和 / 或 396 并经线路 350 将卤素 / 卤化物促进剂 340 注射到位置 355 和 / 或经线路 360 将卤素 / 卤化物促进剂 340 注射到位置 365 和 / 或经线路 370 将卤素 / 卤化物促进剂 340 注射到位置 375。

[0110] 除了或代替在任选的 ESP 单元之前使用促进的碳纳米复合材料，可以使用任选的洗涤器单元通过在该洗涤器中使用促进的碳而除去污染物，如汞，通过在该洗涤器中使用碱性水溶液而除去污染物，如 SO_3，在该洗涤器中除去颗粒物，或它们的任何组合。材料，如促进剂或碳纳米复合吸附剂可以在洗涤器中或在 ESP 和洗涤器之间注射到洗涤器中。促进的吸附剂 320 可以经线路 397 注射到洗涤器中。碳吸附剂 310 可以在飞行中促进，例如通过碳吸附剂 310 经由加热载体线路(未显示)与促进剂 340 一起注射到洗涤器中。卤素 / 卤化物促进剂 340 可以经线路 381 添加到洗涤器中，同时经线路 397 加入碳吸附剂 310，并可以在洗涤器内促进该吸附剂。

[0111] 在组分之间的接触和反应在液相或溶剂相中进行的一些实施方案中，可以提供此类液体和 / 或浆料混合物的搅拌。在一些实施方案中，卤素 / 卤化物促进剂和任选的次要组分以溶液形式注射到碳纳米复合吸附剂中或上。在一些这样的实施方案中，可随后提供如本领域中已知的干燥、过滤、离心、沉降、滗析或其它溶剂脱除法。

[0112] 在该卤素 / 卤化物促进剂是气体或蒸气形式的实施方案中，其可以酌情在空气、氮气或其它气体中稀释。可以使卤化物 / 卤素气体，例如气态 HBr 或 Br_2 经过颗粒或纤维状的碳纳米复合吸附剂的沸腾床或流化床，可以通过气体夹带从该床的顶部取出如此制成的促进的碳吸附剂以供注射。

[0113] 在一些实施方案中，次要组分可包括碘或其它卤素、氢卤化物，包括但不限于 HI、HBr、HCl、与分子卤素结合的第 V 族或第 VI 族元素，如 SCl_2 等。在一些实施方案中，该促进的碳吸附剂可包括大约 1 克至大约 30 克卤素 / 卤化物 /100 克碳纳米复合吸附剂材料。在一些实施方案中，该促进的碳吸附剂可包括占卤素 / 卤化物组分的浓度大约 1 重量％至大约 15 重量％的浓度的次要组分。

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[0114] 在另一些实施方案中，可以将该促进的碳纳米复合吸附剂施加到基底上。在另一些实施方案中，可以使如此制成的基底与污染的烟气或气化系统产物气流接触以减少汞。这样的基底可以是整块的，旋转、移动或以本领域技术人员已知的各种方式暴露在气流中。基底可包括例如蜂窝结构、织物、过滤器、板等。

实施例

[0115] 参照作为示例提供的下列实施例更好地理解本发明。本发明不限于本文中给出的实施例。

[0116] 实施例 1. 来自商业蔗糖蜜的介孔活性炭 (AC) 纳米复合材料

实施例 1.1. NanoG-CM

将获自 Aldrich 的高表面积蒙脱土（粘土）（200 克）快速添加到用更少量的水（200 克 /140 毫升）稀释的 Brer Rabbit 糖蜜（未硫化）中并搅拌以制造稠糊。

[0117] 一旦所有粘土被糖蜜润湿，将该糊在 110℃下干燥整夜以除去过量水。或者，将较少部分的糊在微波中加热 1 分钟。较小批量在炉中在 110℃下更快（1 小时）干燥。

[0118] 将干燥的固体分两批加载到圆柱形钢管中并在管式炉中在氮气流过该床的同时加热至 700℃。将排出的气体鼓过脱水器（water trap）。继续加热 1 小时。该管在氮气下缓慢冷却至环境温度并排空。将所得黑色复合碳块称重并在研钵和研杵中研磨。将产物纳米复合材料分成两个筛分粒度——大于 325 目和大约 325 目。大约 325 目材料用于 Hg 捕获试验。

[0119] 纳米复合材料的产量为 217 克。

[0120] 实施例 1.2. NanoG-CB.

制备类似于 NanoG-CM，只是用高钠膨润土代替蒙脱土。由 10.0 克膨润土获得的产量为 10.1 克。

[0121] 实施例 1.3. 促进剂的浸渍

实施例 1.3.1. 溴化铵

将溴化铵的水溶液（7.3 克 /35 毫升）添加到 54 克 325 目纳米复合材料中并搅拌形成糊。该糊在 110℃下干燥并再研磨。

[0122] 实施例 1.3.2. 溴化氢

将 HBr 水溶液（0.1 N）添加到 NanoG-CM（10 克）中并将该混合物搅拌 1 小时。过滤该浆料并在 110℃下干燥。

[0123] 实施例 1.3.3. 溴 .

将溴蒸气（0.5 克）转移到含有粉状复合材料（10 克）的管瓶中，其吸附到其中。

[0124] 实施例 1.3.4. 硫

将元素硫（1 克）溶解在二硫化碳（20 毫升）中并加入 10 克 NanoG-CM。在搅拌整夜后，除去二硫化碳。

[0125] 实施例 2. 来自 American Crystal Sugar (ACS) Raffinate 的介孔活性碳纳米复合材料

前一版本的 NanoG-CM 碳复合材料使用蔗糖蜜制成。使用当地 ACS 糖蜜会提供更方便的来源；例如可大量（大约 170 吨）供应由糖和甜菜碱提取剩余的低价值残液。但是，溶解

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的无机盐的量比商业蔗糖蜜高得多(>10%)且糖含量较低。

[0126] 使用 ASC 残液和两种类型的粘土制备纳米复合材料:来自 Aldrich 的高溶胀高钠膨润土和低溶胀蒙脱土。两者都细研磨。

[0127] 实施例 2.1. NanoG-ACSB.

通过将 10 克干燥膨润土添加到 80 克水中并用研钵和研杵研磨,使膨润土溶胀。将 ACS 残液(10 克)添加到胶凝的混合物中并通过研磨混合。在静置整夜以使残液中的糖进一步分散到粘土中后,将该混合物在微波中以满功率加热 1 分钟以形成该凝胶中的大孔隙度。将该凝胶在干燥炉中在 110℃下干燥整夜。

[0128] 将干燥的固体分两批加载到圆柱形钢管中并在管式炉中在氮气流过该床的同时加热至 700℃。将排出的气体鼓过脱水器。继续加热 1 小时。该管在氮气下缓慢冷却至环境温度并排空。将所得黑色复合碳块称重并在研钵和研杵中研磨。

[0129] 纳米复合材料的产量为 10.2 克。

[0130] 实施例 2.2. NanoG-2ACSB

制备类似于 NanoG-ACSB,只是添加的残液的重量翻倍。产量为 10.5 克。

[0131] 实施例 2.3. NanoG-2ACSM.

制备类似于 NanoG-CM,使用 10 克 Aldrich 蒙脱土和 20 克 ACS 残液,且量翻倍。产量为 10.5 克。

[0132] 实施例 2.4. NanoG-2ACSB-Washed.

NanoG-2ACSB 的样品用水搅拌整夜,过滤,然后用 0.1 N HBr 搅拌 2 小时。过滤该浆料并将该复合材料在 110℃下干燥。

[0133] 实施例 2.5. 促进剂的浸渍

实施例 2.5.1. 溴化铵.

溴化铵水溶液(1.1 克/5 毫升)添加到 10 克纳米复合材料并搅拌形成糊。该糊在 110℃下干燥并再研磨。

[0134] 实施例 2.5.2. 溴.

将溴蒸气(0.5 克)转移到含有粉状复合材料的管瓶中,其部分吸附(化学吸附)到其中。

[0135] 实施例 3. NanoG吸附剂的实验室规模 Hg吸附试验

进行实验室规模 Hg 吸附试验以评估该吸附剂在床构造下吸附烟气中的元素 Hg 蒸气的性能。这些结果概括在表 1 中。尽管在极短接触时间下对注射模式中的性能的评估不太准确,但初始反应性(作为 %Hg 捕获)和初始斜率给出短时标内的反应性的初步测定。当初始斜率平坦时,存在许多活性位点,并发现较高的反应性。陡峭的初始斜率涉及快速突破和相应的较低反应性。

[0136] 由蔗糖蜜制成的 NanoG 复合吸附剂(NanoG-CM)在实验开始时提供优异的反应性(98%-99% 捕获)并维持高捕获效率 15 分钟(平坦斜率)。另一方面,ACS 残液与由蔗糖蜜制成的复合材料相比提供较低反应性和较低容量(较短的 50% 突破时间)。由于较低的糖含量、较高的盐含量和可能不同的燃尽速率,ACS 复合材料中所含的碳量明显较低。用双倍量的糖蜜制成的复合材料的反应性低于较低剂量。可以通过由 ACS 残液制成的复合材料的孔隙中的盐堵塞解释这些结果。将水添加到该吸附剂中时大量 H_2S 的析出与在孔隙中形成 K_2S(源自硫酸盐的还原以及高钾含量)相一致。当洗涤 ACS 残液吸附剂以溶解掉盐时,反应性

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和容量明显改进。

[0137] 表 1. NanoG吸附剂的固定床筛选的概要结果

吸附剂	促进剂	初始反应性，%Hg捕获	初始斜率	50%突破时间，hr
NanoG-CM	Br_2	98	平坦	0.45
NanoG-CM	NH_4Br	99	平坦	0.38
NanoG-CM	HBr	97	中等	0.29
NanoG-CM	S	92	陡峭	0.06
NanoG-2ACSM	Br_2	67	陡峭	0.02
NanoG-2ACSB	Br_2	95	陡峭	0.16
NanoG-2ACSB	NH_4Br	90	陡峭	0.29
NanoG-ACSB	NH_4Br	97	中等	0.32
NanoG-2ACSB-洗涤过的	Br_2	97	中等	0.53

[0138] 尽管 AC 的硫化产生对 Hg 具有良好反应性的碳，但将硫添加到 NanoG 吸附剂中没有带来良好的容量。硫有可能堵塞这些吸附剂中可提供的有限量孔隙率的孔。

[0139] HBr 与 Br_2 的比较表明 Br_2 产生更高的反应性和容量。其原因可能是在通过气相沉积制成的吸附剂中，这些复合吸附剂中的碳正离子－溴离子对的水合程度更低并更具反应性。

[0140] 溴化铵－促进的吸附剂提供极好的反应性和容量——与在加热时孔隙中的溴化铵分解形成氨和气态 HBr 相一致。HBr 与沉积在邻近的纳米碳表面上的碳结合，以装饰粘土层(片)。氨也截留在该复合材料的酸性粘土层内，在此其可用于在烟气中的 SO_3 在碳表面上氧化之前拦截该 SO_3。

[0141] 实施例 4. 中试评估

在 Center for Air Toxic Metals® (CATM®)－赞助的颗粒物试验燃烧器(PTC)运行过程中以中试规模评估 NanoG-CM。用于该评估的煤是亚烟煤 Montana Powder River Basin (PRB) (Absaloka) 并与市售未处理的碳进行比较。

[0142] 对于市售标准 AC 和两种形式的 NanoG-CM，来自 PTC 试验的结果概括在图 4 中。图 4 显示在总注射吸附剂基础上的 NanoG-CM 测试的 PTC 结果。用中等能量离解技术(moderate energy dissociation technology)(MEDT)吸附剂强化添加剂(SEA)选项测试标准 AC 和未处理过的 NanoG-CM。如附图中所示，标准 AC 的结果较好；但是，该 NanoG-CM 确实表现出飞行中捕获潜力。用 NanoG-CM 的处理过的样品获得更有前途的结果。通过为扩展 MEDT SEA 进行的一组试验确定，用于 NanoG-CM 的预处理在预空气加热器温度下最有效。因此，在该处理过的 NanoG-CM 的评估过程中，将其注射到管道系统中烟气温度为大约 715° F 的点。

[0143] 图 4 表明该 NanoG-CM 材料表现出作为飞行中的汞吸附剂的潜力，但总注射吸附剂

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速率高于标准AC。但是，另一比较是以碳组分为基础评估试验结果，因为对复合吸附剂的基本的经济假设在于，AC组分可能比无机基底贵一个量级。来自图4的结果重新定标在图5中以描绘这三个选项的相当的仅以碳计的注射速率。图5显示以碳组分为基础的NanoG-CM试验的PTC结果。标准AC结果保持不变，因为它们被视为100% AC（没有扣除碳的矿物组分），但NanoG-CM数据表现出低得多的仅以碳计的注射速率，因为NanoG-CM的平均碳含量仅为8%。

[0144] 图5的仅以碳计的结果证实该纳米复合吸附剂的至少一个有益方面：提高的碳利用率。图5中的标准AC和NanoG-CM结果的比较表明标准AC的大部分碳含量（例如内部）未被利用并且没有成为总体汞捕获中的一个因素。这强化了一种机械的理解，即主要是表面和近表面位点对汞在飞行中的捕获是重要的。改进的碳利用率对易消耗的吸附剂成本具有有益影响，例如如果增加的或更复杂的生产步骤没有压倒基础材料的成本优势。此外，改进的碳利用率使得更容易满足飞灰中，例如要用于混凝土的飞灰中的碳含量限制。

[0145] 碳层和内部基底之间的协同效应是该碳纳米复合吸附剂的一个优点。在一个实例中，协同效应来自于包括两种吸附剂的单一粒子：传统AC和对烟气中的酸性气组分具有反应性的无机基底。为了证实纳米复合吸附剂的潜在益处，对具有不同活性炭表面覆盖率的复合吸附剂使用飞行中的捕获的应用模型，结果呈现在图6中。图6显示在高硫烟气（3000 ppm SO_2，15 ppm SO_3）中用复合吸附剂在飞行中捕获汞的模型结果。该烟气模型代表含有显著量的SO_3的高硫煤，其如100%AC参考曲线所示限制了汞捕获。通过50%和10% AC曲线显示该复合吸附剂的协同益处的评估。考虑到所用的保守估计，益处可能超过该模型所表现出的那些。

[0146] 已经使用的术语和措辞用作描述性而非限制性术语，并且在此类术语和措辞的使用中无意排除所展示和描述的特征或其部分的任何等同物，而是要认识，可以在要求保护的本发明的范围内作出各种修改。因此，应该理解的是，尽管已通过优选实施方案和任选特征具体公开了本发明，但本领域技术人员可以采用本文中公开的概念的修改和变动，且这样的修改和变动被认为在如所附权利要求规定的本发明的范围内。

[0147] 附加实施方案

本发明提供下列示例性实施方案，其编号不应被解释为指示重要性的级别：

实施方案1提供了从包含一种材料的气体中分离所述材料的方法，其包括提供或获得碳纳米复合吸附剂；使至少一部分所述材料与所述吸附剂接触以形成材料-吸附剂组合物；和从含所述材料的气体中分离至少一部分所述材料-吸附剂组合物以产生分离的气体。

[0148] 实施方案2提供了实施方案1的方法，其中所述材料是污染物。

[0149] 实施方案3提供了实施方案2的方法，其中所述污染物是汞。

[0150] 实施方案4提供了实施方案2-3任一项的方法，进一步包括提供促进剂；和通过使至少一部分吸附剂材料与所述促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；其中与至少一部分污染物接触的吸附剂包含促进的吸附剂。

[0151] 实施方案5提供了实施方案4的方法，其中所述促进剂是卤素或卤化物促进剂。

[0152] 实施方案6提供了降低含污染物的气体的污染物含量的方法，其包括提供或获得碳纳米复合吸附剂材料；提供或获得卤素或卤化物促进剂；通过使至少一部分吸附剂材料

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与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；使至少一部分促进的吸附剂与含污染物的气体中的污染物接触以形成污染物－吸附剂组合物；和从所述含污染物的气体中分离颗粒物，所述颗粒物包含至少一部分所述污染物－吸附剂组合物，以产生净化气体。

[0153] 实施方案 7 提供了实施方案 6 的方法，其中所述污染物是汞。

[0154] 实施方案 8 提供了实施方案 6-7 任一项的方法，其中获得或提供碳纳米复合吸附剂包括提供或获得碳前体；提供或获得基底材料；使碳前体和基底材料接触以提供纳米复合原材料；加热所述纳米复合原材料以提供碳纳米复合吸附剂。

[0155] 实施方案 9 提供了实施方案 8 的方法，进一步包括使加热的纳米复合原材料与酸或碱反应以提供碳纳米复合吸附剂。

[0156] 实施方案 10 提供了实施方案 8-9 任一项的方法，其中所述碳前体包含碳水化合物。

[0157] 实施方案 11 提供了实施方案 8-10 任一项的方法，其中所述碳前体包含红糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜或糖废品 (sugar waste product)。

[0158] 实施方案 12 提供了实施方案 8-11 任一项的方法，其中所述基底材料包含硅藻土、粘土、沸石或矿物。

[0159] 实施方案 13 提供了实施方案 8-12 任一项的方法，其中所述加热包括加热至超过大约 100℃。

[0160] 实施方案 14 提供了实施方案 6-13 任一项的方法，其中所述吸附剂材料包含与含污染物的气体中的污染物结合的结合位点。

[0161] 实施方案 15 提供了实施方案 6-14 任一项的方法，其中所述吸附剂材料包含已与卤素、卤化氢和第 V 族和第 VI 族卤化物反应或被卤素、卤化氢和第 V 族和第 VI 族卤化物浸渍的碳以形成所述促进的吸附剂中的污染物结合位点。

[0162] 实施方案 16 提供实施方案 15 的方法，其中促进的 AC 中的结合位点与含污染物的气体中的污染物结合以形成污染物－吸附剂组合物。

[0163] 实施方案 17 提供了实施方案 15-16 任一项的方法，其中促进的 AC 中的结合位点与含污染物的气体中的污染物反应以形成污染物－吸附剂组合物。

[0164] 实施方案 18 提供了实施方案 15-17 任一项的方法，其中 AC 的至少一部分结合位点与含污染物的气体中的氧化污染物反应以形成另一污染物－吸附剂化学组合物。

[0165] 实施方案 19 提供了实施方案 6-18 任一项的方法，其中从含污染物的气体中分离颗粒物的步骤包括在包含一个或多个 ESP 的颗粒物分离器中分离。

[0166] 实施方案 20 提供了实施方案 7-19 任一项的方法，其中所述含汞气体中的汞包含元素汞。

[0167] 实施方案 21 提供了实施方案 7-20 任一项的方法，其中所述汞－吸附剂组合物中的汞是氧化汞。

[0168] 实施方案 22 提供了实施方案 7-21 任一项的方法，其中所述促进的吸附剂与所述含汞气体中存在的至少大约 70 重量％的汞结合。

[0169] 实施方案 23 提供了实施方案 6-22 任一项的方法，其中所述卤素或卤化物促进剂是包含蒸气形式、固体形式、在溶剂中或其组合的形式。

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[0170] 实施方案 24 提供了实施方案 6-23 任一项的方法，其中所述卤素或卤化物促进剂包含第 V 族卤化物和第 VI 族卤化物中的至少一种。

[0171] 实施方案 25 提供了实施方案 6-24 任一项的方法，其中所述吸附剂上的或随所述吸附剂注入的促进剂前体转化成与所述吸附剂反应的卤素或卤化物促进剂。

[0172] 实施方案 26 提供了实施方案 6-25 任一项的方法，其中所述卤素或卤化物促进剂是 NH_4Br、NaBr、HBr、NaCl、$CaCl_2$或 HCl。

[0173] 实施方案 27 提供了实施方案 6-26 任一项的方法，进一步包括将碱性组分注入含污染物的气体中。

[0174] 实施方案 28 提供了实施方案 27 的方法，其中所述碱性组分包含碱金属或碱土金属元素的氧化物、氢氧化物、碳酸盐或磷酸盐。

[0175] 实施方案 29 提供了实施方案 6-28 任一项的方法，进一步包括将附加的卤素或卤化物促进剂添加到所述促进的吸附剂中。

[0176] 实施方案 30 提供了实施方案 29 的方法，其中所述附加的卤素或卤化物促进剂包含 HI、HBr、HCl、与卤素结合的第 V 族元素 (a Group V element with halogen) 或与卤素结合的第 VI 族元素。

[0177] 实施方案 31 提供了实施方案 6-30 任一项的方法，进一步包括将稳定剂添加到所述促进的吸附剂中。

[0178] 实施方案 32 提供了实施方案 31 的方法，其中所述稳定剂包含 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2和 P_2S_5中的至少一种。

[0179] 实施方案 33 提供了实施方案 6-32 任一项的方法，其中促进至少一部分吸附剂材料的步骤至少部分在含污染物的气体与促进的吸附剂接触之前进行。

[0180] 实施方案 34 提供了实施方案 6-33 任一项的方法，进一步包括向气流中以一定注射速率注入碳纳米复合吸附剂和以一定注射速率单独注入至少一种促进剂，由此飞行中的反应产生促进的吸附剂，其中所述促进剂选自分子卤素、卤化物及其组合，其中所述促进剂在气相中或作为蒸气反应，其中每大约 100 克碳纳米复合吸附剂材料加入大约 1 至大约 30 克促进剂。

[0181] 实施方案 35 提供了实施方案 34 的方法，其中所述气流是含污染物的气体。

[0182] 实施方案 36 提供了根据实施方案 35 的方法，其中所述气流是输运气体。

[0183] 实施方案 37 提供了实施方案 34-36 任一项的方法，其中注入气体中的促进剂注射速率和吸附剂注射速率至少部分由所述净化气体的监测污染物含量确定。

[0184] 实施方案 38 提供了实施方案 6-37 任一项的方法，进一步包括由所述污染物 - 吸附剂化学组合物再生所述促进的吸附剂的步骤。

[0185] 实施方案 39 提供了实施方案 38 的方法，进一步包括使用再生的促进的吸附剂从含污染物的气体中除去该污染物。

[0186] 实施方案 40 提供了实施方案 6-39 任一项的方法，其中所述促进、所述接触和所述分离中的至少一项在水洗涤器中进行。

[0187] 实施方案 41 提供了实施方案 40 的方法，其中所述促进在洗涤器中进行，其中所述洗涤器包括包含所述促进剂的水性浆料。

[0188] 实施方案 42 提供了实施方案 40-41 任一项的方法，其中所述接触在洗涤器中进

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行，其中所述洗涤器包括包含活性炭纳米复合吸附剂的水性浆料。

[0189] 实施方案 43 提供了降低含汞气体的汞含量的方法，其包括提供或获得碳纳米复合吸附剂，通过下列步骤制造所述碳纳米复合吸附剂：提供或获得碳前体、提供或获得基底材料、使碳前体和基底材料接触以提供纳米复合原材料、和加热所述纳米复合原材料以提供所述碳纳米复合吸附剂；提供或获得卤素或卤化物促进剂；通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；使至少一部分促进的吸附剂与汞接触以形成汞 - 吸附剂组合物；和从含汞气体中分离至少一部分所述汞 - 吸附剂组合物。

[0190] 实施方案 44 提供了制造碳纳米复合吸附剂的方法，其包括提供或获得碳前体；提供或获得基底材料；使碳前体和基底材料接触以提供纳米复合原材料；加热所述纳米复合原材料以提供碳纳米复合吸附剂。

[0191] 实施方案 45 提供了通过实施方案 44 的方法制成的碳纳米复合吸附剂。

[0192] 实施方案 46 提供了通过一种方法制成的促进的碳纳米复合吸附剂，所述方法包括通过使至少一部分实施方案 45 的吸附剂材料与卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。

[0193] 实施方案 47 提供了通过使实施方案 45-46 任一项的碳纳米复合吸附剂与含汞气体接触制成的汞 - 吸附剂组合物。

[0194] 实施方案 48 提供了与汞或氧化汞接触的实施方案 45-47 任一项的碳纳米复合吸附剂。

[0195] 实施方案 49 提供了通过一种方法制成的促进的碳纳米复合吸附剂，所述方法包括通过使至少一部分碳纳米复合吸附剂材料与卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。

[0196] 实施方案 50 提供了实施方案 1-49 任一项或任何组合的装置或方法，其任选构造成使得所叙述的所有要素或选项都可供使用或选择。

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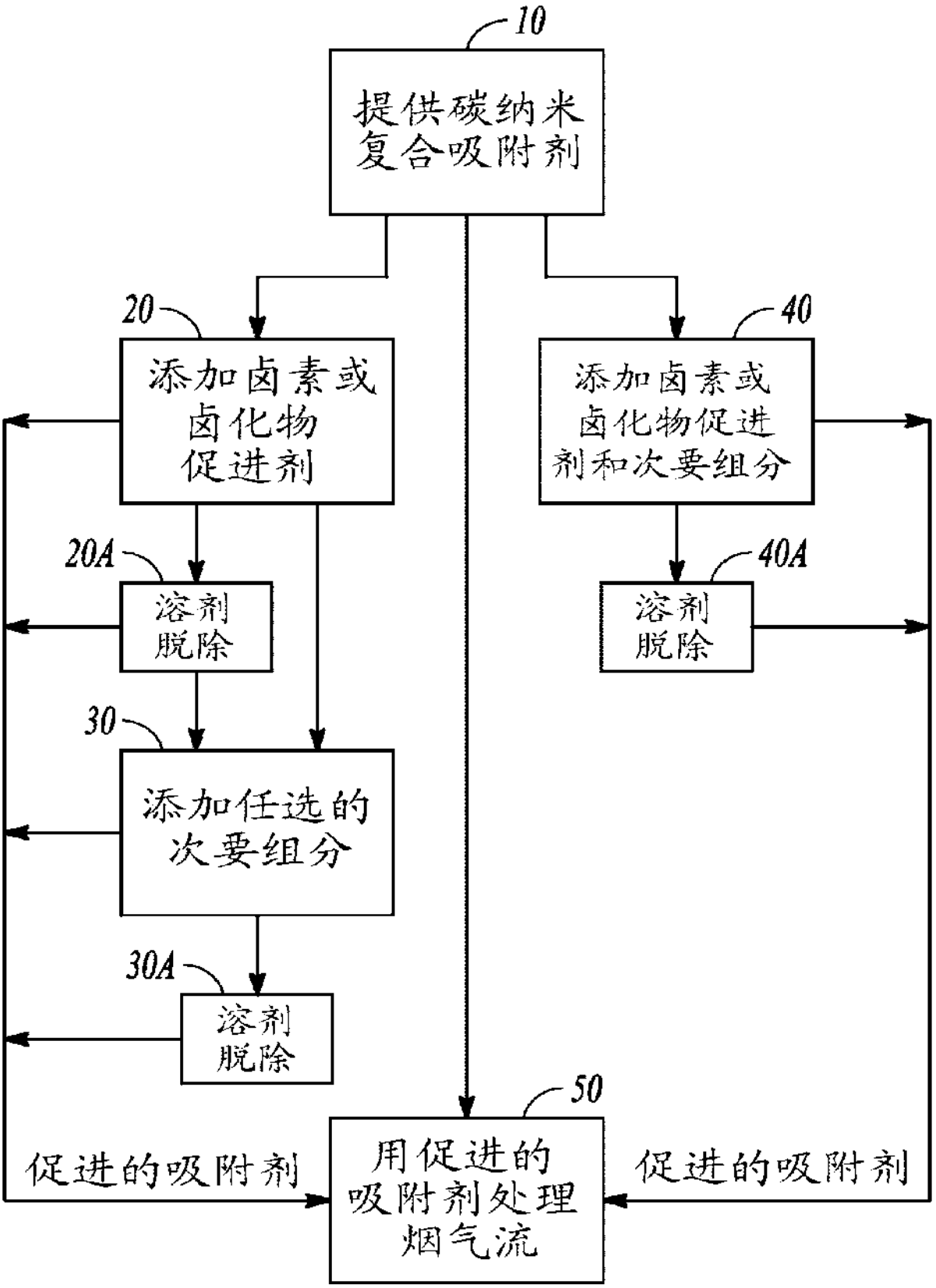


图 1

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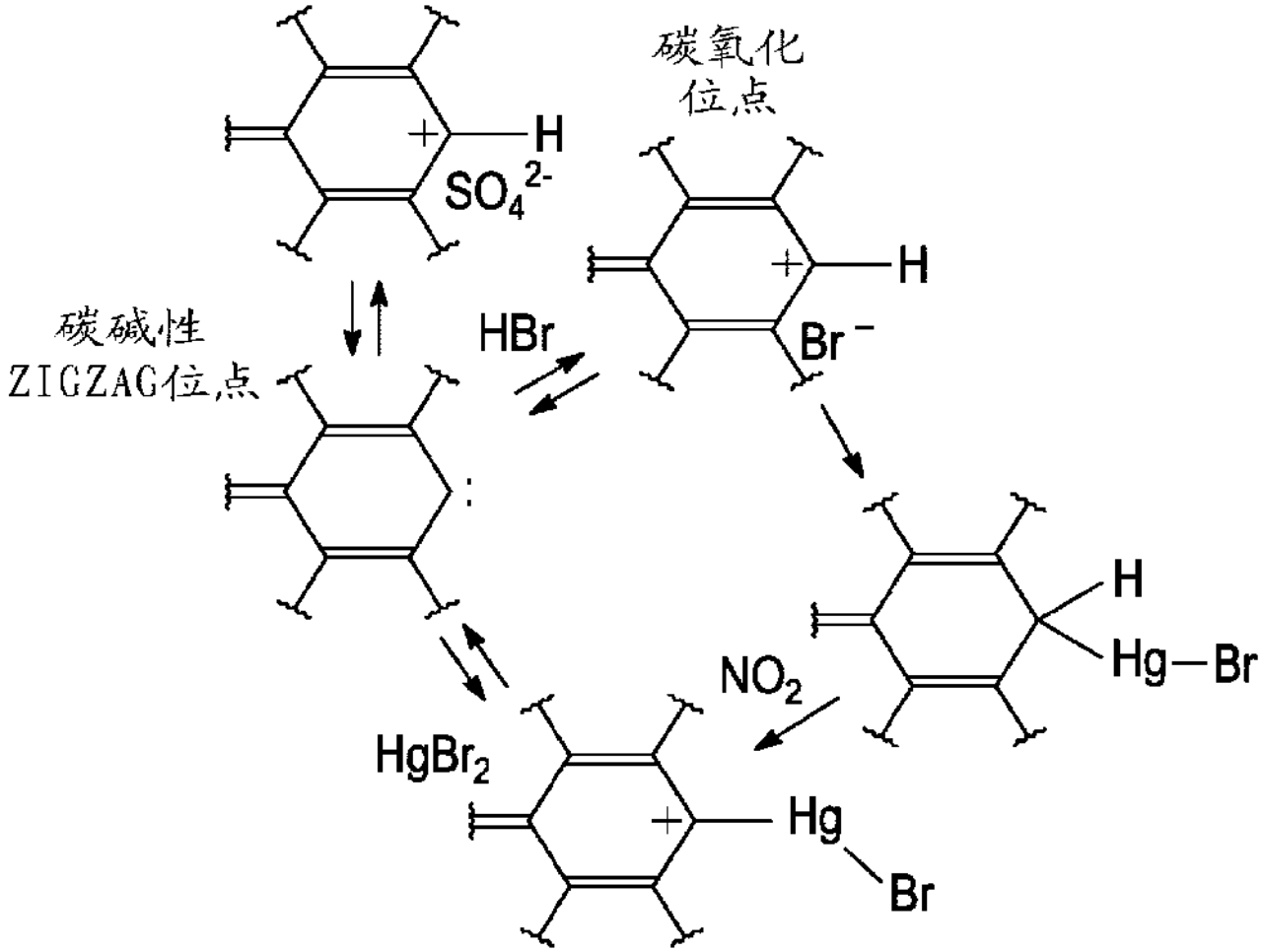


图 2

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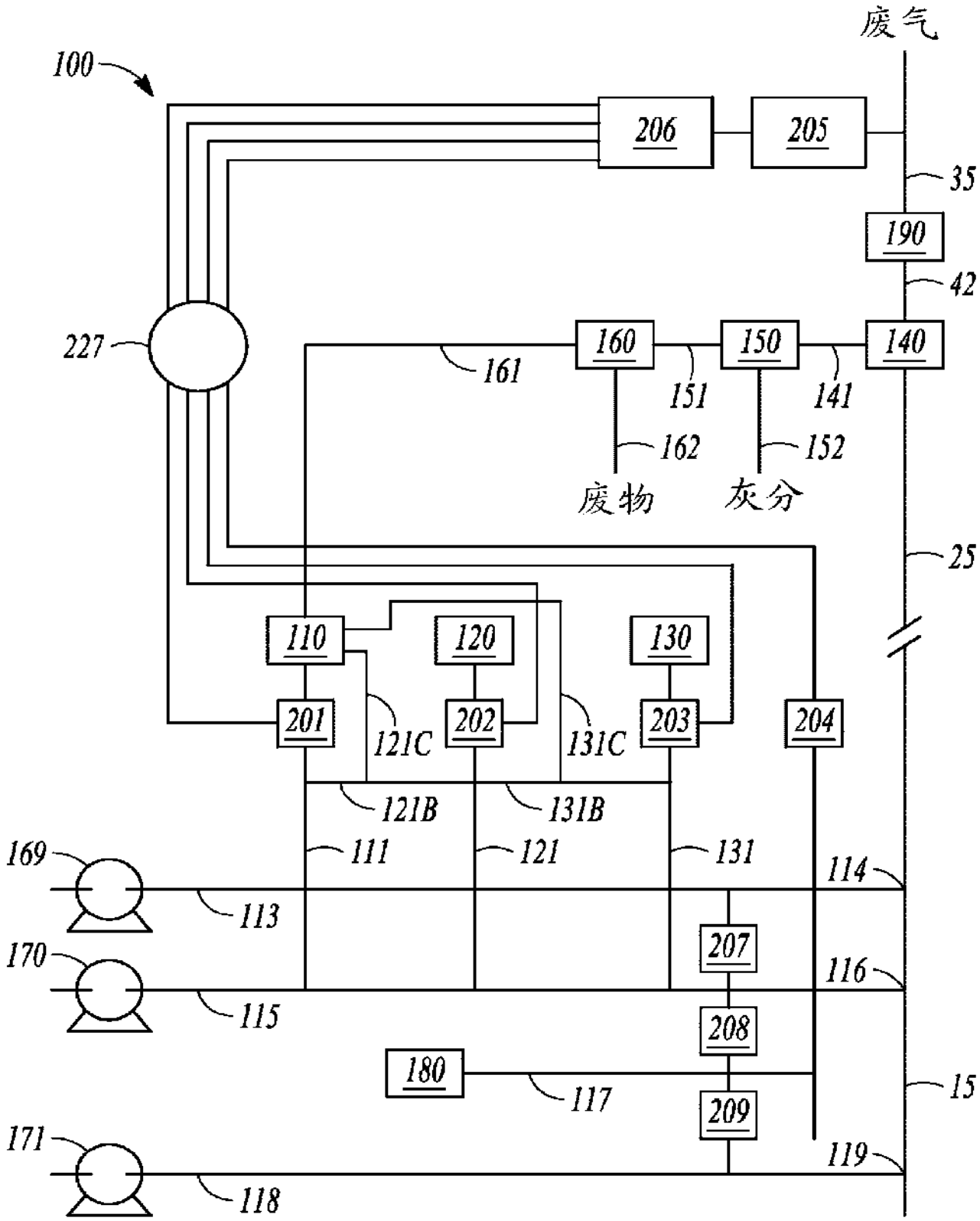


图 3A

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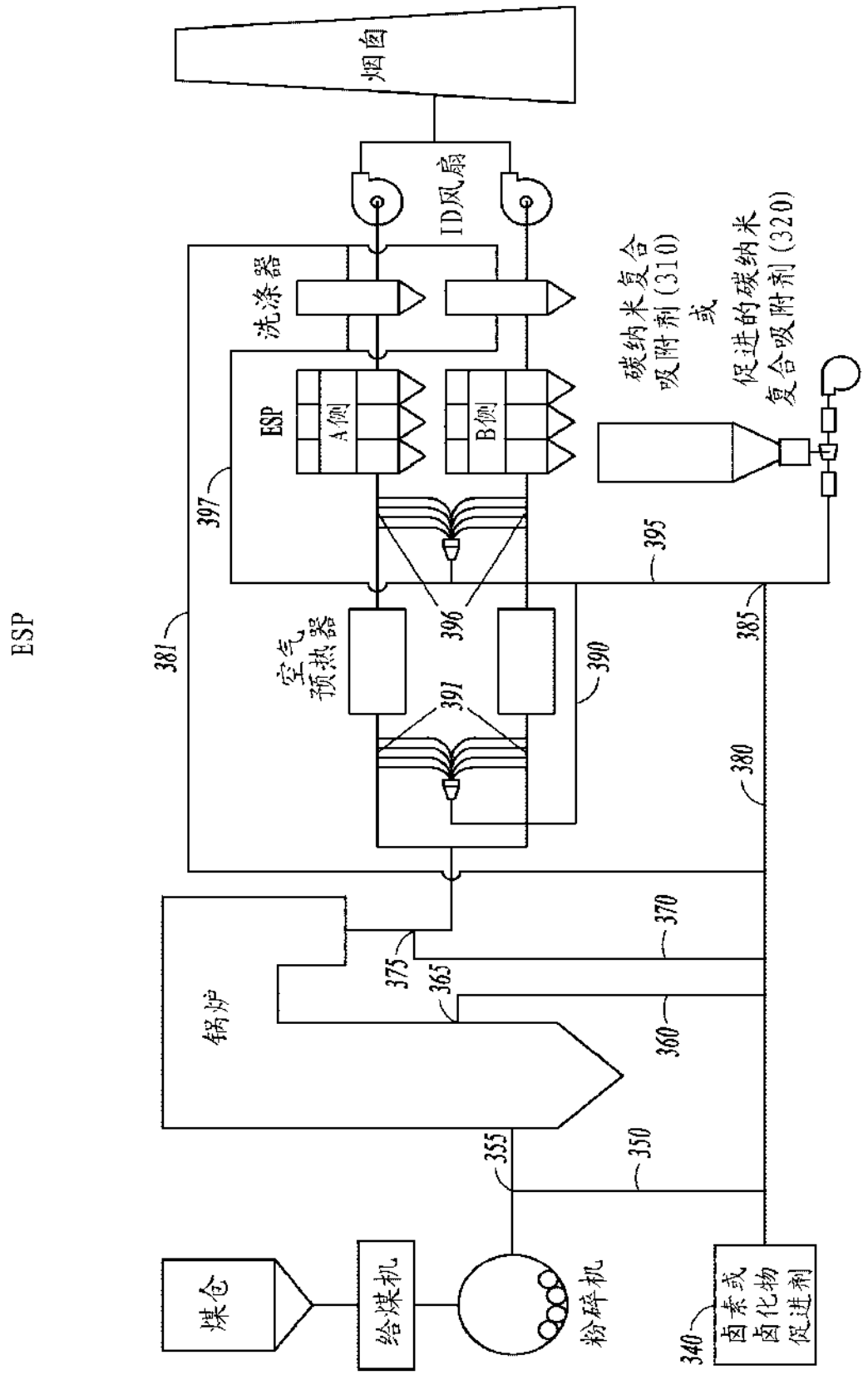


图 3B

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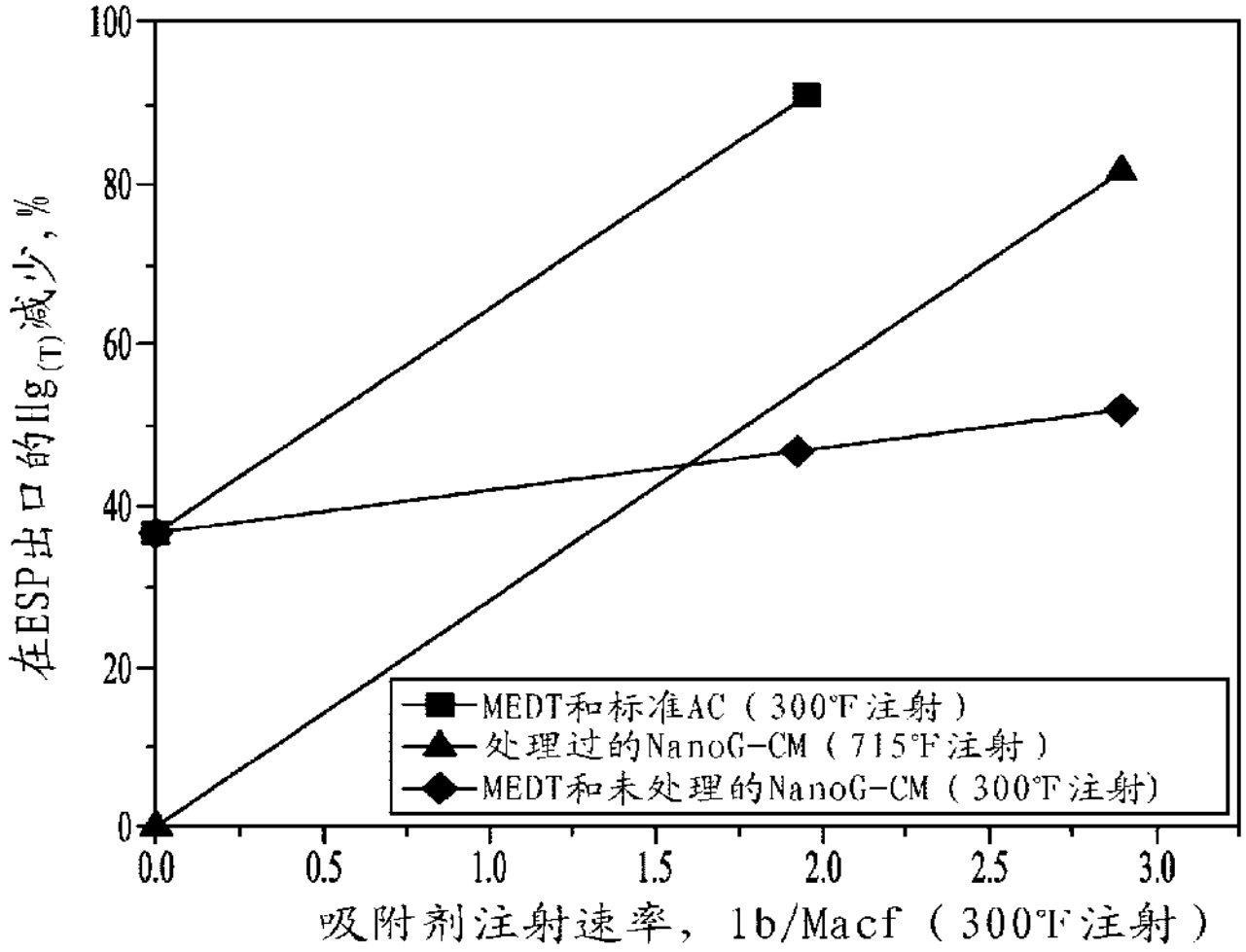


图 4

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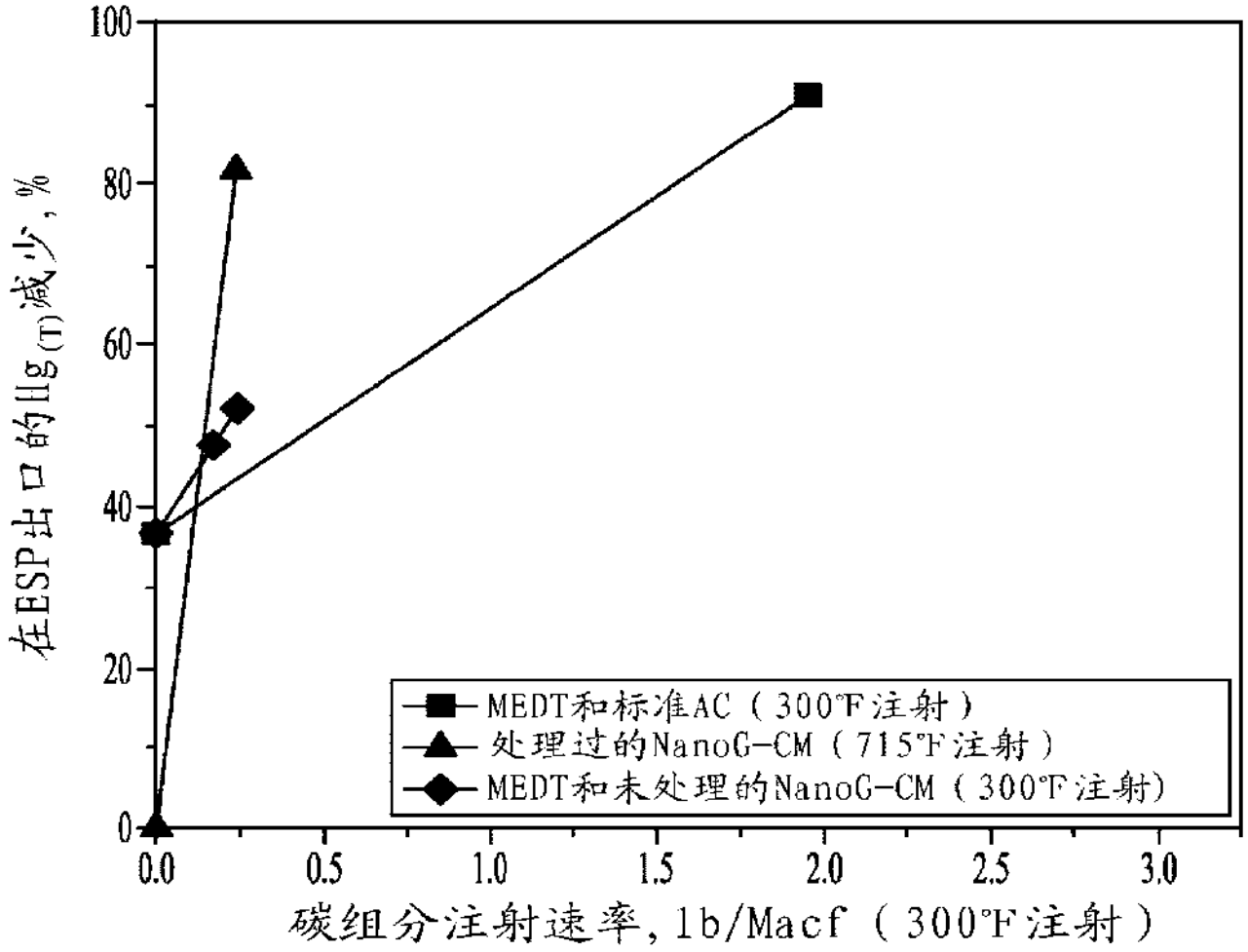


图 5

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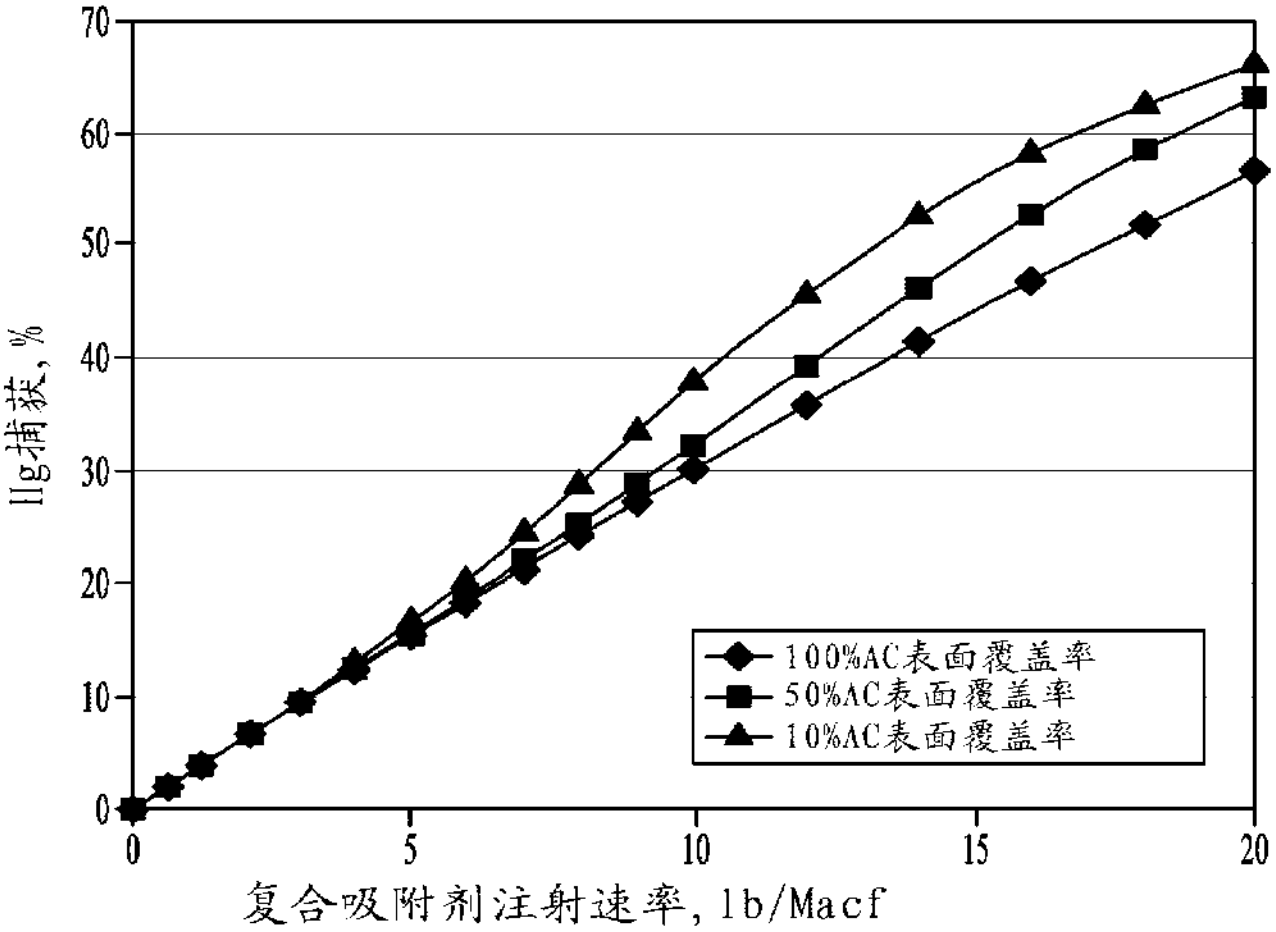


图 6

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Total pages of the description: 7
Total page of drawings: 1

[54] The name of the invention: A catalyst of activated carbon containing iodine and the method to remove and reclaim sulfur dioxide in the industrial exhaust gas with the said catalyst

[57]: Abstract

A catalyst of activated carbon containing iodine and the method used to eliminate and reclaim sulfur dioxide in the industrial exhaust gas with said catalyst comprising these following main stages: dust removal, adsorptions and oxidation, water-washing regeneration and concentrating and so on. This method can effectively eliminate the pollution caused by the exhaust gas from the Sulfur Acid Factory, Smelting Factory, Chemical industry and PowerStation, and moreover, can recycle sulfur acid with 20-30% concentration. This method is particularly suitable for dealing with the exhaust gas containing a great deal of dust and the low concentration sulfur dioxide.

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What is claimed

1. A catalyst of activated carbon containing iodine employed to desulfurization, characterized in that the total pore volume of said activated carbon is 0.60-0.75cc/g, surface area of said activated carbon is 550-750m^2/g, the active component iodine may be iodine or potassium iodide, sodium iodide, ammonium iodine, potassium iodine and other iodide, in which iodine content is 0.15-0.60wt%;
2. A method employed to extract sulfur dioxide from exhaust gas by catalyst of activated carbon containing iodine, characterized in:
   1) If the active component is iodine, said iodine can be attached to the activated carbon by the method sublimation and fumigation.
   2) If the active component is iodine containing compound, said iodine can be attached to the activated carbon by soaking the activated carbon into its aqueous or ethanol solution□and then drying it in the 100-160□hot air after soak.
3. A method to extract sulfur dioxide from exhaust gas by said catalyst according to claim 1or 2 comprising the following main three stages which are: 1 dust removal from the exhaust gas, 2. adsorption and oxidation and regeneration, 3 concentrating sulfuric acid reclaimed, wherein said the adsorption and oxidation is done in the multiple towers, and the temperature of exhaust gas is kept within 50-70□ when the exhaust gas is adsorbed and oxidized in the adsorption tower.
4. The method according to claim 3, wherein the process of regeneration is: right after being washed by dilute sulfuric acid of different concentration and water, the grade bed of catalyst is soaked into water for a certain time.
5. The process of regeneration according to claim 3, wherein, air is firstly pumped into the catalyst to oxidize the iodine ion contained in the grade bed of catalyst into iodine, before regeneration.
6. The process of water washing regeneration about catalyst according to claim 3 or 4, wherein, the water vapor that has been heated to 90 - 100□ is pumped into the catalyst tower to complete the process of regeneration, after water washing regeneration .
7. The process of water washing regeneration according to claim 3, wherein when the activity of catalyst is decreased, the active component should be compensated after said process of water washing regeneration, said compensation is carried out by adding the measured iodide solution from the top of catalyst tower.

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A catalyst of activated carbon containing iodine and the method to remove and reclaim sulfur dioxide in the industrial exhaust gas with said catalyst

A catalyst of activated carbon containing iodine and the method to remove and reclaim sulfur dioxide in the industrial exhaust gas with the said catalyst

The present invention relates to a catalyst of activated carbon containing iodine and the method to turn the sulfur dioxide from coal-fired flue gas into sulfuric acid and thus reclaim it. This method is particularly suitable for eliminating sulfur from the exhaust gas containing low concentration sulfur dioxide and for the purification process.

In industrial field, the exhaust gas from the Sulfur Acid Factory, Smelting Factory, Chemical industry and PowerStation usually contains a certain amount of sulfur dioxide. These exhaust gas from the industrial field causes serious pollution to the environment. To eliminate this influence, the process of catalyzing and oxidizing is often adopted to oxidize sulfur dioxide in the exhaust gas into Sulfur Acid and reclaim it, thus the pollution caused by sulfur dioxide will be eliminated. , The closely related method in the present invention is the process of using the activated carbon containing iodine as catalyst, for example, the method of the activated carbon containing iodine as proposed in the West Germany patent (GB1139817) to recycle the sulfur dioxide from the exhaust gas. However this method of preparing catalyst and the reaction operating are very complicated, and the method of continuously recycling high concentration Sulfur Acid to inhibit the loss of iodine ion, which makes it very difficult to adopt this process in the common factory. In the UK patent BP1090306, in order to decrease the loss of iodine, the process of the adsorption and regeneration is separated, and ammonia water and pure water have to be successively used to wash regeneration so as to maintain the activity of catalyst. The American DU PONT Company proposed the method of using activated carbon containing iodine as the catalyst to treat exhaust gas from Sulfur Acid Factory (Scholte ,W,AICHE 67th Annual meeting Vol 13 85B, 1974). This method needs to recycle the hydrogen iodide from the washing solution of regeneration, so as to be continuously supplemented into the grade bed of catalyst to keep the iodine content in activated carbon around 6%, thus to maintain activity of catalyst. In this method the loss of iodine is serious, and the operation of circularly supplementing iodine is complicated. In these known technologies, the iodine content in activated carbon is relatively high, and the loss of iodine is pretty high during operation. So far, there are still no simple and practical measures in known methods. Furthermore, the stability of catalyst is less satisfying, and it is very difficult to employ this method to purify the exhaust gas containing high concentration dust, for example, the exhaust gas containing high concentration dust from the Smelting Factory or PowerStation which use coal as fuel, due to serious catalyst poisoning.

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One object of the present invention is to prepare a kind of catalyst of activated carbon containing low concentration iodine and with high stability and to figure out a method to eliminate and recycle sulfur dioxide from exhaust gas. The method and catalyst in this invention can be applied to recycle sulfur dioxide not only from the dust-free gas exhausted from sulphuric acid plants and other chemical industries, but also from the exhaust gas of coal-fired which still contains slightly less than $0.2g/m^3$ dust even after dust removal and other industrial exhaust gas containing sulfur dioxide.

In present invention, the content of iodine in the catalyst is 0.15-0.6wt%. The physical properties of activated carbon are as follows: intensity is more than 90%, pore volume is 0.60-0.75 cc/g, surface area is 550-750 m^2/g, bulk density 508-520 g/l. The active component attached to the activated carbon may be iodine or iodide, such as potassium iodide, sodium iodide and ammonium iodine.

The method to prepare catalyst is as follows:

1 If the active component is iodine, said iodine can be attached on the activated carbon by the sublimation of iodine.

2, If the active component is iodine containing compound, said iodine can be attached to the activated carbon by soaking the activated carbon into its aqueous solution or ethanol solution□and then drying it in the 100-160□hot air after soak.

The process to eliminate sulfur dioxide with the catalyst of activated carbon comprises the following three main stages: 1 dust removal from the exhaust gas, 2. adsorption and oxidation and regeneration, and 3 recovering sulfuric acid concentration. The detailed process is as follows:

1) Dust removal from the exhaust gas: the dust removal process is done in the dedusting tower. The relatively low cost wet dedusting or other used methods can be adopted. After dust removal, the dust content needs to be less than $0.2g/m^3$. The sulfur dioxide concentration can be more than 3000ppm. The oxygen content in the exhaust gas is preferably more than 3%. The water vapor concentration in the exhaust gas is preferably 6-12%. To those exhaust gas without need to remove dust and with relatively high oxygen and relatively low vapor content, for example the exhaust gas from the Sulfur Acid Factory, it can be recycled the sulfur dioxide after adjusting the temperature and humidity by the exhaust gas and vapor, according to the present invention.
2) Adsorption-oxidization and water-washing regeneration: after dust removal, the exhaust gas will undergo the process of adsorption and oxidization when passing through the surface of the catalyst, and the sulfur dioxide is adsorbed on the surface of the catalyst and oxidized to sulfuric acid under the action of iodine or iodide. After the desorption of sulfuric acid by water-washing, the catalyst is regenerated and recycled. The process of adsorption is done in the adsorption tower, which is filled with the fixed

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tray containing the catalyst in this invention. The number of trays may be one or more storeys. The adsorption tower may be one, this tower will be alternately used by the adsorption-oxidization and water-washing regeneration, but the multiple towers are generally used and switched by turns for continuous work, that is, often one tower is regenerated by water washing, while the others are under the adsorption operation of different saturated degrees. In order to sufficiently eliminate the sulfur dioxide, the method according to this invention employs the multiple adsorption towers which are switched to work by turns, that is, when one tower is regenerated by water washing, the others are under the adsorption operation of different saturated degrees., When the exhaust gas is adsorbed and oxidized in the tower, the temperature of the exhaust gas keeps 50-70□. After adsorbing a certain amount of sulfuric acid, the catalyst in the adsorption tower must be water washed and regenerated so as to recycle the catalyst.

The process of water washing regeneration of this invention is as follows:

a) Air will be first pumped to oxidize to the iodine ion to iodine before the water washing.
b) The sulfuric acid of different concentration dilute and water will be respectively sprayed into the catalyst tower to wash it, and in the end the catalyst will be soaked in aqueous solution for a certain time to further wash the sulfuric acid away from the surface of catalyst and at the same time remove the dust that covers the surface of catalyst.
c) After water washing, the wet catalyst tower will be heated to 90-100□ by the hot vapor, and the process of regeneration will then complete.
d) Compensation of the active component: After the long time of operation, the activity of catalyst is decreased because of the loss of iodine and the active component should be compensated during the water washing regeneration. In this invention, the iodine and iodide should be compensated, if the iodine content is lower than 0.2%. After the adsorption tower in need of compensation of the active component is regenerated by water-washing, the iodine solution measured will be added into the tower from the top of the catalyst tower, and then the tower is switched to adsorption process with the exhaust gas being pumped into, the activity of this catalyst tower will then be gradually recovered to the original level.

3) Concentration of the reclaimed sulfuric acid: the sulfuric acid of concentration20-30% can be obtained, after the adsorption tower is washed by dilute sulfuric acid of different concentration dilute. The recycled sulfuric acid can be further concentrated by one of the known concentrating methods that result in ideal concentration.

Example 1: the preparation of the catalyst

The catalyst of this invention will be obtained by the following process: to fill the activated carbon in the grade bed of the catalyst, then to add the iodine

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solution measured into the tower to wet all the activated carbon without surplus solution; to pump into the hot air with temperature of 100-200□ from the bottom of the catalyst tower, and stir and dry under the condition of boil, the time of heating is 1-10 h, the velocity of air is 0.1-10m/s, the quantity of air is corresponding to the volume of the catalyst 1000-20000/h.

Example 2: the method to reclaim sulfur dioxide from the exhaust gas

The process to reclaim sulfur dioxide from the exhaust gas is shown in the figure 1: 1, the tower of removal dust; 2,3,4,5 the adsorption tower; 6 the concentrating tower. A is the exhaust gas from factory; B is the exhaust gas after the sulfur dioxide is reclaimed; C is the nozzle by which water or dilute acid are sprayed during the regeneration. D is the exit zone for concentrated sulfuric acid. After the dust removal, the dust content of the exhaust gas is less than 0.2g/m^3, the oxygen content is more than 3%, the vapor content is 6-12%, the temperature of the exhaust gas is 55-75□.The process of adsorption and regeneration is done in the four towers, among which, the 2 to 4 towers are adsorbing and oxidizing the exhaust gas. When the sulfur dioxide content of the exhaust gas reaches 0.3%-0.4%, the space velocity of 400-500/h can be employed and the adsorption and oxidization is done for 18-20 hours in the three towers. The process of regeneration is under way in tower 5: at first, the air is pumped to oxidize, and then the sulfuric acid of different concentration is sprayed□ in the end the catalyst is soaked in the aqueous solution. The process of water-washing regeneration will last for four hours. After the dilute sulfuric acid discharged, the grade bed of the catalyst will be heated to 100□by the hot vapor, and the regenerating process of the adsorption tower will thus complete after heating. The four towers will be switched by turns between adsorption and water washing regeneration, therefore the entire process of reclaiming sulfur dioxide will work continuously.

Example 3: to reclaim the sulfur dioxide from the exhaust gas of PowerStation.

The flux of exhaust gas is 5000m^3/h, and said the equipments, the process and method in the example 2 will be employed, and the volume of catalyst is approximate 4.5m^3, the time of operation is 1800 hours, the regeneration in the four towers is done approximate 100 times, the active component of the catalyst need not to be compensated. The result of operation for the two times is shown in the table 1.

Table 1 Recycle of the sulfur dioxide from the exhaust gas and purification

	First time	Second time
The concentration of Sulfur dioxide (ppm)	3530	3860
The Space velocity (h^{-1})	414	502
The average conversion of Sulfur dioxide (%)	95	91
The amount of Sulfur dioxide adsorbed (g/100g catalyst)	13.3	15.4

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Example 4: reclamation of the Sulfur dioxide from the exhaust gas of the sulfuric acid factory

The flux of the exhaust gas treated is 15,000m^3/h, the time of operation is 2,000 h, and said the amount of catalyst and the equipments in the example 2, 3 will be employed. The result of operation for the two times is shown in the table 2:

Table 2 Recycle of the sulfur dioxide from the exhaust gas and purification

	First time	Second time
The concentration of Sulfur dioxide (ppm)	3372	5971
The Space velocity (h^{-1})	450	450
The average conversion of Sulfur dioxide(%)	96.6	98.0
The amount of Sulfur dioxide adsorbed (g/100g catalyst)	20.2	19.5

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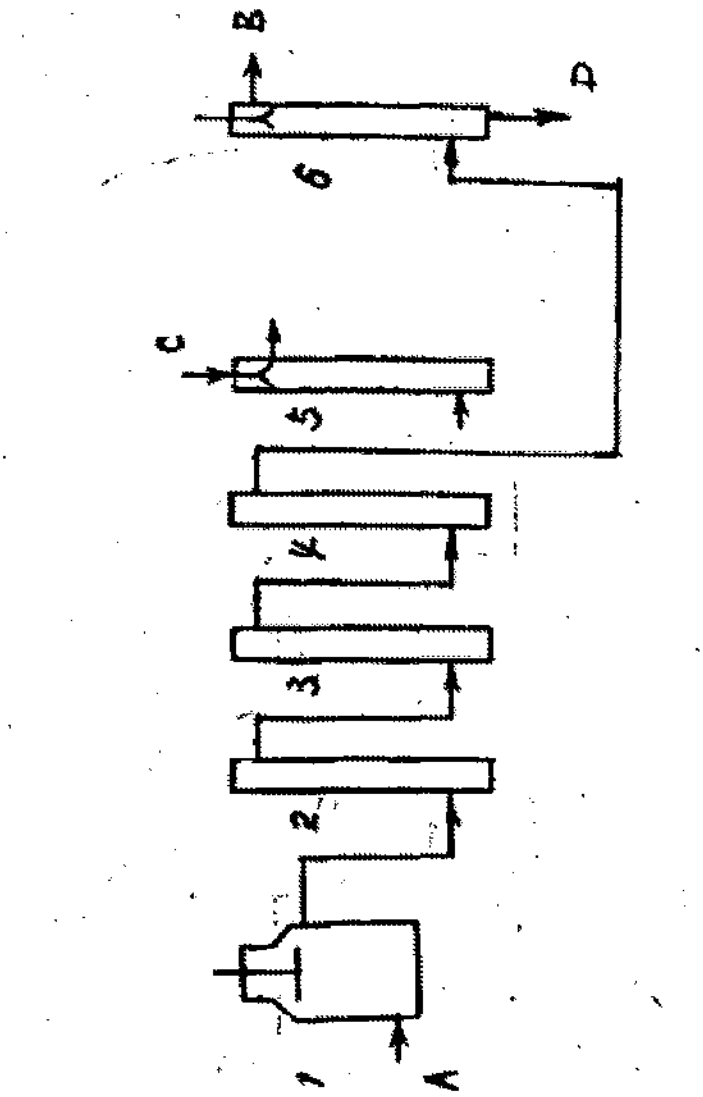


Figure 1

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Espacenet

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Process for removing mercury from flue gases

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Mercury is removed from flue gases of high-temperature plants by feeding bromine and/or a bromine compound to a multi-stage furnace and/or to the flue gas, and subjecting the flue gas to a multi-stage clean-up. The combustion takes place in the presence of a sulfur compound, particularly sulfur dioxide, with or without the addition of sulfur and/or a sulfur compound and/or a mixture of various sulfur compounds. The removal of mercury from flue gases of high-temperature plants, comprises feeding bromine and/or a bromine compound and/or a mixture of various bromine compounds to a multi-stage furnace and/or to the flue gas in a plant section downstream of the furnace, the temperature during the contact of the bromine compound with the flue gas being at least 500degreesC, preferably at least 800degreesC.; The combustion takes

place in the presence of a sulfur compound, particularly sulfur dioxide, with or without the addition of sulfur and/or a sulfur compound and/or a mixture of various sulfur compounds. The flue gas is subjected to a multi-stage clean-up comprising a wet scrubber and/or a dry clean-up.

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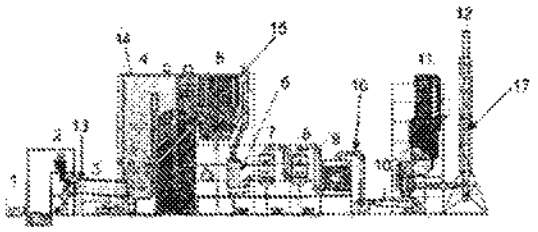
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Prüfungsantrag gemäß § 44 PatG ist gestellt.

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: **Verfahren zur Abscheidung von Quecksilber aus Rauchgasen**

(57) Zusammenfassung: Die Erfindung beschreibt ein Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen, bei dem der, gegebenenfalls mehrstufigen, Feuerung und/oder dem Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil eine bromhaltige Verbindung zugeführt wird, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt. Die Verbrennung erfolgt in Gegenwart einer schwefelhaltigen Verbindung, insbesondere Schwefeldioxid. Im Anschluss an die Feuerung wird das Rauchgas einer, gegebenenfalls mehrstufigen, Reinigung zur Abtrennung von Quecksilber aus dem Rauchgas unterzogen, welche eine Nasswäsche und/oder eine Trockenreinigung umfasst.



Beschreibung

[0001] Die Erfindung betrifft ein Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen.

Stand der Technik

[0002] Aufgrund der hohen Toxizität von Quecksilber, insbesondere von organisch gebundenem Quecksilber, das direkt oder indirekt über die Nahrungskette auch vom Menschen aufgenommen wird, existieren strenge Grenzwerte für die gesetzlich zulässige Emission von Quecksilber z.B. aus Verbrennungsanlagen und Kraftwerken. Trotz der heute bereits niedrigen Quecksilber-Reingaskonzentrationen – der derzeit in Deutschland zulässige Halbstundenmittelwert für Quecksilberemissionen aus Abfallverbrennungsanlagen beträgt 30 $\mu g/m^3$ i. N. tr. (i. N. tr.: im Normalzustand trocken) – werden aufgrund großer Volumenströme, beispielsweise aus Großkraftwerken, beachtliche Quecksilberfrachten erzielt, so dass eine weitere Minderung der derzeit zulässigen Grenzwerte angestrebt wird.

[0003] Diverse Verfahren zur Minderung von Quecksilberemissionen aus Kraftwerken, Abfallverbrennungsanlagen oder dgl. sind aus der Literatur bekannt. Welches der Verfahren für eine bestimmte Anwendung zweckmäßig ist, hängt stark von der eingebrachten Fracht und vom Chlorgehalt des Feuerungsgutes ab. Bei hohem Chlorgehalt ist der Anteil an ionischem Quecksilber im Rauchgas hoch. Ionisches Quecksilber lässt sich gut in Wäschern abscheiden. Das quasi-wasserunlösliche metallische Quecksilber kann beispielsweise durch den Zusatz von Oxidationsmitteln, wie Peroxide, Ozon oder Natriumchlorit, im Kesselrohgas vor der Rauchgasreinigung oder im entstaubten Kesselrohgas in ionisches Quecksilber überführt und anschließend in Wäschern abgeschieden werden. Weitere Verfahren zur Abscheidung des Quecksilbers sind: der Zusatz von Reaktionsmitteln, wie Natriumtetrasulfit, zur Bindung des Quecksilbers mittels Schwefel im Kesselrohgas vor Rauchgasreinigung oder im teilgereinigten Reingas; die verbesserte Auswaschung von ionischem Quecksilber durch pH- bzw. pCl-Absenkung in der sauren Wäsche oder durch Beaufschlagung mit 1,3,5-Triazin-2,4,6-trithiol (Trimercapto-S-triazin, TMT) in der schwach sauren oder schwach alkalischen Wäsche; die sorptive Abscheidung von ionischem und metallischem Quecksilber unter Zusatz von pulvrigen Sorbentien oder zerstäubten Suspensionen.

[0004] Bisherige Techniken zur Minderung sind nicht ausreichend effektiv und sind aufgrund ihrer z.T. hohen Zusatzinvestitionen und dem zusätzlichen Betriebsmittelverbrauch relativ teuer.

Aufgabenstellung

[0005] Aufgabe der Erfindung ist es, ein Verfahren zur Abscheidung von Quecksilber, insbesondere zur weitgehend vollständigen Abscheidung von Quecksilber (Hg), aus Rauchgasen von Hochtemperaturprozessen bereitzustellen. Das Verfahren soll breitestmögliche Anwendung finden, wie im Falle von im Wesentlichen konstanten niedrigen Hg-Konzentrationen, z.B. in Kohlekraftwerken, aber auch im Falle von relativ hohen Hg-Konzentrationen, z.B. in der Klärschlammverbrennung, oder sehr hohen Hg-Konzentrationen z.B. in der Hausmüll- oder Sondermüllverbrennung. Des Weiteren sollte das Verfahren keiner umfangreichen Nachrüstung der Hochtemperaturanlagen bedürfen sowie möglichst geringer zusätzlicher Betriebsmittel, so dass das Verfahren kostengünstig implementiert und betrieben werden kann.

[0006] Gegenstand der Erfindung ist ein Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen, welches darin besteht, dass der, gegebenenfalls mehrstufigen, Feuerung und/oder dem Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil Brom und/oder eine bromhaltige Verbindung und/oder eine Mischung verschiedener bromhaltiger Verbindungen zugeführt wird, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt, die Verbrennung in Gegenwart einer schwefelhaltigen Verbindung, insbesondere Schwefeldioxid, gegebenenfalls unter Zusatz von Schwefel und/oder einer schwefelhaltigen Verbindung und/oder einer Mischung verschiedener schwefelhaltiger Verbindungen erfolgt und anschließend das Rauchgas einer, gegebenenfalls mehrstufigen, Reinigung zur Abtrennung von Quecksilber aus dem Rauchgas unterzogen wird, welche eine Nasswäsche und/oder eine Trockenreinigung umfasst.

[0007] Die Abscheidung von Quecksilber aus Rauchgasen in einer der Verbrennung oder einem ähnlichen Hochtemperaturprozess nachgeschalteten Rauchgasreinigung hängt entscheidend davon ab, in welcher Speziesform das Quecksilber vor Eintritt in die Rauchgasreinigung vorliegt. Ein möglichst hoher Anteil an ionischem Quecksilber ist von Vorteil, da das ionische Quecksilber gut wasserlöslich, also auswaschbar, sowie an diversen Adsorbentien gut adsorbierbar ist. Der Zusatz von Brom bzw. bromhaltigen Verbindungen zur Feuerung bewirkt unter den gegebenen Bedingungen eines Hochtemperaturprozesses oder dgl. in Gegenwart einer schwefelhaltigen Verbindung, insbesondere in Gegenwart von Schwefeldioxid, eine weitgehende, im Wesent-

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lichen vollständige, Oxidation des Quecksilbers und erlaubt daher eine starke Abscheidung des Quecksilbers aus Rauchgasen.

[0008] Unter Hochtemperaturanlagen werden im Sinne der vorliegenden Erfindung insbesondere Abfallverbrennungsanlagen, beispielsweise Hausmüll-, Sondermüll- und Klärschlammverbrennungsanlagen, sowie Kraftwerke, beispielsweise Steinkohle- oder Braunkohlekraftwerke, aber auch sonstige Anlagen für Prozesse hoher Temperatur, wie z.B. das Zementbrennen, sowie Abfall mitverbrennende Hochtemperaturanlagen oder kombinierte (mehrstufige) Hochtemperaturanlagen, wie z.B. Kraftwerke oder Zementdrehrohröfen mit vorgeschalteter Abfallpyrolyse oder Abfallvergasung, verstanden. Die Dimension der Hochtemperaturanlage spielt für das erfindungsgemäße Verfahren keine Rolle. Vorteilhaft an dem erfindungsgemäßen Verfahren ist gerade, dass es auf unterschiedliche Typen von Hochtemperaturanlagen und auf Hochtemperaturanlagen von unterschiedlicher Größenordnung anwendbar ist. Dies schließt Anlagen mit einem Rauchgasvolumenstrom von nur $15 \cdot 10^3$ m³ i. N. tr./h, beispielsweise zur Klärschlammverbrennung, oder von $50 \cdot 10^3$ m³ i. N. tr./h, z.B. in Sondermüllverbrennungsanlagen, oder von $150 \cdot 10^3$ m³ i. N. tr./h, z.B. in der Hausmüllverbrennung, ebenso ein wie Großkraftwerke mit z.B. $2\text{-}3 \cdot 10^6$ i. N. tr./h.

[0009] Für das erfindungsgemäße Verfahren ist es unerheblich, in welcher Form das zugeführte Brom vorliegt. Es ist möglich, freies oder organisch gebundenes oder anorganisch gebundenes Brom einzusetzen. Das Brom oder die bromhaltigen Verbindungen können einzeln oder im Gemisch zugeführt werden. Besonders bevorzugt wird eine wässrige Lösung von Bromwasserstoff oder ein Alkalibromid, insbesondere Natriumbromid, oder eine wässrige Lösung des Alkalibromids verwendet. Durch diese Ausführungsform ist das Verfahren wirtschaftlich besonders interessant, da die Kosten für zusätzliche Betriebsmittel niedrig gehalten werden können. Weiterhin bevorzugt ist eine Ausführungsform, in der die bromhaltige Verbindung bzw. das Gemisch verschiedener bromhaltiger Verbindungen aus bromreichen Abfallstoffen, wie z.B. niedrig- oder hochhalogenierte Flüssigabfälle, bestehen, welche Teil des Verbrennungsguts sind oder dem Verbrennungsgut, beispielsweise Sondermüll, beigemengt werden.

[0010] Das erfindungsgemäße Verfahren findet in Gegenwart einer schwefelhaltigen Verbindung statt. Die Zugabe einer bromhaltigen Verbindung nach dem erfindungsgemäßen Verfahren führt zu einer Gasphasenreaktion zwischen Quecksilber und Brom in Gegenwart von Schwefeldioxid. Da bei den im Sinne dieser Erfindung üblichen Verbrennungs- und sonstigen Hochtemperaturprozessen in der Regel Schwefeldioxid entsteht, ist für das erfindungsgemäße Verfahren in der Regel ein ausreichendes Angebot einer schwefelhaltigen Verbindung vorhanden. Ein ausreichendes Angebot im Sinne dieser Erfindung liegt vor, wenn unter Zugabe einer bromhaltigen Verbindung zu der Feuerung der Gehalt an Schwefeldioxid im Rauchgas vor der Rauchgasreinigung deutlich größer als Null ist. Wird bei einem Verbrennungsprozess jedoch kein oder nicht ausreichend Schwefeldioxid gebildet, muss dem Prozess eine schwefelhaltige Verbindung zugeführt werden. Dies kann in Form von freiem oder gebundenem Schwefel, beispielsweise Schwefelgranulat, Abfallschwefelsäure oder andere schwefelreiche Abfallstoffe, erfolgen. Darüber hinaus kann insbesondere auch zur Minderung eines zu hohen Gehalts an freien Halogenen im Rauchgas eine schwefelhaltige Verbindung zugesetzt werden, wenn z.B. mehr bromhaltige Verbindung zugeführt worden ist, als zur Oxidation des vorliegenden Quecksilbers notwendig ist. Die Zudosierung einer schwefelhaltigen Verbindung kann z.B. nach dem in der bisher unveröffentlichten Patentanmeldung DE 10131464 beschriebenen Verfahren zur korrosions- und emissionsarmen Mitverbrennung hochhalogenierter Abfälle in Abfallverbrennungsanlagen erfolgen. Nach diesem Verfahren wird in den primären und/oder sekundären Feuerraum Schwefel oder ein entsprechender Schwefelträger geregelt zudosiert. Die Regelung der Schwefelmenge erfolgt im Wesentlichen proportional zur mit den Abfällen eingetragenen aktuellen Halogengesamtfracht im Kesselrauchgas. Der zudosierte Schwefel verbrennt im Feuerraum zu Schwefeldioxid, was kesselintern zu einer weitgehenden Unterdrückung zwischenzeitlich gebildeter freier Halogene im Kesselrauchgas sowie nachfolgend zur stabilen Halogeneinbindung in der alkalischen Wäsche führt. Die Zudosierung von Schwefel wird so geregelt, dass der Soll-Schwefeldioxidgehalt im Rauchgas am Kesseleingang oder der Soll-Schwefeldioxidrestgehalt am Kesselende, d.h. im Kesselrohgas vor einer beispielsweise nassen Rauchgasreinigung, im stationären Betriebszustand über einen einfachen primären Regelkreis eingehalten werden.

[0011] Wird speziell Natriumbromid der Feuerung zugesetzt, so ist ein Mehrverbrauch an Schwefeldioxid zu beobachten, welcher auf die Sulfatierung des Natriumbromids im Hochtemperaturbereich zurückzuführen ist.

[0012] Andererseits stellt ein relativ hoher Gehalt einer schwefelhaltigen Verbindung, insbesondere an Schwefeldioxid, im Rauchgas keinen Nachteil für das erfindungsgemäße Verfahren dar. Ein hoher Gehalt an Schwefeldioxid kann beispielsweise bei der Verbrennung von Steinkohlen auftreten, welche üblicherweise zwischen 0,5 und 1 Gew.-% Schwefel enthalten, oder bei einer geregelten Zudosierung einer schwefelhaltigen Verbindung, welche zur Unterdrückung zwischenzeitlich gebildeter freier Halogene (s.o.) zugesetzt wird. Unter den gegebenen Bedingungen eines Hochtemperaturprozesses findet auch in Gegenwart von überschüssigem Schwefeldioxid die Oxidation des Quecksilbers statt, welche nach dem erfindungsgemäßen Verfahren durch den Zusatz einer oder mehrerer bromhaltiger Verbindungen erzielt wird. Darin liegt ein besonderer Vorteil des vorliegenden Verfahrens, denn die Oxidation des Quecksilbers durch den Zusatz von bromhaltigen Verbindun-

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gen zeigt sich – anders als durch den Zusatz von chlorhaltigen Verbindungen – weitgehend unempfindlich gegenüber einem Überschuss an Schwefeldioxid.

[0013] Die Zugabe einer bromhaltigen Verbindung sowie gegebenenfalls einer schwefelhaltigen Verbindung erfolgt erfindungsgemäß zur Feuerung und/oder zum Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt. Die bromhaltige Verbindung, z.B. Natriumbromid, kann entweder in fester, z.B. als Salz, oder flüssiger Form, z.B. als wässrige Lösung, dem zu verfeuernden Abfallgemisch, der Kohle oder dgl. vor der Feuerung beigemengt werden. Die Zugabe kann auch in einen der Feuerung vorgeschalteten Anlagenteil erfolgen, beispielsweise einer Pyrolysetrommel, welche z.B. dem thermischen Aufschluss mitverbrannter Abfallstoffe dient, oder einer Kohlemühle. Die Verbindung kann ebenso während des Verbrennungsprozesses zugeführt werden. Umfasst die Feuerung mehrere Stufen, z.B. eine primäre und eine sekundäre Feuerung, kann die bromhaltige Verbindung in eine oder beide Brennkammern, beispielsweise in den Drehrohrofen und/oder die Nachbrennkammer, ebenfalls in fester oder flüssiger Form eingeführt werden. Vorzugsweise wird eine wässrige Lösung der Verbindung in einer der Brennkammern eingedüst. Ferner kann die Zugabe auch nach der Verbrennung, z.B. in einem nachgeschalteten Abhitzekessel, erfolgen, sofern die Temperatur des Rauchgases ausreichend hoch ist, d.h. mindestens 500°C, insbesondere mindestens 800°C, beträgt. In anderen Hochtemperaturprozessen, wie z.B. dem Zementbrennen, wird beispielsweise der heiße Ofenkopf des Zementdrehrohrofens und/oder die befeuerte Entsäuerungsstufe des nachgeschalteten Zementrohmehlvorwärmers mit der bromhaltigen Verbindung bestückt.

[0014] In einer weiteren Ausführungsform des erfindungsgemäßen Verfahrens ist es auch möglich, die bromhaltige Verbindung, beispielsweise eine wässrige Lösung von Bromwasserstoff oder von Natriumbromid, fein dispergiert der Verbrennungsluft und/oder gegebenenfalls einem rückgeführten Teilstrom, insbesondere rückgeführtem Rauchgas, rückgeführter Asche und rückgeführten Flugstäuben, zuzuführen.

[0015] Um eine möglichst vollständige, insbesondere 100%ige, Oxidation des Quecksilbers durch die Zugabe einer bromhaltigen Verbindung zu erzielen, wird die bromhaltige Verbindung bevorzugt in einem Massenverhältnis von Brom zu Quecksilber im Bereich von 10^3 bis 10^6 zugegeben. Wird die bromhaltige Verbindung in großem Überschuss zugefügt, wirkt sich dies nicht nachteilig auf das erfindungsgemäße Verfahren aus. Ein zu großer Überschuss muss jedoch vermieden werden, nicht zuletzt aus Kostengründen. Gegebenenfalls müssen zwischenzeitlich gebildete freie Halogene, wie z.B. freies Brom, durch die Zugabe einer schwefelhaltigen Verbindung unterdrückt bzw. stabil eingebunden werden (s.o.), da auch Bromemissionen in der Regel gesetzlich festgelegten Grenzwerten unterliegen.

[0016] Die Oxidation von Quecksilber kann prinzipiell auch durch chlorhaltige oder jodhaltige Verbindungen erfolgen. Es zeigt sich jedoch, dass bromhaltige Verbindungen Quecksilber unter den gegebenen Bedingungen von Hochtemperaturprozessen, wie der Temperatur, und insbesondere auch bei einem hohen Gehalt an Schwefeldioxid (s.o.) wirksamer oxidieren als chlorhaltige Verbindungen. Jodhaltige Verbindungen oxidieren im Vergleich zu bromhaltigen Verbindungen Quecksilber wirksamer. Aus wirtschaftlichen Gesichtspunkten werden in dem erfindungsgemäßen Verfahren allerdings bromhaltige Verbindungen bevorzugt eingesetzt. Gegebenenfalls in den Abfallstoffen, z.B. in Sondermüll, vorliegende chlor- oder jodhaltige Verbindungen tragen demnach zur Oxidation des Quecksilbers bei. In einer bevorzugten Ausführungsform erfolgt das erfindungsgemäße Verfahren zusätzlich zu den bromhaltigen Verbindungen in Gegenwart von Chlor und/oder Jod und/oder einer chlorhaltigen Verbindung und/oder einer jodhaltigen Verbindung und/oder einem Gemisch solcher Verbindungen. Die chlorhaltige und/oder jodhaltige Verbindung kann beispielsweise in Form von chlor- oder jodreichen Abfallstoffen in Ergänzung zu oder unter teilweisem Ersatz der zugesetzten bromhaltigen Verbindung zugeführt werden.

[0017] Nach dem erfindungsgemäßen Verfahren folgt nach der Verbrennung oder einem ähnlichen Hochtemperaturprozess unter Zusatz einer bromhaltigen Verbindung eine Reinigung des Rauchgases, wodurch das oxidierte Quecksilber möglichst weitgehend aus dem Rauchgas abgeschieden wird. Verschiedene Rauchgasreinigungsverfahren zur Abscheidung von u.a. ionischem Quecksilber sind aus dem Stand der Technik bekannt. Sie basieren entweder auf einer Nasswäsche oder einer Trockenreinigung oder einer Kombination beider und kann ggf. mehrstufig sein. Die Nasswäsche umfasst z.B. eine saure Wäsche, welche beispielsweise in einer mit Kreislaufwaschwasser beaufschlagten Quenche, einem Druckdüsen- oder Rotationszerstäuberwäscher oder einem Füllkörperwäscher erfolgt. Eine Wäsche kann aber ggf. auch nur schwachsauer oder alkalisch ausgeführt sein, beispielsweise im Fall niedriger Chlorwasserstofffrachten, aber hoher Schwefeldioxidfrachten.

[0018] In einer bevorzugten Ausführungsform umfasst die Rauchgasreinigung eine mehrstufige nasse Rauchgaswäsche mit mindestens einer stark sauren (pH kleiner 1) und/oder mindestens einer schwach sauren (pH 3–4) und/oder mindestens einer alkalischen Waschstufe.

[0019] Die Rauchgasreinigung kann auch eine auf der Adsorption von ionischen Quecksilberverbindungen basierende Trockenreinigung umfassen. Eine solche Reinigung kann beispielsweise durch quasitrockene Entschwefelung in einem Sprühtrockner durchgeführt werden, welcher mit einer Kalkmilch-Kohle-Suspension beaufschlagt ist, oder mit Hilfe von Festbettadsorbern, z.B. auf Basis von körniger Aktivkohle oder von Herdofen-

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koks oder von Mischungen derartiger Adsorbentien mit gekörntem Kalk, oder mit Hilfe von Flugstromadsorbern, z.B. elektrostatischen Gasreinigungsfiltern (EGR-Filter), oder mit Hilfe von Gewebefiltern, welche mit einem eingeblasenen feinpulvrigen Kalkhydrat-Aktivkohle- oder Kalkhydrat-Herdofenkoks-Gemisch beaufschlagt sind. Auch Zeolithe eignen sich zur Abscheidung von quecksilberhaltigen Verbindungen. Im Bezug auf die trockene Rauchgasreinigung zeigt sich ein weiterer Vorteil des erfindungsgemäßen Verfahrens. Die Anwendung des Verfahrens ist insbesondere auch für jene Hochtemperaturanlagen interessant, welche über keine nasse Rauchgasreinigung, sondern ausschließlich über eine trockene Reinigung mit einer Quecksilbersorptionsstufe verfügen. Quecksilberbromid $HgBr_2$ adsorbiert stärker an Trockensorbentien als Quecksilberchlorid $HgCl_2$. Beispielsweise verstärkt sich die Adsorption von Quecksilber am Flugstaub von EGR-Filtern.

[0020] In einer bevorzugten Ausführungsform umfasst die Rauchgasreinigung daher mindestens eine trockene oder quasitrockene, auf Adsorption basierende Reinigungsstufe, insbesondere unter Verwendung von elektrostatischen oder filternden Staubabscheidern.

[0021] Des weiteren werden die mit Quecksilber beladenen Flugstäube aus gegebenenfalls vorhandenen Staubabscheidern zwecks Quecksilberentfrachtung vorzugsweise thermisch nachbehandelt, insbesondere in einer auf Temperaturen von mindestens 200°C beheizten Drehtrommel.

[0022] Bevorzugt wird in dem erfindungsgemäßen Verfahren der Quecksilbergehalt des Rauchgases, insbesondere der Gehalt an metallischem Quecksilber, nach der Rauchgasreinigung kontinuierlich gemessen und anhand des gemessenen Quecksilbergehalts die Menge an zugeführtem Brom und/oder bromhaltigen Verbindungen und/oder der Mischung bromhaltiger Verbindungen sowie gegebenenfalls Schwefel und/oder schwefelhaltigen Substanzen und/oder der Mischung schwefelhaltiger Substanzen geregelt. Ein relativ hoher Gehalt an metallischem Quecksilber im Rauchgas ist ein Indikator dafür, dass die Oxidation des Quecksilbers unvollständig verläuft und damit das Quecksilber in der Rauchgasreinigung unvollständig abgetrennt wird. Um Quecksilber möglichst vollständig zu oxidieren, muss in einem solchen Fall mehr bromhaltige Verbindung zugeführt werden. Zusätzlich kann der Gehalt an ionischem Quecksilber nach der Rauchgasreinigung gemessen werden und daraus der Abscheidegrad des ionischen Quecksilbers in der Rauchgasreinigung bestimmt werden. Der Gehalt an metallischem Quecksilber und ggf. an Quecksilber insgesamt im Kesselrohgas kann nach entsprechender Gasaufbereitung beispielsweise mit Hilfe eines Differenz-Absorptionsphotometers gemessen werden. Die kontinuierliche Messung von metallischem Quecksilber und ggf. auch von Quecksilber insgesamt im Reingas nach der nassen und/oder trockenen Rauchgasreinigung erfolgt vorzugsweise vor einer gegebenenfalls vorhandenen, nachgeschalteten SCR-Entstickungsanlage (SCR: selective catalytic reduction), da der metalloxidreiche Festbettkatalysator erhebliche Mengen an metallischem Quecksilber adsorbiert.

[0023] Nachfolgend wird die Erfindung anhand der Beispiele unter Bezugnahme auf die anliegenden Figuren näher erläutert. Es zeigen:

[0024] **Fig. 1** ein Schema einer Sondermüllverbrennungsanlage.

[0025] **Fig. 2** ein Diagramm, welches den Gehalt von metallischem Quecksilber (Hg_{met}) im gewaschenen Kesselrauchgas, d.h. im Reingas, nach der Nasswäsche in µg/m³ i. N. tr. (Kurve 21, linke Ordinate) sowie den Gesamtgehalt von Brom (Br_{ges}) im Kesselrauchgas in mg/m³ i. N. tr. (Kurve 22, rechte Ordinate) in Abhängigkeit von der Zeit darstellt.

[0026] **Fig. 3** ein Diagramm, welches den Gesamtgehalt von Quecksilber (Hg_{ges}) im Kesselrauchgas, d.h. zugleich im Kesselrohgas, vor der Nasswäsche in µg/m³ i. N. tr. (Kurve 31, linke Ordinate) sowie den Gehalt von metallischem Quecksilber (Hg_{met}) im Reingas nach der Nasswäsche in µg/m3 i. N. tr. (Kurve 32, rechte Ordinate) in Abhängigkeit von der Zeit darstellt.

[0027] **Fig. 4** ein Diagramm, welches den Gesamtgehalt von Brom (Br_{ges}) im Kesselrauchgas, d.h. zugleich im Kesselrohgas, vor der Nasswäsche in mg/m³ i. N. tr. (Kurve 41, linke Ordinate) sowie den Gehalt von metallischem Quecksilber (Hg_{met}) im Reingas nach der Nasswäsche in µg/m³ i. N. tr. (Kurve 42, rechte Ordinate) als Funktion der Zeit darstellt,

[0028] **Fig. 5** ein Diagramm, welches das Massenverhältnis von Brom zu Quecksilber im Kesselrauchgas (Kurve 51, linke Ordinate) sowie den erzielten Gesamtabscheidegrad von Quecksilber in der mehrstufigen Nasswäsche in (Kurve 52, rechte Ordinate) als Funktion der Zeit darstellt,

[0029] **Fig. 6** ein Diagramm, welches das Gewichtsverhältnis von metallischem Quecksilber zur Summe aus metallischem und ionischem Quecksilber (Hg_{met}/Hg_{ges}), d.h. den Hg_{met}-Speziesanteil im Kesselrohgas, in Gew.-% als Funktion des Gesamtgehaltes an Chlor (Kurve 61) bzw. an Brom (Kurve 62) im Kesselrohgas in mg/m³ i. N. tr. darstellt,

[0030] **Fig. 7** ein Diagramm, welches den Gesamtgehalt an Quecksilber (Hg_{ges}) im entstaubten Rohgas nach der elektrostatischen Gasreinigung (Kurve 71, linke Ordinate) bzw. den Gehalt an metallischem Quecksilber (Hg_{met}) nach der elektrostatischen Gasreinigung (Kurve 72, linke Ordinate) sowie die durch Quecksilberzudosierung herbeigeführte Anhebung des Gesamtgehalts an Quecksilber (Hg_{ges}) im Kesselrauchgas (Kurve 73, rechte Ordinate) als Funktion der Zeit darstellt.

[0031] **Fig. 8** ein Diagramm, welches das Gewichtsverhältnis von metallischem Quecksilber (Hg_{met}) zu der Summe aus metallischem und ionischem Quecksilber (Hg_{ges}), d.h. den Hg_{met}-Speziesanteil (Hg_{met}/Hg_{ges}), im

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entstaubten Kesselrohgas nach der elektrostatischen Gasreinigung in Gew.-% (Kurve 82) sowie den Gesamtgehalt an Brom (Br_{ges}) im Kesselrauchgas in mg/m^3 i. N. tr. (Kurve 81) als Funktion der Zeit darstellt.

[0032] **Fig. 9** ein Schema eines Industriekraftwerks mit zwei Schmelzkammerkesseln.

Beispiele

[0033] Die Beispiele 1–4 wurden in einer dem Schema in **Fig. 1** entsprechenden Sondermüllverbrennungsanlage der Bayer AG in Leverkusen durchgeführt. Der Drehrohrofen **3** als primärer Feuerraum wird mit Feststoffabfällen aus dem Bunker **1** über einen Krangreifer **2**, mit Flüssigabfällen aus einem Flüssigabfalltank sowie mit Abfallgebinden über eine Gebindeaufgabe befeuert. Auch die Nachbrennkammer **4** als sekundärer Feuerraum wird mit Flüssigabfällen befeuert. Das Rauchgas wird über den Abhitzekessel **5** abgekühlt und anschließend, als sogenanntes Kesselrohgas, der nassen Rauchgasreinigung (mehrstufige Wasche) zugeführt, welche eine Quenche **6**, einen sauren Rotationszerstäuberwäscher **7**, einen alkalischen Rotationszerstäuberwäscher **8** und eine elektrostatische Gasreinigung mit Wasserdampf-Teilkondensation **9** (KEGR) umfasst. Über Saugzüge **10** gelangt das gewaschene Rauchgas, als sogenanntes Reingas, in die nachgeschaltete katalytische Entstickungsanlage **11** (selektive katalytische Entstickung des Reingases mittels Ammoniak) und wird von dort über den Kamin **12** emittiert. Der Gehalt an metallischem Quecksilber (Hg_{met}) sowie gegebenenfalls der Gesamtgehalt an Quecksilber (Hg_{ges}) im gewaschenen Reingas nach KEGR wurde – nach entsprechender Aufbereitung – an der Messstelle **16** mit Hilfe eines Differenz-Absorptionsphotometers kontinuierlich bestimmt. Der Gehalt an Quecksilber insgesamt (Hgges) im emittierten Reingas wurde an der Messstelle **17**, d.h. in einer Kaminhöhe von 22 m, quasikontinuierlich bestimmt durch Amalgamierung an einer periodisch ausgeheizten Goldfolie mit nachfolgendem Differenz-Absorptionsphotometer.

[0034] Beispiel **5** beschreibt die Anwendung des erfindungsgemäßen Verfahrens in einem Kohlekraftwerk der Bayer AG in Uerdingen, welches im Wesentlichen einen Schmelzkammerkessel und eine kraftwerkstypische Rauchgasreinigung, bestehend aus einer trockenen elektrostatischen Gasreinigung (EGR), einem schwachsauren, auf Kalkstein basierten Nasswäscher zur Rauchgasentschwefelung sowie einer SCR-Entstickungsanlage (SCR: selective catalytic reduction), umfasst.

Ausführungsbeispiel

Beispiel 1

[0035] Über einen Zeitraum von 116 Minuten wurde dem sekundären Feuerraum (Nachbrennkammer **4**) über die Schauluke **15** eine Serie von Proben von metallischem Quecksilber in Kunststoffkapseln zugeführt (in Summe 3400 g, siehe Tabelle 1). Die Zugabe erfolgte in Abständen von ca. 5–10 Minuten mit zunehmender Quecksilbermenge. Das eingeworfene Quecksilber verdampft innerhalb von ca. 2–4 Minuten; demzufolge können die im Kesselrauchgas mit einem Volumenstrom von ca. 45-103 m^3 i. N. tr./h aufgetretenen momentanen Spitzenkonzentrationen an Quecksilber abgeschätzt werden. Die Abschätzung liefert zum Versuchsende hin Spitzenkonzentrationen von mehr als $130 \cdot 10^3$ $\mu g/m^3$ i. N. tr.

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Tabelle 1: Zugabe der Hg-Proben

Uhrzeit	Hg-Menge [g]	Uhrzeit	Hg-Menge [g]
9:24	5	10:32	180
9:32	10	10:37	200
9:38	15	10:43	220
9:49	20	10:48	240
9:54	40	10:53	260
9:59	60	10:58	280
10:04	80	11:03	300
10:09	100	11:08	310
10:15	120	11:13	320
10:20	140	11:20	340
10:26	160		
Versuchsdauer [min]		**Hg-Gesamtmenge [g]**	
116		**3400**	

[0036] Während des Versuchszeitraums wurde durch Mitverbrennung eines hochbromierten Flüssigabfalls (Zugabe zum Drehrohrofenkopf) im Kesselrauchgas von $45 \cdot 10^3$ m³ i.N. tr./h ein Bromgehalt von ca. $4 \cdot 10^2$ mg/m³ i. N. tr. aufrechterhalten, wie die Kurve 22 (rechte Ordinate) in **Fig. 2** zeigt (Bestimmung anhand des Durchsatzes und Bromgehaltes des hochbromierten Flüssigabfalls). Der Rest-SO_2-Gehalt im Kesselrohgas vor der Quenche war dabei mittels Zudosierung von Schwefelgranulat zum Drehrohrofenkopf auf $5,5 \cdot 10^3$ mg/Nm³ i. N. tr. ungewöhnlich hoch eingestellt (direkte SO_2-Messung im Kesselrohgas vor der Quenche). Damit war sichergestellt, dass für das erfindungsgemäße Verfahren ein ausreichendes Angebot an Schwefeldioxid vorhanden war. Das sonstige Verbrennungsgut bestand aus Festabfällen und schwachchlorierten Lösemitteln. Vor, während und nach der Quecksilberzugabe wurde an der Messstelle **16**, d.h. nach der Rauchgasreinigung, der Gehalt an Quecksilber im Rauchgas gemessen. Wie die Kurve **21** (linke Ordinate) in **Fig. 2** zeigt, steigt trotz der Zugabe von erheblichen Quecksilbermengen der Gehalt an metallischem Quecksilber, welches durch die Wäsche durchschlägt, praktisch nicht an.

[0037] Darüber hinaus sind in Tabelle 2 die momentanen Austragungsströme von Quecksilber um 11:30 Uhr, d.h. kurz nach der Zugabe der letzten Quecksilberprobe und damit zum Zeitpunkt der höchsten Quecksilberkonzentration, aufgeführt, welche mit den Wäscherabwässern der nassen Rauchgasreinigung ausgetragen wurden. Umfangreiche abwasserseitige Messungen belegen, dass ca. 99,93 % des insgesamt ausgetragenen Quecksilbers als ionisches Quecksilber mit dem Abwasser der stark sauren Quenche (pH-Wert kleiner 1) und ca. 0,066 % mit dem Abwasser des alkalischen Rotationszerstäuberwäschers (pH-Wert ca. 7,5) ausgetragen wurden. Der geringe, nicht ausgewaschene Rest von nur 0,004 % des insgesamt ausgetragenen Quecksilbers wurde mit dem gewaschenen Reingas als metallisches Quecksilber ausgetragen. Nachweislich war im gewaschenen Reingas praktisch kein Hg_{ion} zu finden (Hg_{ion} = Null, d.h. vollständige Auswaschung des ionischen Quecksilbers und somit $Hg_{ges} = Hg_{met}$).

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Tabelle 2: Momentane Quecksilber-Austragungsströme [g/h] um 11:30 Uhr

Quenche (einschließlich dem sauren Rotationszerstäuberwäscher)	1931
(Saurer Rotationszerstäuberwäscher, dessen Abwasser zur Quenche rückgeführt wird)	(468)
Alkalischer Rotationszerstäuberwäscher	1,32
Gewaschenes Reingas nach KEGR	0,069

Beispiel 2:

[0038] Über einen Zeitraum von 130 Minuten wurde dem sekundären Feuerraum (Nachbrennkammer **4**) über eine Düse in der Nachbrennkammerdecke kontinuierlich eine wässrige $HgCl_2$-Lösung zugeführt. Dabei wurde die zudosierte Menge in Zeitschritten von etwa 5 Minuten angehoben. **Fig. 3** zeigt den so herbeigeführten Anstieg der Konzentration von Quecksilber im Kesselrauchgas in der Zeit zwischen ca. 10:45 und 13:00 Uhr. Das eindosierte Quecksilber wird in der Nachbrennkammer unverzüglich als metallisches Quecksilber $Hg_{0,g}$ freigesetzt. Die Gesamtkonzentration von Quecksilber im Kesselrauchgas stieg auf diese Weise bis auf Werte von $18 \cdot 10^3$ µg/m³ i. N. tr. an (Kurve **31** und linke Ordinate). Die Hg-Konzentration im Kesselrauchgas wurde aus dem zugegebenen Quecksilbermengenstrom und dem betrieblich gemessenen Rauchgasvolumenstrom berechnet. Während des Versuchszeitraums wurde durch Mitverbrennung eines hochbromierten Flüssigabfalls (Zugabe über einen Brenner am Drehrohrofenkopf) im Kesselrauchgas von $45 \cdot 10^3$ m³ i.N. tr./h ein Bromgehalt von ca. $9 \cdot 10^3$ mg/m³ i. N. tr. aufrechterhalten (Bestimmung anhand des Durchsatzes und Bromgehalt des mitverbrannten hochbromierten Flüssigabfalls). Der Rest-SO_2-Gehalt im Kesselrohgas vor Quenche war dabei mittels Zudosierung von Schwefelgranulat zum Drehrohrofenkopf auf ca. $4 \cdot 10^3$ mg/Nm³ i. N. tr. eingestellt (direkte SO_2-Messung im Kesselrohgas vor der Quenche).

[0039] Im Zeitraum zwischen ca. 11:00 und 13:00 Uhr wurde im gewaschenen Reingas nach der KEGR eine Konzentration von metallischem Quecksilber von weniger als 10 µg/m³ i. N. tr. beobachtet. Nachweislich war im gewaschenen Reingas auch hier praktisch kein Hg_{ox} zu finden (Hg_{ox} = Null, d.h. vollständige Auswaschung des ionischen Quecksilbers und somit $Hg_{ges} = Hg_{0,g}$). Bei einem kurzzeitigen Ausfall der Bromzugabe gegen 13:05 Uhr stieg die Konzentration von $Hg_{0,g}$ sprunghaft auf ca. 800 µg/m³ i. N. tr. an und kehrte aber unverzüglich auf ihren niedrigen Ausgangswert von weniger als 10 µg/m³ i. N. tr. zurück, als die Bromzugabe wieder einsetzte (Kurve **32** und rechte Ordinate).

Beispiel 3:

[0040] In der Zeit zwischen ca. 8:30 und 14:45 Uhr, d.h. über einen Zeitraum von 675 Minuten, wurde dem sekundären Feuerraum (Nachbrennkammer **4**) über eine Düse in der Nachbrennkammerdecke kontinuierlich eine wässrige $HgCl_2$-Lösung zugeführt. Dabei wurde nunmehr aber der zudosierte Hg-Mengenstrom konstant gehalten, entsprechend einer Konzentration von Quecksilber im Kesselrauchgas von ca. $9{,}6 \cdot 10^3$ µg/m³ i. N. tr.

[0041] In diesem Versuchszeitraum (vgl. **Fig. 4** bzw. **Fig. 5**) wurde Brom in Form eines hochbromierten Flüssigabfalls über einen Brenner am Drehrohrofenkopf zugegeben, jedoch wurde die zugegebene Brommenge schrittweise verringert, womit der Bromgehalt im Kesselrauchgas stufenweise von ca. $9 \cdot 10^3$ auf ca. $3 \cdot 10^3$ mg/m³ i. N. tr. abgesenkt wurde (Kurve **41** in **Fig. 4** und linke Ordinate). Der mittels Zudosierung von Schwefelgranulat herbeigeführte Rest-SO_2-Gehalt im Kesselrohgas war mit ca. $4{,}3 \cdot 10^3$ mg/m³ i. N. tr in diesem Versuchszeitraum wiederum sehr hoch gewählt worden. Neben dem hochbromierten Flüssigabfall wurde auch ein chlorierter Flüssigabfall mitverbrannt.

[0042] Wie **Fig. 4** bzw. **Fig. 5** zu entnehmen ist, war der Gehalt an metallischem Quecksilber im gewaschenen Reingas nach KEGR deutlich kleiner als 2 µg/m³ i. N.

[0043] tr. (Kurve **42** in **Fig. 4** und rechte Ordinate). Nachweislich war im gewaschenen Reingas auch hier praktisch kein Hg_{ox} zu finden (Hg_{ox} = Null, d.h. vollständige Auswaschung des ionischen Quecksilbers und somit $Hg_{ges} = Hg_{0,g}$). Entsprechend war der Abscheidegrad von Quecksilber in der Nasswäsche deutlich größer als 99,98 % (Kurve **52** in **Fig. 5** und rechte Ordinate), solange der Bromgehalt größer als $3 \cdot 10^3$ mg/m³ i. N. tr.

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(Kurve **41** und linke Ordinate) bzw. das Brom-Quecksilber-Massenverhältnis größer als 500 µg Brom/µg Quecksilber betrug (Kurve **51** in **Fig.** 5 und linke Ordinate). Gegen 13:30 Uhr sinkt der Bromgehalt im Rauchgas auf $3 \cdot 10^3$ mg/m³ i. N. tr. bzw. das Brom-Quecksilber-Massenverhältnis auf ca. 335 µg Brom/µg Quecksilber. Dabei steigt die Konzentration von metallischem Quecksilber nach der Nasswäsche auf bis zu 20 µg/m³ i. N. tr. (Kurve **42** in **Fig.** 4 und linke Ordinate) bzw. nimmt der Hg-Abscheidegrad auf 99,8 % ab (Kurve **52** in **Fig.** 5 und rechte Ordinate). Darüber hinaus führt eine kurzzeitige Unterbrechung der Chlor-Zugabe kurz nach 14:30 Uhr zu einer Spitzenkonzentration von metallischem Quecksilber nach der Wäsche von ca. 117 µg/m³ i. N. tr. (Kurve **42** in **Fig.** 4 und linke Ordinate) bzw. zu einem kurzzeitigen Abfall des Abscheidegrades auf ca. 98,4 % (Kurve **51** in **Fig.** 5 und rechte Ordinate). Hieran wird die gegenüber Brom vergleichsweise geringe Wirkung von Chlor deutlich.

Beispiel 4:

[0044] **Fig.** 6 illustriert einen Versuch zum Vergleich der Wirkung von Brom und Chlor auf die Oxidation von Quecksilber im Kesselrauchgas der oben beschriebenen Sondermüllverbrennungsanlage. Dabei lagen ein durch Zudosierung von $HgCl_2$ eingestellter Hgges Gehalt von 130 µg/m³ i. N. tr. bei einem durch Mitverbrennung chlorarmer Lösemittel eingestellten Chlorgehalt (Cl_{ges}) im Kesselrauchgas von $1,35 \cdot 10^3$ mg/m³ i. N. tr. sowie einem durch Zudosierung von Schwefelgranulat eingestellten Restgehalt an Schwefeldioxid im Kesselrohgas von $1,5 \cdot 10^3$ mg/m³ i. N. tr. vor. Der Messpunkt **63** zeigt den zunächst ohne Bromzusatz, d.h. allein durch Chlor, erzielten Hg_{elem}-Speziesanteil von ca. 63 Gew.-% im Kesselrohgas vor der Nasswäsche. Die anlagenspezifische Kurve **61**, welche auf ca. 20 Betriebsversuchen an einer Sondermüllverbrennungsanlage mit Verbrennung hochchlorierter Flüssigabfälle basiert, zeigt, wie der Hgmet-Speziesanteil (Hg_{elem}/Hg_{ges}) mit wachsendem Chlorgehalt Cl_{ges} im Kesselrauchgas zurückgeht.

[0045] Ausgehend von einem Hgmet-Speziesanteil von ca. 63 Gew.-% im Kesselrohgas vor der Nasswäsche (Messpunkt **63** mit Cl_{ges}-Gehalt als Abszisse bzw. Messpunkt **63'** mit Brges Gehalt als Abszisse) wurde dann in drei Schritten eine zunehmende Menge einer bromhaltigen Verbindung zudosiert (vgl. Pfeil **64**, der den Übergang von der Darstellung des Hg_{elem}-Speziesanteil in Abhängigkeit von dem Cl_{ges} Gehalt zu der Darstellung in Abhängigkeit von dem Br_{ges}-Gehalt markiert). Dabei wurde der Bromgehalt im Kesselrauchgas von zunächst 0 mg/m³ i. N. tr. (Messpunkt **63'** mit Br_{ges}-Gehalt als Abszisse) durch Zudosierung von wässriger Bromwasserstofflösung bzw. von wässriger Natriumbromidlösung (Eindüsung an der Nachbrennkammerdecke **14**, **Fig.** 1) in drei Schritten auf 50, 100 und 120 mg/m³ i. N. tr. (Messpunkte **62** mit Brges Gehalt als Abszisse) angehoben. Dabei ging der Hg_{elem}-Speziesanteil (Hg_{elem}/Hg_{ges}) im Kesselrohgas vor der Nasswäsche – ausgehend von ca. 63 Gew.-% – bis auf 30 Gew.-% zurück.

[0046] Der Vergleich weist die deutlich effektivere Oxidation des Quecksilbers durch bromhaltige Verbindungen im Vergleich zu chlorhaltigen Verbindungen am Beispiel einer Sondermüllverbrennungsanlage nach. Um allein mittels Chlor einen Hg_{elem}-Speziesanteil von nur 30 Gew.-% zu erreichen, müsste man den Cl_{ges}-Gehalt gemäß der Chlorierungskurve **61** auf $4 \cdot 10^3$ mg/m³ i. N. tr. erhöhen. Statt dessen erreicht man dies mit nur 120 mg/m³ i. N. tr. an Brom. Brom erscheint daher etwa 25-fach wirksamer als Chlor. Die Hg-Bromierungskurve **65** (Br_{ges}-Gehalt als Abszisse) entspricht unter Berücksichtigung dieses Faktors der vollständig vermessenen Hg-Chlorierungskurve **61** (Cl_{ges}-Gehalt als Abszisse). Gleiches gilt für im Fall von Kraftwerksrauchgasen, wo allerdings die anlagenspezifische Hg-Chlorierungskurve und die entsprechende Hg-Bromierungskurve **65** zu wesentlich niedrigeren Halogengehalten hin verschoben sind.

Beispiel 5:

[0047] **Fig.** 7 und **Fig.** 8 illustrieren Versuche zum Nachweis der Wirkung von Brom auf die Quecksilberabscheidung in einem Kohlekraftwerk der Bayer AG in Uerdingen (vgl. **Fig.** 9). In dem Kohlekraftwerk erfolgte ein Versuch mit Zudosierung von wässriger $HgCl_2$-Lösung und von wässriger NaBr-Lösung in den Feuerraum zum Nachweis der Wirkung von Brom auf die Hg-Oxidation. Das Kraftwerk umfasst zwei parallele Schmelzkammerkessel **91**, **91'** mit Temperaturen im Feuerraum um 1450°C. Die Schmelzkammerkessel **91**, **91'** werden mit Kohle **92**, **92'** bestückt. Über die jeweiligen Luftvorwärmer **93**, **93'** wird den Schmelzkammerkesseln **91**, **91'** Frischluft **94**, **94'** zugeführt. Das Kesselrohgas **95**, **95'** wird über elektrostatische Gasreiniger (EGR) **96**, **96'** dem gemeinsamen schwachsauren (pH = 5,3) Nasswäscher als Rauchgasentschwefelungsanlage (REA-Wäscher) **97** zugeführt. Das gewaschene Kesselrauchgas (Reingas) wird anschließend in zwei parallele katalytisch wirkende Entstickungsanlagen (SCR-Entstickungsanlage) **98**, **98'** überführt, bevor es über Kamine **100**, **100'** emittiert wird. Der in den EGR abgeschiedene Flugstaub **99**, **99'** wird zu 100 % in die Feuerung des jeweiligen Schmelzkammerkessels zurückgeführt. An der Messstelle **101** nach der EGR **96** wurden die Gehalte an Hg_{ges} und Hgges im entstaubten Kesselrohgas kontinuierlich erfasst.

[0048] Es wurde kein Schwefel zudosiert. Der Gehalt an Schwefeldioxid im Kesselrauchgas von $1,3 \cdot 10^3$ i. N. tr. resultierte ausschließlich aus dem verbrannten Kohleschwefel selbst. Der Gesamtquecksilbergehalt im ent-

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staubten Rohgas nach der EGR, d.h. vor der Nasswäsche, betrug zu Beginn bei reiner Kohleverbrennung (polnische Steinkohle) im Mittel nur 22,5 µg/m³ i. N. tr., vgl. **Fig. 7**, Kurve **71** (Gesamtgehalt an Quecksilber Hg_{ges}) um 8:30 Uhr, der Gehalt an metallischem Quecksilber im Mittel nur 8,8 µg/m³ i. N. tr., vgl. **Fig. 7**, Kurve **72** (Gehalt an metallischem Quecksilber Hg_{met}) um 8:30 Uhr. Die Zahnung beider Kurven **71**, **72** im 10-Minuten-Takt beruht auf der regelmäßigen Abklopfung der EGR; wodurch unmittelbar nach Abreinigung der Staubschichten im entstaubten Kesselrohgas hinter der EGR höhere Gehalte auftreten. Um 9:15 Uhr wurde mit der Zudosierung von Quecksilber (als wässrige $HgCl_2$-Lösung) und um 10:30 dann auch mit der Zudosierung von Brom (als wässrige NaBr-Lösung) in den Feuerraum begonnen. Die Kurve **73** (**Fig. 7**, rechte Ordinate) stellt die durch Zudosierung von Quecksilber herbeigeführte Erhöhung des Hg_{ges}-Gehalts im Kesselrauchgas dar. Zwischen ca. 9:30 und 13:00 Uhr betrug die mittels $HgCl_2$-Zudosierung herbeigeführte Anhebung des Gesamtgehalts an Quecksilber im Rauchgas vor der EGR mindestens ca. 220 µg/m³ i. N. tr. (Kurve **73**, rechte Ordinate). Die Kurve **81** in **Fig. 8** stellt die durch Zudosierung von wässriger NaBr-Lösung herbeigeführte Erhöhung des Br-Gehalts im Kesselrauchgas dar. Um 10:30 Uhr wurde der Bromgehalt im Rauchgas vor der EGR zunächst um mindestens 75 mg/m³ i. N. tr. angehoben und schrittweise wieder abgesenkt. Um 16:10 Uhr erfolgte eine neuerliche Anhebung des Bromgehalts um ca. 43 mg/m³ i. N. tr. Wegen der Rückführung der Flugasche in die Schmelzkammerfeuerung und somit auch der Rückführung von an der Flugasche sorbiertem Quecksilber bzw. Brom handelt es sich hierbei um Mindestanhebungen, wie sie sich aus den zudosierten Mengenströmen und dem Rauchgasvolumenstrom (ca. 110·10³ m³ i. N. tr./h) ergeben. Die tatsächlichen Hg- und Br-Gehalte im Rohgas vor der EGR liegen demzufolge (Kreislauf zwischen Schmelzkammerfeuerung und EGR) etwas höher.

[0049] Die Kurven **71** bzw. **72** (linke Ordinate) in **Fig. 7** zeigen, wie mit dem Zusatz der bromhaltigen Verbindung der Gehalt an Quecksilber im Rauchgas deutlich zurückgeht. Dies gilt einerseits für das ionische Quecksilber (Differenz zwischen Hg_{ges} und Hg_{met}), welches in Anwesenheit der bromhaltigen Verbindung vermehrt gebildet und offensichtlich am rückgeführten Flugstaub adsorbiert wird, und gilt andererseits aber stärker noch für das metallische Quecksilber, dessen Gehalt im entstaubten Rohgas nach EGR trotz des Zusatzes von Quecksilber annähernd auf den Ausgangsgehalt vor der Quecksilberzugabe zurückkehrt. Von 10:30 Uhr bis 13:00 Uhr (Ende der Br-Zudosierung) und weit darüber hinaus betrug der Gehalt an Hg_{met} weniger als 10 µg/m³ i. N. tr. Erst mit dem Ende der neuerlichen Zugabe der Natriumbromidlösung gegen 19:00 Uhr steigt der Gehalt von Hg_{ges} deutlich an. Weiterhin zeigt die Kurve **82** in **Fig. 8** den zunächst schlagartigen Rückgang des Spezies-anteils an metallischem Quecksilber mit der Zugabe von Brom (Absenkung von ca. 40 Gew.-% auf ca. 10 Gew.-% gegen 10:30 Uhr). Entsprechendes zeigt sich nach ca. 17:00 Uhr bei der neuerlichen Quecksilber- und Bromzugabe an dem allmählichen Rückgang des Hg_{met}-Speziesanteils bis auf nur ca. 5 Gew.-% gegen 20:45 Uhr. Infolge der Hg-Zudosierung und der verstärkten Hg-Adsorption stieg der Hg-Gehalt im zur Schmelzkammer rückgeführten EGR-Flugstaub von anfänglich ca. 2–5 mg/kg im Laufe des Versuchs auf 55 mg/kg an.

Patentansprüche

1. Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen, **dadurch gekennzeichnet**, dass
– der, gegebenenfalls mehrstufigen, Feuerung und/oder dem Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil Brom und/oder eine bromhaltige Verbindung und/oder eine Mischung verschiedener bromhaltiger Verbindungen zugeführt wird, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt,
– die Verbrennung in Gegenwart einer schwefelhaltigen Verbindung, insbesondere Schwefeldioxid, gegebenenfalls unter Zusatz von Schwefel und/oder einer schwefelhaltigen Verbindung und/oder einer Mischung verschiedener schwefelhaltiger Verbindungen erfolgt
– und anschließend das Rauchgas einer, gegebenenfalls mehrstufigen, Reinigung zur Abtrennung von Quecksilber aus dem Rauchgas unterzogen wird, welche eine Nasswäsche und/oder eine Trockenreinigung umfasst.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die bromhaltige Verbindung eine wässrige Lösung von Bromwasserstoff und/oder ein Alkalibromid, insbesondere Natriumbromid, und/oder eine wässrige Lösung von Alkalibromid ist.

3. Verfahren nach einem der Ansprüche 1 bis 2, dadurch gekennzeichnet, dass die bromhaltige Verbindung und/oder die Mischung bromhaltiger Verbindungen flüssige und/oder feste bromreiche Abfallstoffe sind.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass das Brom und/oder die bromhaltige Verbindung und/oder die Mischung bromhaltiger Verbindungen der Verbrennungsluft und/oder gegebenenfalls einem rückgeführten Teilstrom, insbesondere dem rückgeführtem Rauchgas und den rückgeführten Flugstäuben, zugesetzt wird.

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5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass das Massenverhältnis von Brom zu Quecksilber im Bereich von 10^2 bis 10^5 liegt.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass die Verbrennung zusätzlich in Gegenwart von Chlor und/oder einer chlorhaltigen Verbindung und/oder einer Mischung verschiedener chlorhaltiger Verbindungen und/oder Jod und/oder einer jodhaltigen Verbindung und/oder einer Mischung verschiedener jodhaltiger Verbindungen durchgeführt wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass die Rauchgasreinigung eine mehrstufige nasse Rauchgaswäsche mit mindestens einer stark sauren und/oder mindestens einer schwach sauren und/oder alkalischen Waschstufe umfasst.

8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, dass die Rauchgasreinigung mindestens eine trockene oder quasitrockene, auf Adsorption basierende Reinigungsstufe umfasst, insbesondere unter Verwendung von elektrostatischen oder filternden Staubabscheidern.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, dass die mit Quecksilber beladenen Flugstäube aus gegebenenfalls vorhandenen Staubabscheidern zwecks Quecksilberentfrachtung thermisch nachbehandelt wird, insbesondere in einer auf Temperaturen von mindestens 200°C beheizten Drehtrommel.

10. Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, dass der Quecksilbergehalt des Rauchgases, insbesondere der Gehalt an metallischem Quecksilber, nach der Rauchgasreinigung kontinuierlich gemessen wird und anhand des gemessenen Quecksilbergehalts die Menge an zugeführtem Brom und/oder bromhaltigen Verbindungen sowie gegebenenfalls Schwefel und/oder schwefelhaltigen Verbindungen geregelt wird.

Es folgen 9 Blatt Zeichnungen

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Anhängende Zeichnungen

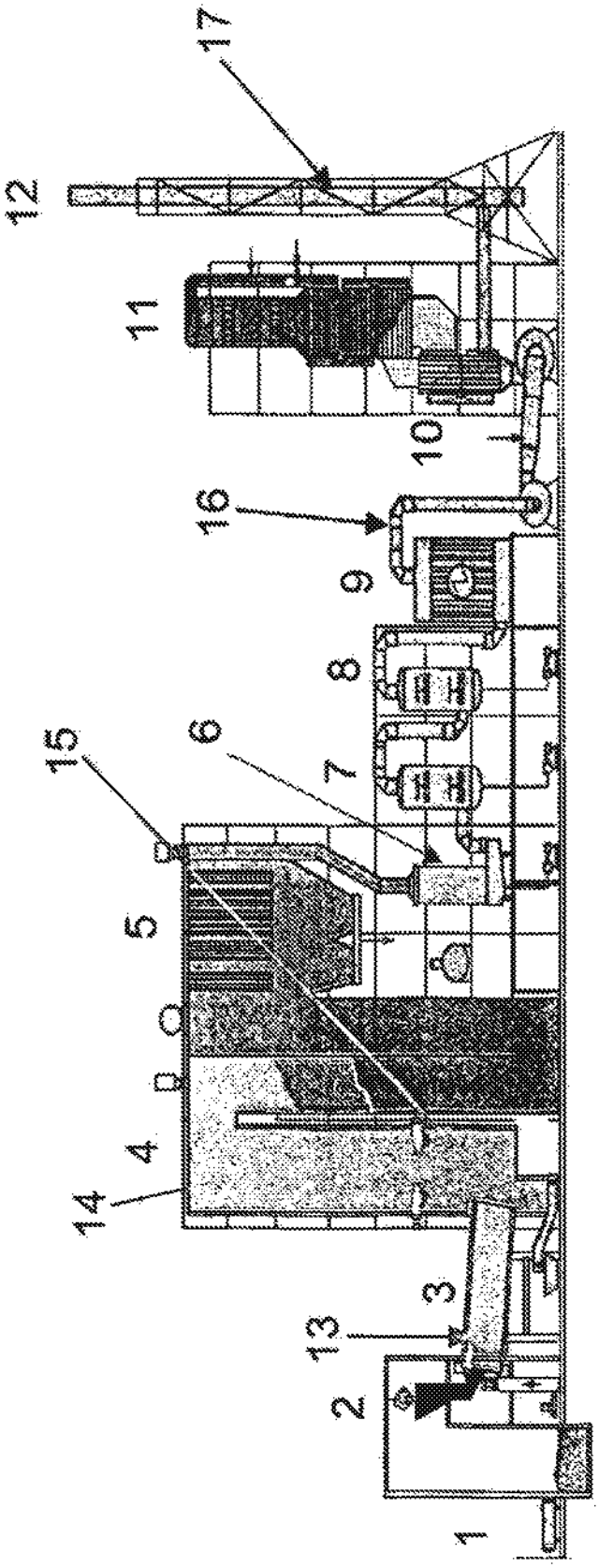


Fig. 1

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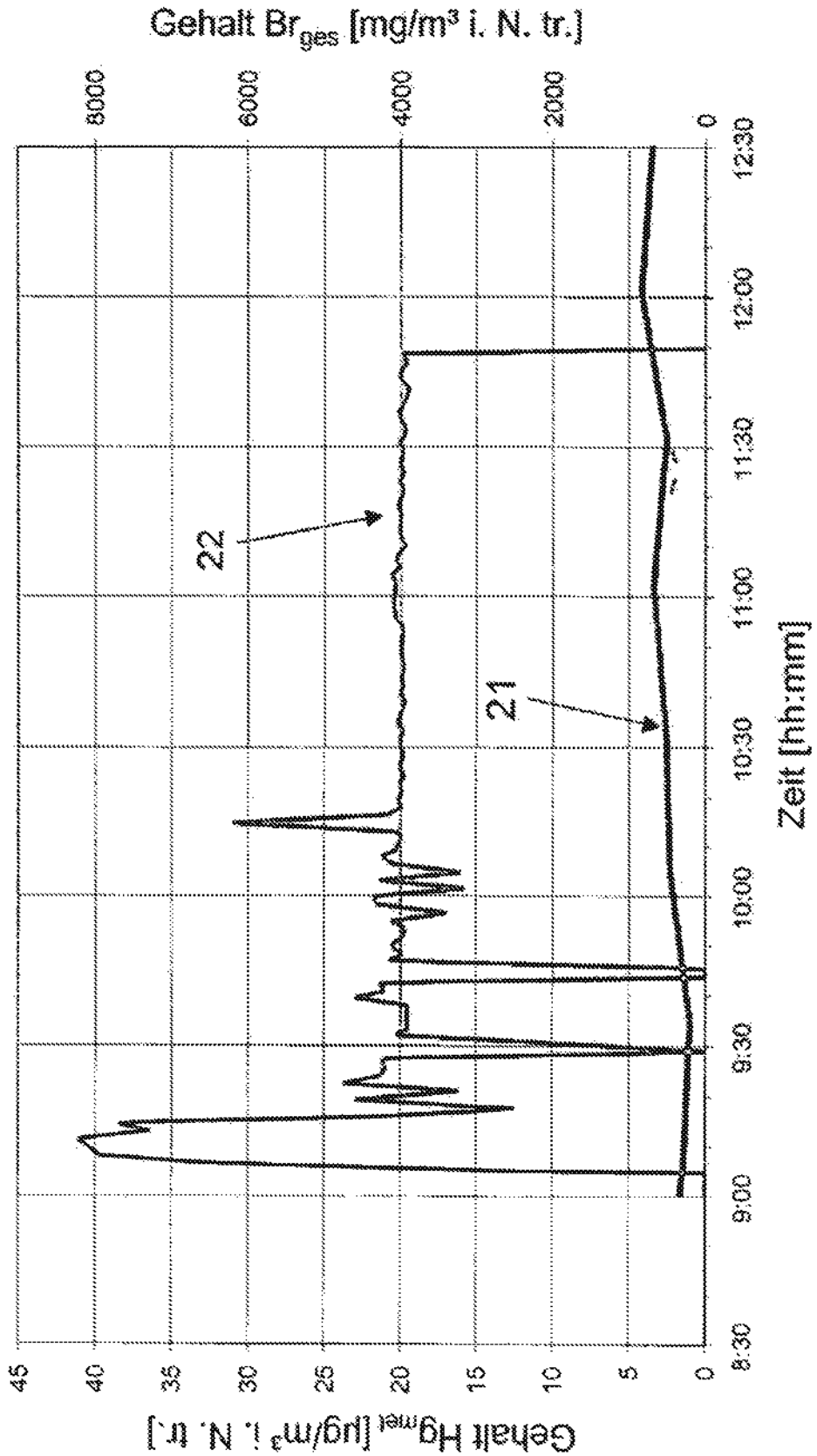

Gehalt Br_{ges} [mg/m³ i. N. tr.]
8000
6000
4000
2000
0
22
21
Gehalt Hg_{met} [µg/m³ i. N. tr.]
45
40
35
30
25
20
15
10
5
0
8:30
9:00
9:30
10:00
10:30
11:00
11:30
12:00
12:30
Zeit [hh:mm]

Fig. 2

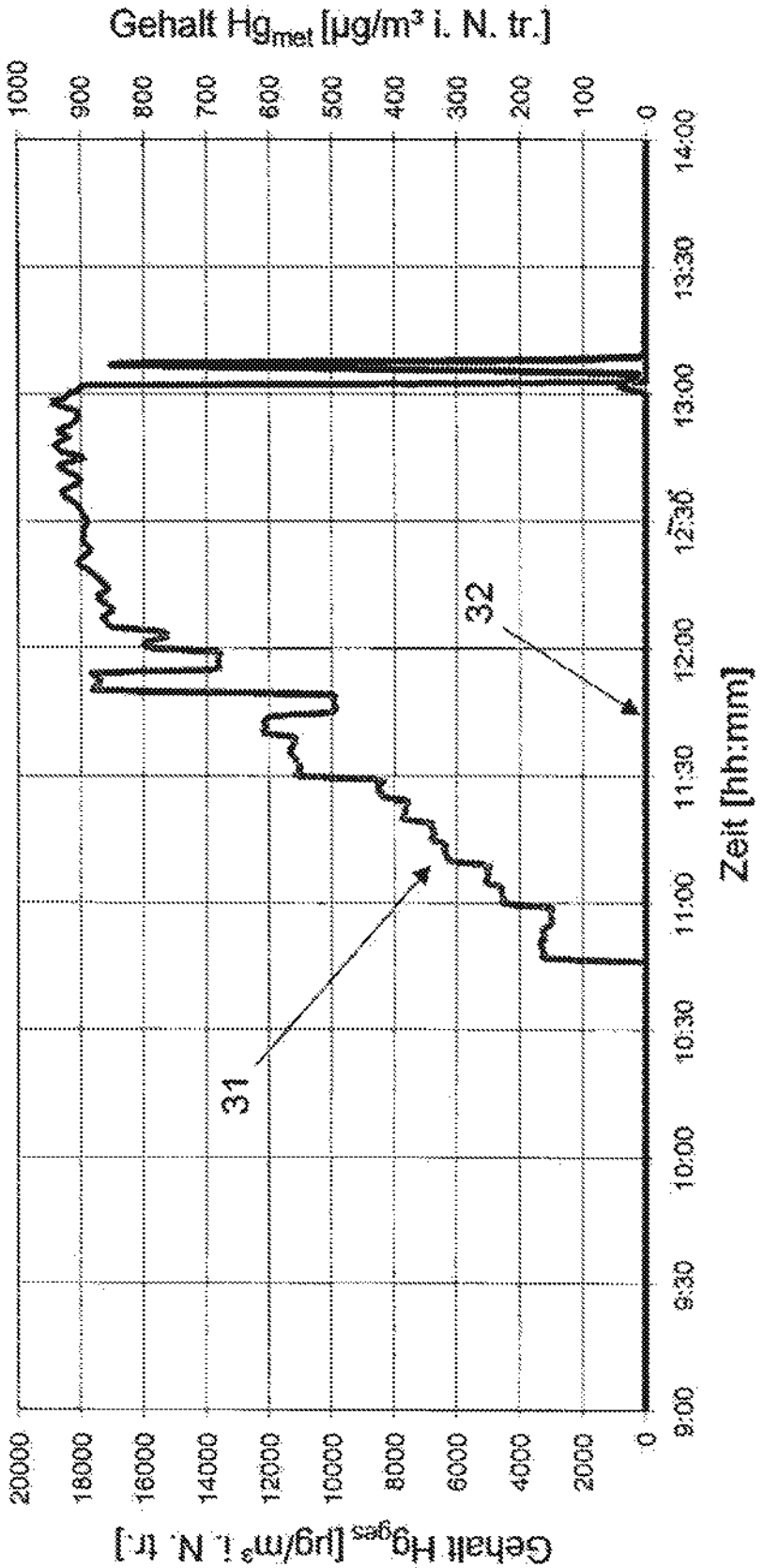


Fig. 3

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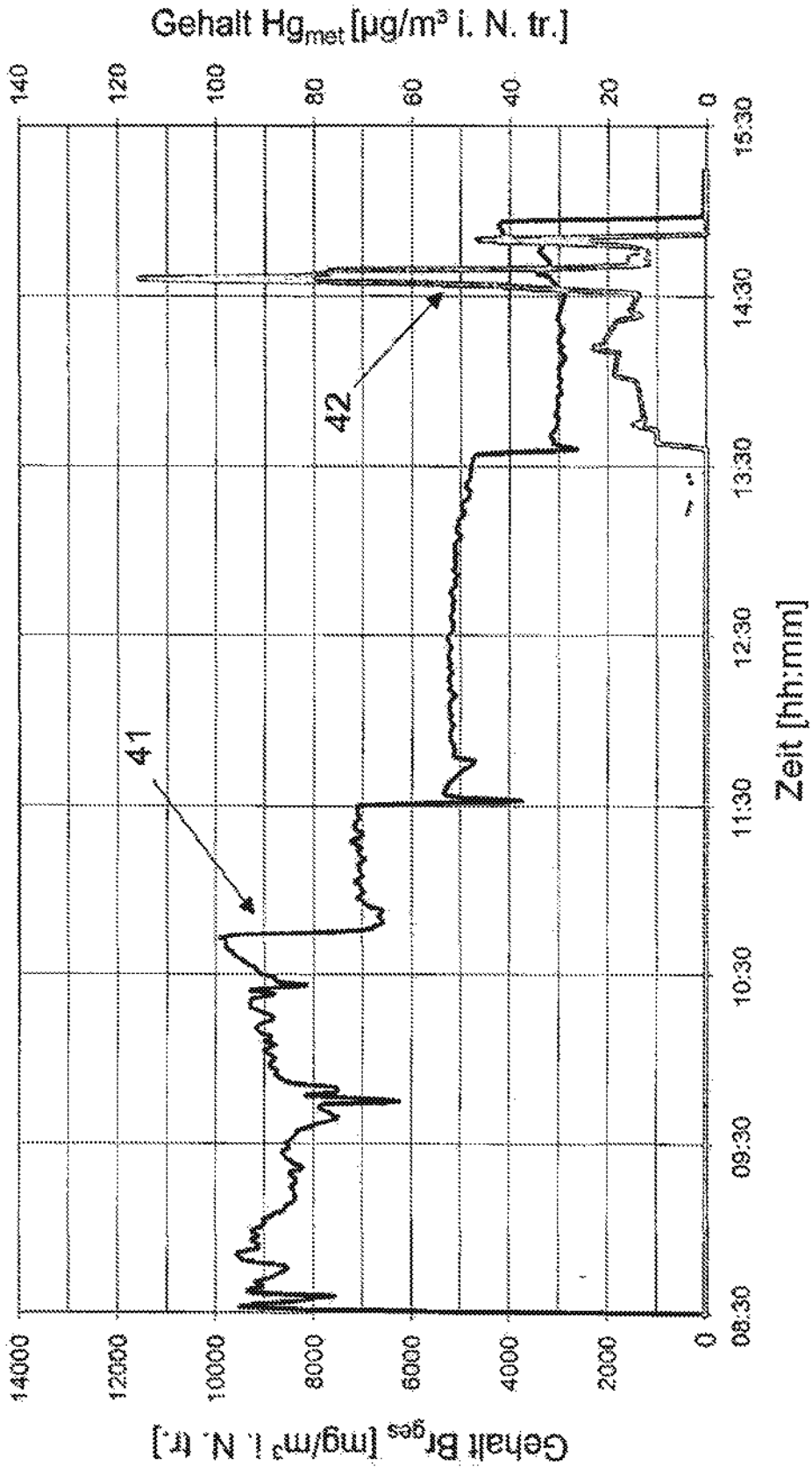


Fig. 4

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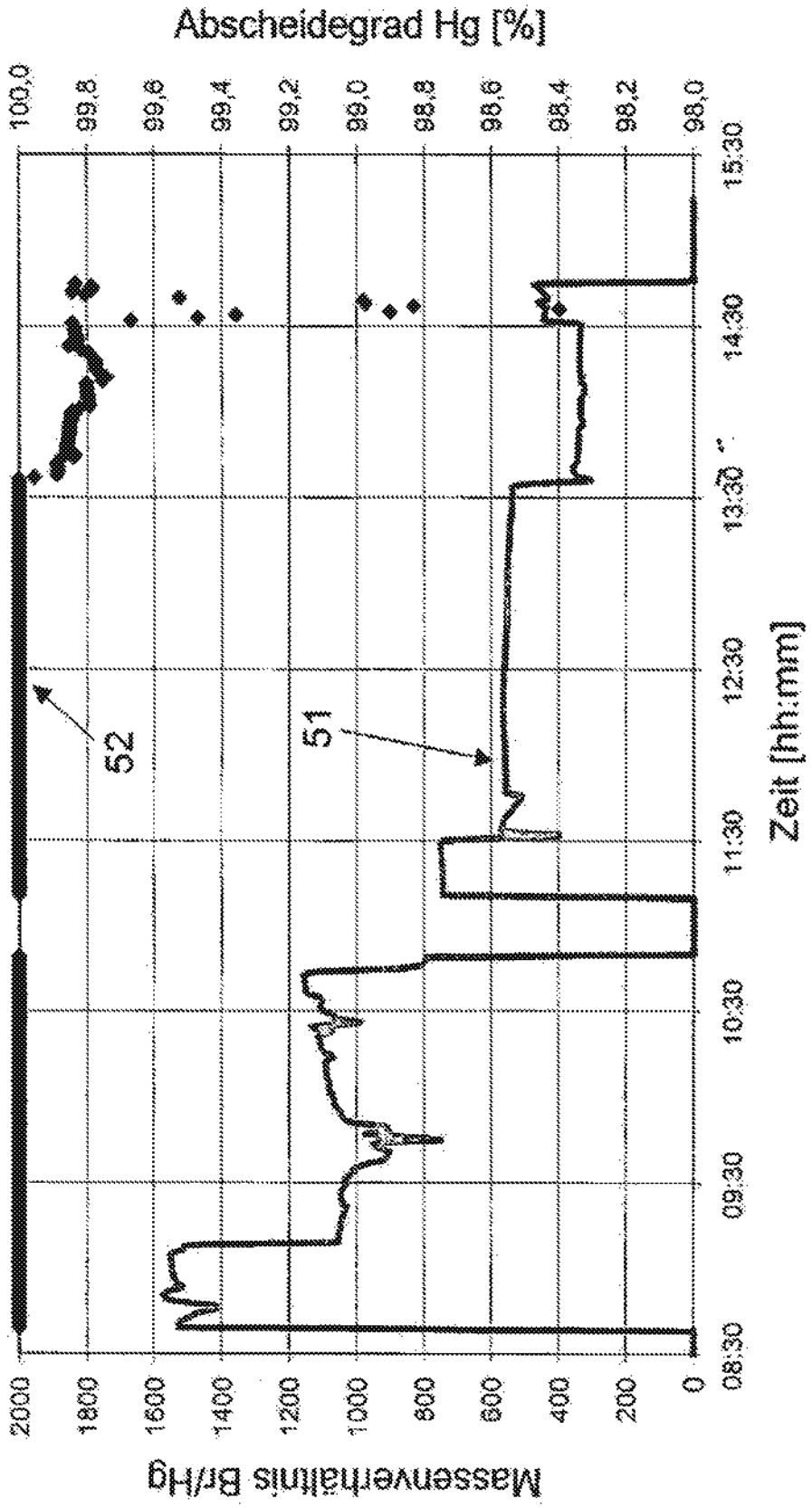


Fig. 5

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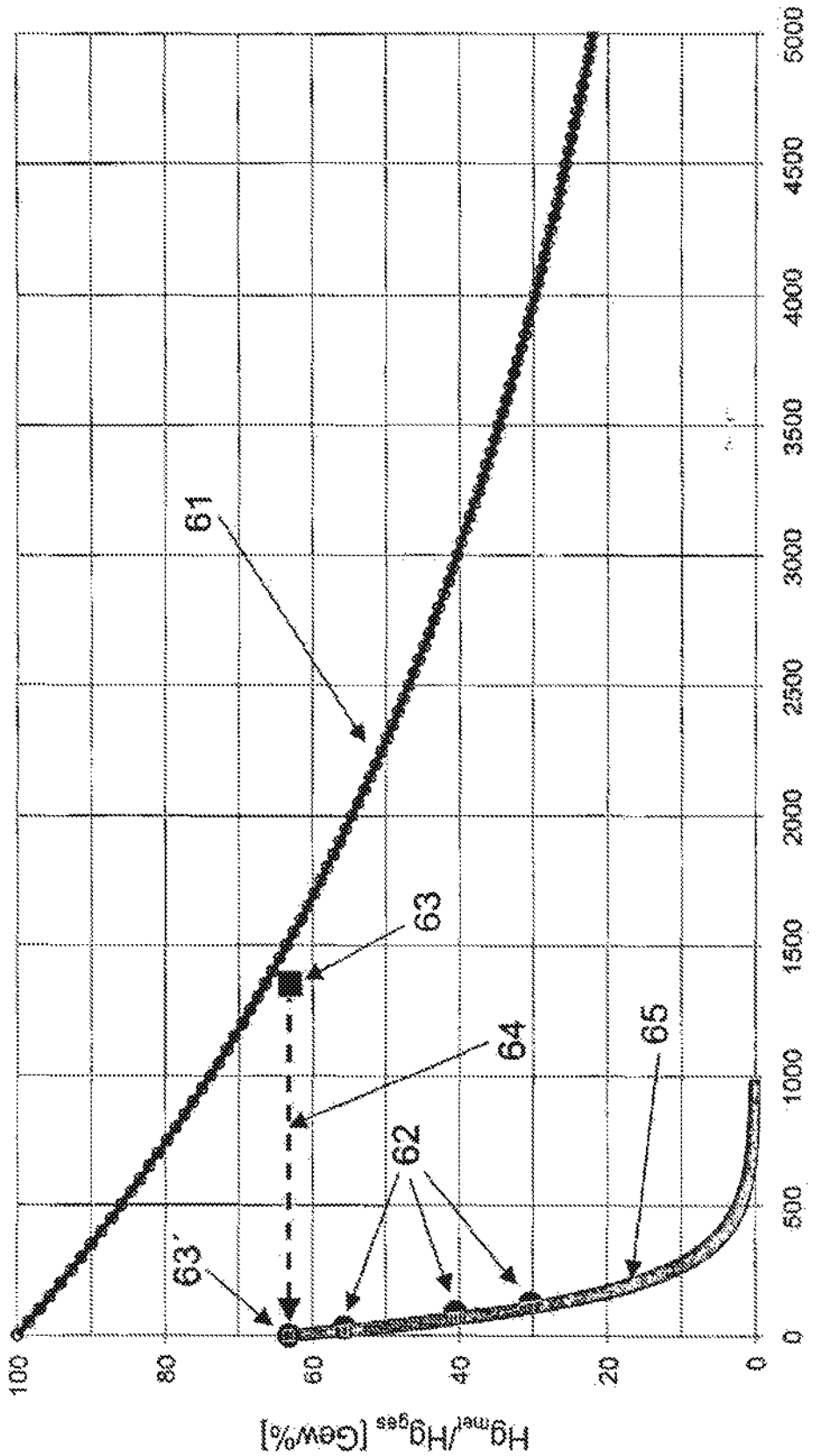


Fig. 6

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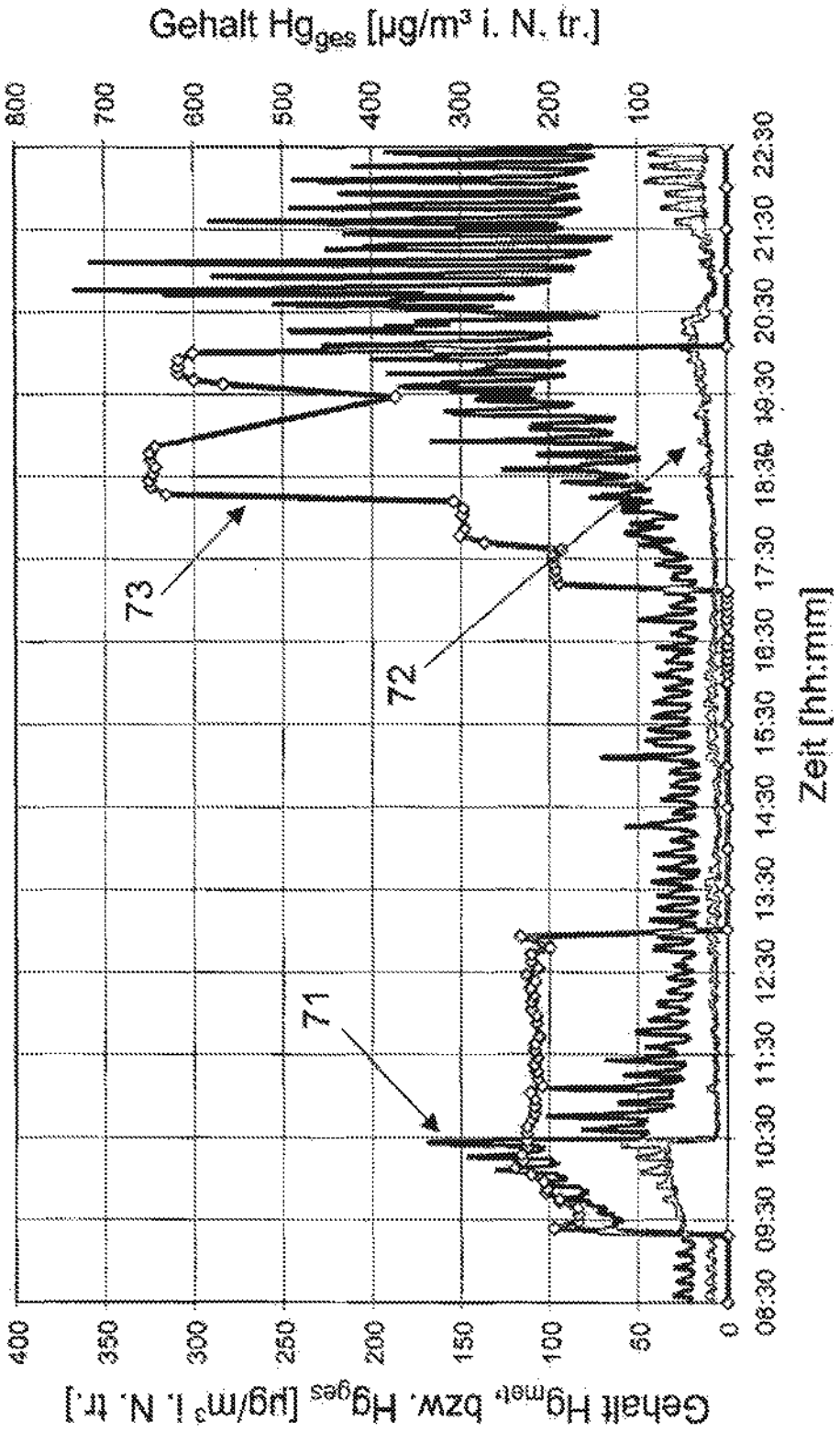


Fig. 7

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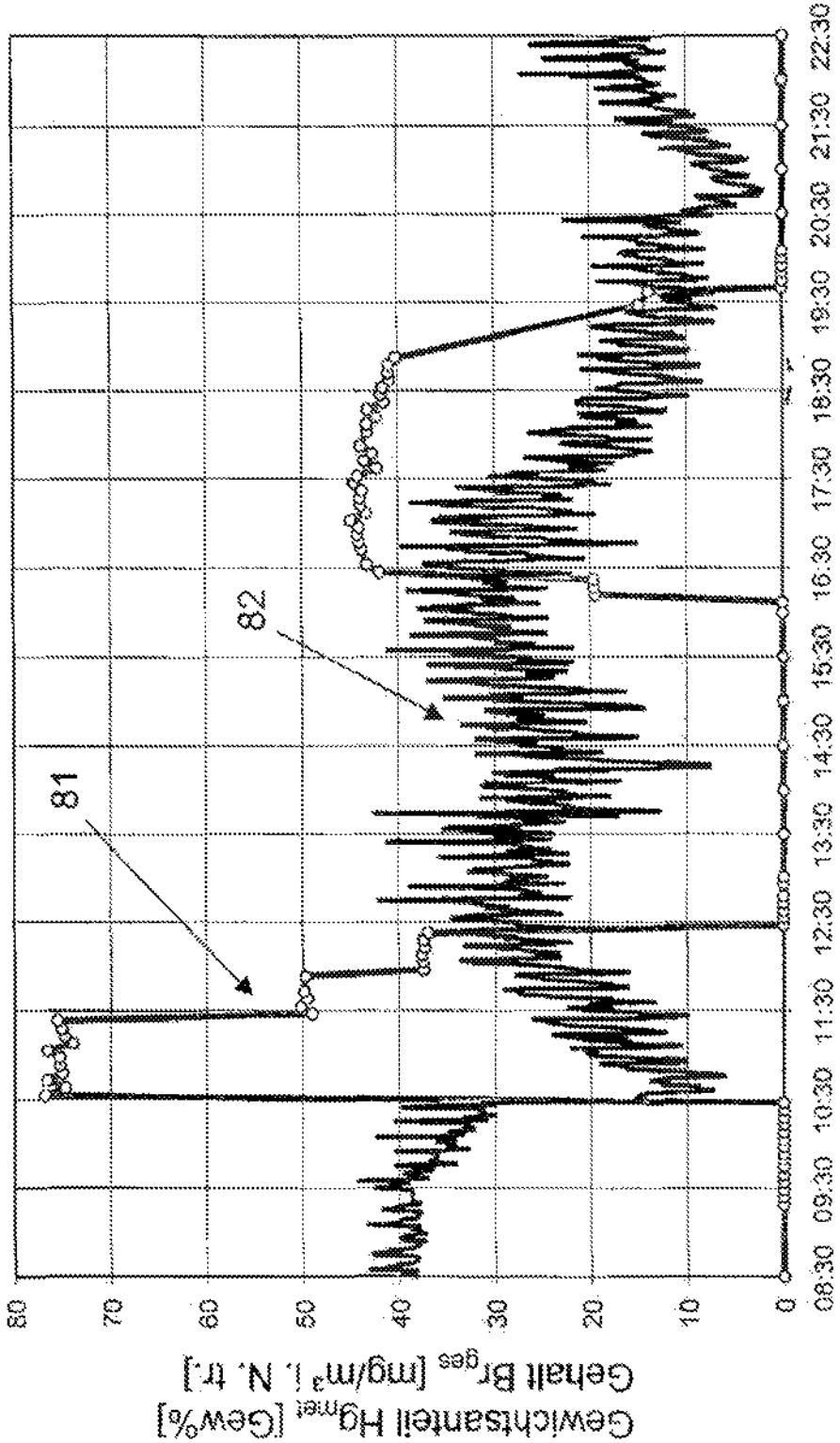


Fig. 8

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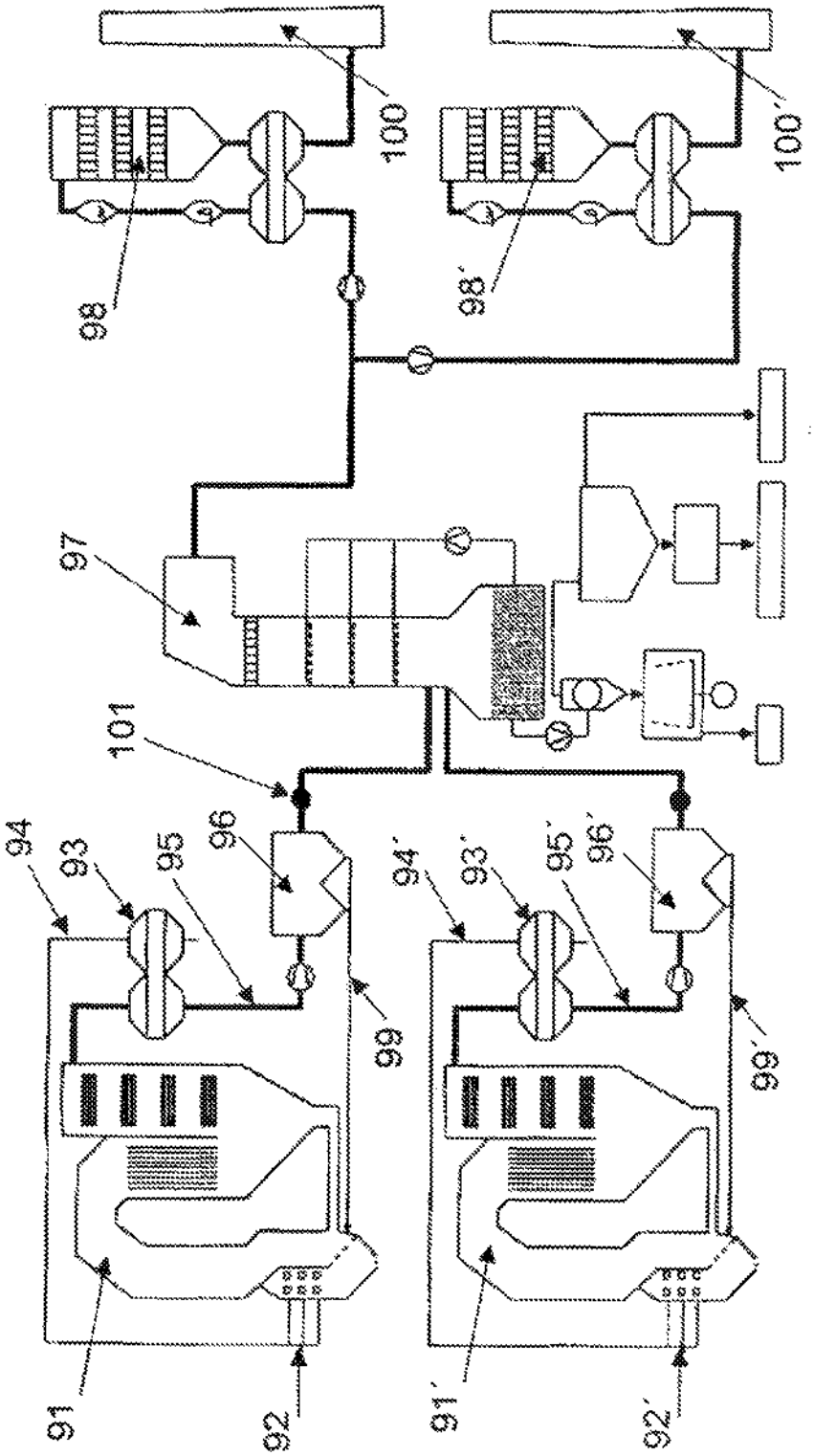


Fig. 6

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(54) **A process for removal of mercury vapor and vapor of chlorodibenzodioxins and -furans from a stream of hot flue gas.**

(57) Mercury vapor and/or vapor of chlorodibenzodioxins and/or vapor of chlorodibenzofurans are removed from a stream of hot flue gas together with acidic components of the flue gas in a spray absorption process. The absorbent used in said process is an aqueous liquid which besides alkaline components contains suspended activated carbon.

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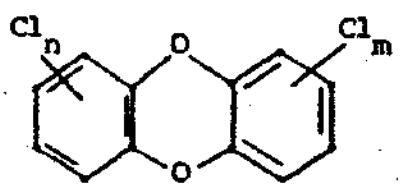
A process for removal of mercury vapor and vapor of chlorodibenzo-dioxins and -furans from a stream of hot flue gas.

FIELD OF THE INVENTION.

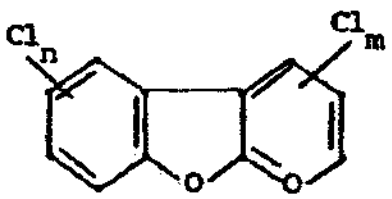
It is a well recognized fact that flue gases often contain mercury vapor in such amounts that their release into the atmosphere is regarded as being hazardous. This especially applies to flue gases from incineration plants where domestic refuse is incinerated but also flue gas formed by combustion of certain coals may contain mercury vapor in such amounts that it is highly desirable to remove a substantial part of said mercury vapor before releasing the flue gas into the atmosphere.

In the present specification and the attached claims the term mercury vapor means elementary mercury as well as mercury-containing chemical compounds in the vapor phase.

In recent years a growing concern has arisen as to the presence in flue gases of the toxic polychlorodibenzodioxines (PCDD) and polychlorodibenzofurans (PCDF). Said two series of compounds may be represented by the following formulae



PCDD



PCDF

wherein n and m each independently is an integer from 0 through 4 provided that n + m is at least 2.

PCDD and PCDF are present in flue gases from incineration plants and in minor proportion also in the

flue gases from power plants. In flue gases these compounds are primarily present in vapor phase and in the present specification the above abbreviations denote the compounds as vapors.

The extremely high toxicity of certain of these compounds makes it desirable to avoid their release into the atmosphere.

DESCRIPTION OF PRIOR ART.

Numerous methods have been suggested for removing or recovering mercury from gases. However, the majority of the prior art processes have been created with the purpose of removing mercury from relative small amounts of gas having high mercury concentration. These processes are not suitable for cleaning flue gas since costs of chemicals would be prohibitive or operation would be impracticable in connection with large volumes of flue gas.

Processes for removing mercury from air of relatively low mercury content have also been suggested. Such a process is disclosed in published European Patent Application No. 1.456. (Akzo N.V.). Said process which is described as particularly suitable for the removal of mercury from air which is vented from buildings, is based on the principle that mercury vapor is absorbed as mercury chloride when passing a bed of activated carbon having a specific chlorine content. According to the specification to said European application high moisture content of the gas from which mercury is to be removed, should be avoided since the effectiveness of the activated carbon is reduced thereby. From said specification it also appears that activated carbon used in a stationary bed without chlorine is unsatisfactory as absorbent for mercury and has a very low capacity for that purpose.

The process of said European application seems unsuitable for treating flue gas since it would require the total amount of flue gas to be passed through a bed of activated carbon to which gaseous chlorine is added, which obviously involves the risk that a surplus of chlorine may be entrained with the flue gas to the atmosphere.

A process for removing mercury vapor from a hot hydrogene chloride-containing flue gas is disclosed in published European patent application no. 13.567, (Svenska Fläktfabriken). According to said process the gas which contains hydrogen chloride and minor amounts of mercury vapor, is contacted with powdered calcium hydroxide, preferably in a fluidized bed. The hydrogen chloride in the gas reacts with the calcium hydroxide to form calcium chloride which apparently is essential to the removal of mercury. Said process is restricted to gases having a substantial contents of hydrogen chloride. This condition will often be fulfilled by the flue gas from a waste incineration plant while flue gasses from other sources may be deficient in that respect.

US patent specification 4.273.747 (Rasmussen) discloses removal of mercury from hot waste gasses by atomizing an aqueous liquid into the waste gasses in the presence of fly ash suspended in the gas and subsequently separating the fly ash together with a substantial part of the mercury originally present as vapor. It is essential that by said treatment the gas stream is cooled from a temperature of at least 200°C to a temperature below 160°C. The aqueous liquid may be just water or it may be an aqueous solution or suspension of an alkaline compound, preferably calcium hydroxide.

Obviously said method will not be suitable in case it is not acceptable to cool the gas to the

extent required or if the amount of fly ash is insufficient due to the use of a preceding fly ash separation. Even when the conditions as to fly ash contents of the flue gas and cooling are satisfied it would in certain applications be desired to increase the efficiency of the removal of mercury vapor in said process.

Efforts to reduce the PCDD and PCDF levels in flue gas have hitherto mainly concentrated on thermal destruction. A reliable thermal destruction is, however, difficult to establish, since a very high temperature is required to ensure a complete destruction.

According to a paper of A.J. Teller and J. D. Lauber : "Control of Dioxin Emissions from Incineration" presented at the 76th annual meeting of the Air Pollution Control Association, Atlanta, Georgia, June 19 - 24, 1983, dioxin theoretic estimations indicate that emission may be reduced by condensing the dioxin thereof. However, A. Nottrodt et al: "Emissionen von polychlorierten Dibenzodioxinen und polychlorierten Dibenzofuranen aus Abfallverbrennungsanlagen", Müll und Abfall 11/84, p. 313-327 (Erich Schmidt Verlag GmbH Berlin, Bielefeld, München) state results showing high vapor phase concentrations after several wet scrubbings with flue gas temperatures lower than those obtained in the theoretic estimations made in said paper by Teller and Lauber.

Consequently a need excists for efficient measures for removing not only mercury vapor but also PCDD and PDCF vapors from flue gases.

SUMMARY OF THE INVENTION.

The present invention is directed to a novel process for efficient removal of mercury vapor and PCDD

and PCDF from a stream of hot flue gas, which process provides a simultaneous removal of acidic components of the flue gas.

It has turned out that incorporation of a relatively small amount of activated carbon in an alkaline feed suspension to be spraydried in a spray absorption process enables a surprising improvement of the ability of the process to remove mercury, PCDD and PCDF.

Consequently the process according to the invention is characterized in that an aqueous liquid which besides alkaline components comprises suspended activated carbon is spray dried in the flue gas which subsequently is freed from the resulting particulate material.

The amount of activated carbon to be used depends on the amount of mercury vapor as well as PCDD and PCDF in the flue gas, on the limits for emission which it is intended to meet, on the extent to which cooling of the gas is permissible, on the proportion of fly ash and the character thereof, etc.

Usually the amount of activated carbon will correspond to at least 5 mg per Nm^3 flue gas to be treated. For economic reasons the amount will usually not exceed 500 mg per Nm^3 flue gas, peferrably not 200 mg per Nm^3.

Since the prior art describes activated carbon as not being very suitable for absorption of mercury vapor when no chlorine is present and since high moisture conditions are described as harmful to mercury sorption by means of activated carbon together with chlorine it could not be predicted that a very efficient mercury removal is obtained by the very simple measures prescribed by the present process. It is also surprising that the rather small additions of activatet carbon to

the aqueous liquid to be atomized, which come into consideration by the present process, enables a reduction of PCDD and PCDF levels to extremely low values.

The preferred alkaline component for the simultaneous removal of acidic components of the gas is calcium hydroxide which by chemical reaction absorbs e.g. sulphur oxides and hydrogen chloride. However, it is to be observed that by the process of the invention presence of hydrogen chloride and consequently production of calcium chloride is not necessary to achieve an efficient removal of mercury vapor.

The fact that in the present process the activated carbon is initially present in aqueous suspension in the atomized droplets and subsequently is embedded in the particulate material comprising the reaction products of e.g. calcium hydroxide and the acidic components of the gas, apparently does not have any substantial adverse influence on the absorption ability of the activated carbon, as would have been expected.

The process of the present invention may be performed using those measures which are conventional in spray absorption processes for desulfurization of flue gases, e.g. as described in US patent 4,279,873 (Felsvang et al), incorporated herein by reference.

In the typical embodiment the process of the invention is performed on a stream of flue gas the fly ash of which has previously been removed in a particle collector, e.g. an electrostatic precipitator. However, the absorption of mercury vapor by activated carbon may be used as a supplement to the absorption by means of fly ash as described in the above cited US specification 4,273,747, in which case at least a portion of the fly ash present in the flue gas stream remains in said stream during the spray absorption process and is re-

covered together with the particulate material formed by the spray absorption process.

It is also possible to add fly ash to the liquid to be atomized, thereby utilizing the sorption ability of the fly ash to reduce the requirement for activated carbon.

Also other absorbents such as silicates may be added to the liquid to be atomized to minimize the requirement as to activated carbon.

As indicated above the amount of activated carbon necessary to achieve a substantial reduction of the concentration of mercury vapor and PCDD and PCDF in the flue gas is surprisingly small. The actual amounts to be used in each individual case may easily be fixed by a person skilled in the art on the basis of a few tests.

It is an important feature of the invention that by very simple measures a very flexible process is obtained since even flue gases with substantially varying levels of Hg, PCDD and PCDF may be coped with just by changing the amount of activate carbon added to the liquid to be atomized.

The particulate material formed in the spray absorption process and typically comprising calcium sulfite, calcium sulfate, calcium hydroxide and activated carbon and possibly fly ash is preferably separated from the flue gas in a baghouse which enables a prolonged contact between the particulate material and the flue gas.

In the following the process according to the invention will be further illustrated by means of examples.

In these examples analysis was performed on flue gas withdrawn by means of a heated probe with glass lining and equipped with a glass wool filter. The mercury was collected in two impinger flasks in series

containing an aqueous 5% potassium permanganate - nitric acid solution. Mercury was analyzed by flameless atomic absorption using $NaBH_4$ as a reductant (MHS-20, Mercury/ Hydride System by Perkin Elmer, ref. 338 - A2-M 294/ 12.79).

It is to be observed that methods previously used for determination of Hg in flue gases have not always been accurate and have often indicated values lower than the actual ones. Consequently the reults obtained as to removal of Hg vapor in the following examples may not be comparable with prior art results determined by means of less accurate methods of analysis.

EXAMPLE 1

Eight test runs were performed using a partial stream of the flue gas from an incineration plant wherein domestic waste was incinerated.

The spray absorption process was performed in a spray absorber the chamber of which comprised a cylindrical portion having a diameter of 1.2 m and a hight of 0.8 m, and a conical bottom portion the cone angle of which was 60°. The spray absorber was provided with a rotary atomizer. Downstream of the spray absorber particle separation was performed using a baghouse.

An aqueous suspension of slaked lime or an aqueous solution of sodium carbonate (solids content of the suspension or solution app. 5%) was used as feed for the atomizer.

The temperature of the flue gas when led to the spray absorber was 225-300°C and the amount of fly ash therein was 0.5-1.0 g/Nm^3 in run nos. 1-5 whereas run nos. 6-8 were performed using flue gas with substantially no fly ash. The flue gas was supplied in an amount of 300 kg/h.

The concentration of mercury vapor was measured upstream of the spray absorber, between the spray ab-

sorber and the baghouse filter and downstream of the baghouse filter.

Run nos. 1 and 7 were performed for comparison and no activated carbon was added to the feed suspension of slaked lime or feed solution of sodium carbonate. In runs 2 through 6 and in run 8 activated carbon was added to said feed solution in an amount of app. 2% by weight of the solids content, corresponding to 0,04-0,05 g/Nm^3 of flue gas.

The following results were obtained:

	Run no. 1	2	3	4	5	6	7	8
Upstream of spray absorber								
Hg vapor, µg/Nm^3	241	290	725	517	314	423	213	405
Absorbent	Slaked lime	Slaked lime + activated carbon	slaked lime + activated carbon	slaked lime + activated carbon	slaked lime + activated carbon	slaked lime + activated carbon	Na_2CO_3	Na_2CO_3 + activated carbon
Between spray absorber and baghouse								
Gas temperature, °C	130	130	100	160	175	165	130	130
Hg vapor, µg/Nm^3	77	46	not analysed	not analysed	not analysed	not analysed	not analysed	not analysed
Downstream the baghouse								
Hg vapor, µg/Nm^3	30	20	11	42	63	80	96	47
% removal	87.6	93	98.9	92.9	79.9	81.1	54.9	88.4

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The above results clearly indicate that activated carbon acts as a very efficient absorbent for mercury vapor when utilized in the process of the present invention.

EXAMPLE 2

Two further test runs was made in the same plant and under similar conditions as described in example 1, except that the flue gas temperature varied between 280 and 300°C.

The results obtained are listed in the following table:

	Run No. 9	Run No. 10
Upstream of spray absorber		
PCDD[1] +PCDF, µg/Nm³	0.38	0.53
Absorbent	slaked lime	slaked lime + activated carbon
Between spray absorber and baghouse		
Gas temperature, °C	150	150
PCDD[1] +PCDF, µg/Nm³	not analysed	0.28
Downstream the baghouse		
PCDD[1] +PCDF, µg/Nm³	0.047	0.01
% removal	87.8	98.1

[1] The PCDD contents were approximately 35-45% of the total contents of PCDD and PCDF.

CLAIMS

1. A process for removal of mercury vapor and/or vapor of chlorodibenzodioxins and/or vapor of chlorodibenzofurans from a stream of hot flue gas combined with a simultaneous removal of acidic components of the flue gas, characterized in that an aqueous liquid, which besides alkaline components comprises suspended activated carbon is spray dried in the flue gas which subsequently is freed from the resulting particulate material.

2. The process of claim 1, wherein the amount of activated carbon in said aqueous liquid amounts to 5-500 mg per Nm^3 flue gas being treated.

3. The process of claim 1, wherein the amount of activated carbon in said aqueous liquid amounts to 5-200 mg per Nm^3 flue gas being treated.

4. The process of claim 1, wherein said alkaline components comprise calcium hydroxide in a quantity at least sufficient to neutralize a substantial part of the acidic components, such as sulfuroxides and hydrogen chloride, of the flue gas.

5. The process of claim 1, wherein said particulate material is recovered in a baghouse.

6. The process of claim 1, wherein at least a portion of any fly ash present in the flue gas stream remains in said stream during the spray absorption process and is recovered together with the particulate material formed by the spray absorption process.

7. The process of claim 1, wherein at least a portion of any fly ash present in the flue gas stream is collected from said stream before said aqueous liquid is spray dried therein, and at least a part of the collected fly ash is suspended in said aqueous liquid before spraying thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 86 30 5054 0208490

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.4)
A	US-A-4 049 399 (TELLER ENVIRONMENTAL SYSTEMS)		B 01 D 53/34
A	US-A-2 886 131 (J.R. CONLISK)		
D,A	US-A-4 273 747 (E. RASMUSSEN)		
A	US-A-4 246 242 (C.H.S. BUTLER)		
A	CHEMICAL ABSTRACTS, vol. 88, no. 2, 9th January 1978, page 125, abstract no. 9181j, Columbus, Ohio, US; T. HALMOE: "Micropollutants from an incineration plant lower than expected", & FAST AVFALL 1977, (1), 29-31		TECHNICAL FIELDS SEARCHED (Int. Cl.4) B 01 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26-08-1986	PYFFEROEN K.

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
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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
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(54) Method and system for removal of mercury emissions from coal combustion

(57) A method to reduce emissions in flue gas due to combustion of coal in a combustion unit (12) including the steps of: combusting coal in a primary combustion zone (25) of the combustion unit; releasing elemental mercury from the combustion into the flue gas; injecting NH_4Cl, NH_4Br, or NH_4I (36) into the flue gas; oxidizing the elemental mercury with halogen from the additive; adsorbing the oxidized mercury generated by the combustion of the coal with an adsorbent in the flue gas, and collecting the adsorbent with the oxidized mercury in a combustion waste treatment system (32).

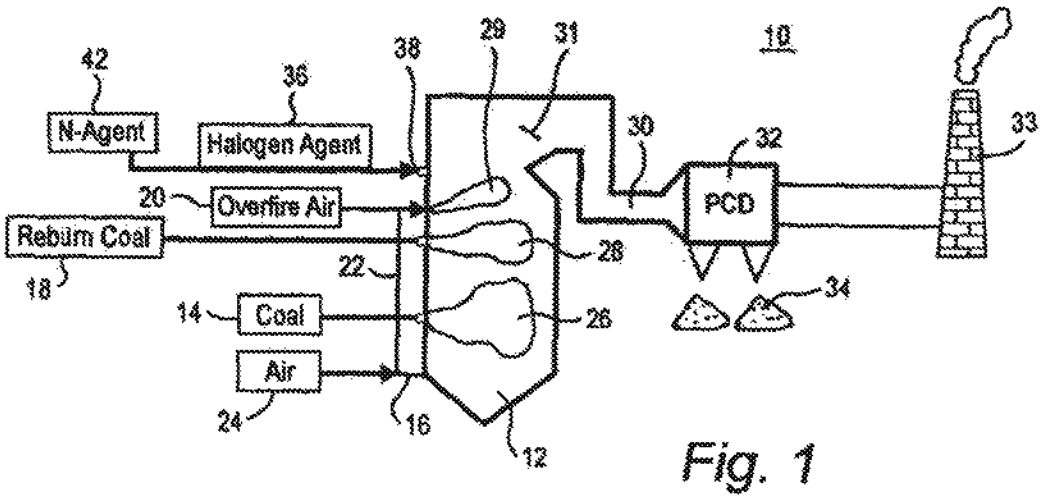


Fig. 1

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Description

[0001] This invention relates to the combustion of coal and in particular to the reduction of mercury (Hg) and nitrogen oxides (NOx) in flue gas generated during coal combustion.

[0002] Emissions from coal combustion can contain oxides of nitrogen (NOx) and volatile metals such as mercury (Hg). There is a long felt need to reduce Hg and NOx in gaseous emissions from coil-fired boilers and other industrial coal combustion systems.

[0003] As mercury volatizes during coal combustion, it enters the flue gas generated by combustion. Some of the volatized mercury can be captured by coal fly ash and removed via a particulate collection system. The volatized mercury that is not captured in the particulate collection system, or by some other control system, passes into the atmosphere with the stack gases from the coil boiler. It is desirable to capture as much of mercury in flue gas before the stack discharge.

[0004] Mercury volatizes as elemental mercury (Hg^0) during coal combustion. Oxidized mercury (Hg^{+2}) is more easily collected by emission control devices than is elemental mercury. Oxidization of mercury is a known technique to capture mercury and remove it from flue gases. As flue gases cool, mercury is partially oxidized by chlorine which is present in coal and released during combustion. It is believed that most oxidized mercury (Hg^{+2}) in flue gas is present as mercury chloride ($HgCl_2$). Oxidation of mercury occurs in combustion gas-phase reactions and on the surface of fly ash. It is believed that mercury oxidation on the surface of fly ash is a predominant channel of mercury oxidation.

[0005] Oxidized mercury ($HgCl_2$ or Hg^{+2}) is water soluble and is easily adsorbed on high carbon fly ash or activated carbon. The oxidized mercury captured by fly ash may be collected with the ash and removed via a particulate collection system. Oxidized mercury is also easily removed by wet scrubbers that are used to control sulfur dioxide (SO_2) emissions. Mercury control is generally most effective when the mercury in flue gas is mostly oxidized.

[0006] Controlling mercury emissions is complicated because mercury is present in flue gases in several different forms, such as elemental mercury (Hg^0) and oxidized mercury (Hg^{+2}). Mercury changes forms throughout the combustion process. To effectively control mercury emissions, a control system should take into account the form or speciation of the mercury present in the flue gases at the location of the control system in the flue gas stream. In addition, it would be beneficial if mercury emission controls reduced NOx in stack gases discharged by a power plant.

[0007] There is a special need to control mercury emission from boilers firing low-rank coals, such as coal from the Powder River Basin (hereinafter PRB) and lignite coals. These low-rank coals represent a significant portion of the coal energy market, especially in the U.S. These low-rank coals often have low sulfur content, which minimize SO_2 emissions. Mercury emissions from the burning of low-rank coals tends not to oxidize because of the low chlorine (Cl) content of the coal and the presence of other constituents in the coal that tend to suppress Hg oxidation. Chlorine assists in the oxidation of mercury in flue gas. The low chlorine levels in low rank coal results in relatively high levels of elemental mercury in the flue gas from low rank coal. There is a long felt need to reduce the levels of elemental mercury in flue gas in coal fired plants, especially when low-rank coals are fired.

[0008] The invention may be embodied as a method to reduce emissions in flue gas due to combustion of coal in a combustion unit including the steps of: combusting coal in a primary combustion zone of the combustion unit; releasing elemental mercury from the combustion into the flue gas; injecting NH_4Cl, NH_4Br, or NH_4I into the flue gas; oxidizing the elemental mercury with a halogen (chlorine, bromine, or iodine) from the injected additive; adsorbing the oxidized mercury generated by the combustion of the coal with an adsorbent in the flue gas, and collecting the adsorbent with the oxidized mercury in a combustion waste treatment system.

[0009] The invention may also be embodied as a method to reduce mercury in gas emissions from the combustion of coal in a combustion system, said method comprising: combusting the coal in a primary combustion zone of the combustion system, wherein elemental mercury (Hg^0) is released in the flue gas produced by the combustion; staging combustion air supplied to the combustion system by adding a portion of the combustion air to the primary combustion zone and a second portion of the combustion air to an overfire air zone downstream of the combustion zone; maintaining a stoichiometric ratio in the primary combustion zone of no greater than 1.1 so as to form active carbon in the fly ash generated by the combustion of coal; oxidizing the elemental mercury by injection of NH_4Cl, NH_4Br or NH_4I in the flue gas to generate oxidized mercury (Hg^{+2}); adsorbing the oxidized mercury in the flue gas by the active carbon in the fly ash, and collecting the fly ash with adsorbed mercury in a combustion waste treatment system.

[0010] The invention may be further embodied as a system to treat mercury in flue gas emissions from a coal fired furnace comprising: a primary combustion zone receiving combustion air and having a downstream passage for flue gases and fly ash generated during combustion; a coal injector adapted to inject coal into the primary combustion zone; an air injector adapted to introduce combustion oxygen into the combustion zone, wherein an stoichiometric ratio in the zone is no greater than 1.1 so as to form active carbon in the fly ash generated by the combustion of coal; an overfire air burnout zone downstream of the combustion zone and included in the downstream passage, wherein combustion air is injected into the burnout zone; an NH_4Cl, NH_4Br or NH_4I

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injector downstream of the primary combustion zone; a combustion treatment waste system coupled to the flue gas output and a discharge for captured particulate waste, and wherein said primary combustion zone burns the coal, and elemental mercury released in the flue gas reacts with injected additive to oxidize the mercury

[0011] Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:

FIGURE 1 is a schematic diagram of a coal fired power plant having a primary combustion zone with an additive injection system downstream of the primary combustion zone.

FIGURE 2 is a schematic diagram of coal fired power plant similar to the plant shown in Figure 1 wherein the additive injection is performed in cooperation with an overfire air (OFA) system.

FIGURE 3 is a schematic diagram of coal fired power plant similar to the plant shown in Figure 1 where the additive injector is in a conductive pass of the plant and the conductive pass also includes a Selective Catalytic Reduction (SCR) unit.

FIGURE 4 is a chart of the effects on mercury and NO_x emissions due to the injection of NH_4Cl at different flue gas temperatures.

FIGURE 5 is a chart of the effects on NOx and Hg emissions due to air staging and NH_4Cl injection.

FIGURE 6 is a schematic diagram of a computer model for predicting flue gas reactions due to the injection of NH_4Cl.

FIGURE 7 is a chart of predicted NOx reduction due to NH_4Cl injection.

FIGURE 8 is a chart of the predicted effects of NH_4Cl injection on, elemental an oxidized mercury in flue gas.

FIGURE 9 is a chart of the predicted effect of chlorine and bromine containing species on mercury oxidation.

[0012] Available mercury control technologies for coal-fired power plants tend to be more effective at removing oxidized mercury from flue gas than in removing elemental mercury. A technique has been developed to increase the fraction of oxidized mercury in flue gas by injecting an oxidizing a halogen additive, e.g., ammonium chloride (NH_4Cl), NH_4Br or NH_4I, into the flue gas. By increasing the fraction of oxidized mercury, the halogen additive increases the amount of mercury removal by activated carbon injection, wet scrubbers and other mercury control technologies. Simultaneously, the halogen additive injection decreases NOx emissions by reducing oxides of nitrogen to molecular nitrogen.

[0013] The presence of chlorine containing compounds in flue gas is an important factor in the oxidation of mercury. Chlorine is a halogen that oxidizes mercury. Low rank coals tend to have low chlorine content, e.g., less than 100 ppm, and a high content of alkali metals. These alkali metals tend to react with and remove the chlorine in the low rank coal flue gas. Mercury oxidation is suppressed during combustion of low rank coals because of the lack of chlorine in the flue gas. Adding chlorine to flue gas of low rank coal should assist in the oxidation of elemental mercury.

[0014] Other halogens including bromine (Br) and iodine (I) oxidize mercury to form $HgBr_2$ and HgI_2, respectively. Because of very low bromine and iodine contents in coal, these halogens typically contribute very little if any to mercury oxidation in flue gas. However, adding bromine or iodine to flue gas of low rank coals should improve mercury oxidation.

[0015] It has been discovered that mercury removal can be significantly improved by injecting ammonium chloride (NH_4Cl), NH_4Br or NH_4I into flue gas, especially in the flue gas from low-rank coals. The hot flue gas causes the additive to thermally decompose to form HCl, HBr or HI which results in more significant mercury oxidation. The increase in mercury oxidation allows for improved efficiency of mercury removal by activated carbon (AC) injection, wet flue gas desulfurization (FGD) systems, and other mercury control technologies.

[0016] The injected additive also reduces NOx emissions in a selective catalytic reduction (SCR) and/or (SNCR) process, especially if the additive is injected with a nitrogen agent (N-agent) into NOx and O_2 containing flue gas at flue gas temperatures in a range of 1600°F (Fahrenheit) to 2300°F. Injection of additive can also oxidize elemental mercury and improve the performance of the SCR process especially if the additive is injected with N-agent before the SCR unit.

[0017] FIGURE 1 shows a coal-fired power plant 10 comprising a coal combustion furnace 12, e.g., a boiler, having a coal fuel injection system 14, primary air injectors 16, reburn coal injectors 18 and overfire air (OFA) injectors 20. An exterior air duct 22 may distribute air provided by an air source 24, e.g., ambient air, to the primary combustion air injectors 16 and overfire air injectors 20. The coal injection system 14 and combustion air injectors 16 may be included in a low NOx burner (LNB) system.

[0018] The hot gas path through the furnace 12 includes a primary combustion zone 26, a reburn zone 28, an overfire air zone 29, and a convective pass 30. The power plant 10 further includes a particulate control device (PCD) 32 and a fly ash collection unit 34. Most of the coal is burned in a primary combustion zone 36 of

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the boiler 12. The remaining coal (or fuel) is injected downstream into the reburn zone 28 through the reburn injectors 18 to provide fuel-rich combustion in the reburn zone 28. Overfire air (OFA) is injected into the OFA burnout zone 29 to complete combustion. The hot flue gases flow through the post-combustion zone 31 of the boiler and to a conductive pass 30. Gas emissions are ultimately discharged through a smoke stack 33.

[0019] A halogen additive, e.g., ammonium chloride (NH_4Cl), NH_4Br or NH_4I, is injected as an aqueous solution 36 by nozzles 38 into the flue gas. The halogen assists in the oxidation of elemental mercury in the flue gas. The injection is made downstream from the primary combustion zone 26 at flue gas temperatures of, for example, 1600°F to 2300°F. The halogen additive can be co-injected with air, recycled flue gas, nitrogen or another carrier gas to increase the penetration of the additive aqueous solution across the flue gas path and to improve mixing of the additive aqueous solution and flue gas. Optionally, the halogen additive can be added to ammonia, urea or other N-agent solution 42 (in a SNCR process) to increase the efficiency of NOx reduction. A SNCR process is a selective non-catalytic reduction process in which ammonia, urea or another N-agent solution is injected into flue gas to reduce NOx emissions.

[0020] FIGURE 2 schematically shows a second coal fired power plant 44. Common reference numbers are used to identify components of the second plant that are common to the first plant 10. In the second plant 44, a halogen containing additive agent, an NH_4Cl aqueous solution 36 is injected through nozzles 46 into the boiler along with the OFA 20 into the burnout zone 29. As with the first plant, the boiler 12 of the second plant 44 can be retrofitted with OFA 20 and/or a reburn system 18. The additive can be injected separately downstream of the primary combustion zone, such as with or downstream of the OFA unit. The halogen additive can also be added with ammonia, urea or other N-agent solution 42 (SNCR process) to increase efficiency of NOx reduction.

[0021] FIGURE 3 schematically shows a third coal fired power plant 48. Common reference numbers are used to identify components of the third plant that are common to the first plant 10. In the third plant 48, the halogen containing additive is an aqueous NH_4Cl solution 36 that is injected via nozzles 50 into the conductive pass 30 of the boiler and upstream of a selective catalytic reduction (SCR) unit 52. SCR units are conventionally used to minimize NOx emissions by injecting a nitrogenous reducing agent (hereinafter N-agent), such as ammonia or urea, on the surface of a catalyst exposed to flue gas. An SCR unit is typically positioned in the conductive pass 30 where the flue gas is at a temperature of about 700° F. An SCR can relatively easily achieve 80% NOx reduction. As with the first plant, the boiler 12 of the third plant 48 can be retrofitted with OFA 20 and a reburn system 18. The additive can be added with ammonia, urea or other N-agent solution (SNCR process) to increase efficiency of NOx reduction.

[0022] To evaluate the injection of a NH_4Cl (a halogen containing additive) downstream of a primary combustion zone of a boiler, tests were performed in a 1.0 MMBTU/hr Boiler Simulator Facility (hereinafter BSF) to determine effect of NH_4Cl injection on Hg oxidation and NOx removal. The BSF is described in U.S. Patent 6,280,696.

[0023] Tests were conducted with and without air staging, e.g., with and without OFA. In tests without air staging, the stoichiometric ratio in the primary combustion zone 26 (SR1) was 1.16 which corresponded to about 2% excess air in the flue gas at the BSF emission discharge. The stoichiometric ratio is defined as the ratio of the O_2 to fuel concentrations to the ratio of O_2 to the fuel concentration that results in complete consumption of O_2 and fuel. Combustion of coal without air staging generated about 880 parts-per-million (ppm) of NOx. In the BSF test, the NH_4Cl was injected as an aqueous solution at a nitrogen stoichiometric ratio (NSR) of 0.6. The nitrogen stoichiometric ratio is defined as the ratio of the NH_4Cl concentration to the NO concentration in the flue gas at the location of NH_4Cl injection.

[0024] FIGURE 4 is a chart showing the effect of the injection of a NH_4Cl additive on mercury oxidation and on NOx reduction. During the tests reported in Figure 4, the BSF plant had no air staging. The test results shown in Figure 4 are for: no NH_4Cl additive (66), an NH_4Cl additive added at a flue gas temperature of 1700° F (68), and the NH_4Cl additive added to flue gas at 1850° F (60). Figure 4 shows the percentage of elemental mercury of the total mercury in the flue gas, and the percentage reduction in NOx due to the NH_4Cl injection. Without NH_4Cl injection, the concentration of elemental mercury in flue gas was about 60% of total mercury. No NO_x reduction was observed without NH_4Cl injection. Injection of the NH_4Cl additive at a flue gas temperature of 1700° F resulted in about a 30% NOx reduction and a decrease in the concentration of elemental mercury (Hg^0) from 60% to about 30% of total mercury indicating that the additive oxidized some mercury. Injection of the NH_4Cl additive at 1850° F resulted in more significant mercury oxidation while NOx reduction slightly decreased.

[0025] FIGURE 5 is a chart showing test conducted while BSF plant operated with air staging. In these tests, the SR_1 was 0.7, and SR2 was 1.16. SR_1 is the stoichiometric ratio in the primary combustion zone. SR2 is the stoichiometric ratio at the overfire air injection zone. Overfire air was injected at a flue gas temperature of 2200°F. NH_4Cl was injected as an aqueous solution where the flue gas temperature was at 1600° F. The amount of chlorine in the flue gas provided by NH_4Cl was 120 ppm, and the NSR was 1.5. Figure 5 shows the effect of the NH_4Cl additive injection on NOx reduction and the reduction of the concentration of the elemental mercury. The test results 62,64 presented in Figure 5 demonstrate that staging reduces NOx emissions by about 80% in comparison to no staging of combustion

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air, injection of the NH_4Cl additive 54 in conjunction with staging increased the efficiency of NOx reduction by an additional 7% (as compared to no NH4Cl-62) and decreased the percentage of elemental mercury (Hg^0) of the total mercury in flue gas from about 40% to about 20%. The BSF test results show in Figures 4 and 5 demonstrate that the injection of NH_4Cl at flue gas temperatures of 1700° F to 1850° F reduces NOx emissions and decreases the concentration of elemental mercury in flue gas.

[0026] A computer simulation process model was developed to predict the effect of NH_4Cl on NOx reduction and Hg oxidation. This process model is described in U. S. Patent No. 6,280,695.

[0027] FIGURE 6 illustrates a computer model used to describe the mixing of reagents with flue gas to the stream of NH_4Cl (so-called inverse mixing). The model treated the injection of gases introduced to the reaction over a certain period of time (mixing time) rather than instantaneously. FIGURE 6 schematically shows a process model 70 that treats the reacting system as a series of two plug-flow reactors R1 (72) and R2 (74). Each reactor describes one of the physical and chemical processes occurring in a boiler: addition of NH_4Cl, NOx reduction by N-agent, and mercury oxidation by chlorine compounds. The first reactor R1 describes mixing of flue gas and NH_4Cl using the model of inverse mixing. The mixture entering R1 consisted of NH_4Cl.

[0028] The flue gas was added to NH_4Cl at a constant rate over period of 120 ms. The flue gas added to R1 corresponds to products coming out of the OFA zone in a typical boiler with OFA. The second reactor R2 describes reactions in the burnout zone.

[0029] The mixing time and temperature profile in the mixing region R1 of the model were estimated using a single jet in a cross flow model. The mixing time was determined by evaluating the entrainment rate of fluid from the crossflow into the jet. For the NH_4Cl jet, the mixing time was estimated to be 110 ms (millisecond) to 120 ms. Variation of mixing time within the range of 120 ms ± 20 ms showed little effect on modeling results. A mixing time of 120 ms was used for NH_4Cl injection in the modeling results shown in Figures 7 and 8.

[0030] The initial amount of NO in the modeled flue gas was 500 ppm. The concentration of NH_4Cl in flue gas after injection was 500 ppm, which corresponded to an NSR of 1.0. The temperature of the flue gas decreased at a linear rate of 550 degrees Fahrenheit per second (F/s). Variations in the temperature gradient within ±50° F showed little effect on modeling predictions.

[0031] FIGURE 7 is a chart of the results of modeling that show the predicted temperature effect of NH_4Cl injection on NOx reduction. Figure 7 shows that NH_4Cl injection in a temperature range of 1600° F to 2300° F reduces NOx emissions. An optimal range according to the modeling for NOx reduction is 1750° F to 1950° F. The maximum predicted NOx reduction is about 73% where NSR is 1.0.

[0032] FIGURE 8 shows a predicted effect of NH_4Cl injection on mercury in flue gas. The NH_4Cl shows the predicted effect of injecting a spray of 500 ppm NH_4Cl in flue gas on mercury speciation. Total mercury concentration of mercury in the flue gas was 10 ppbv. It was assumed that all mercury was present in elemental form (Hg^0) prior to NH_4Cl injection. Modeling predicted that about 12% of the Hg^0 was oxidized by chlorine compounds in the gas phase due to NH_4Cl injection. Mercury oxidation during coal combustion can be catalyzed by minerals present in fly ash. Mechanism of that heterogeneous process is not well understood and was not considered in modeling. Accordingly, the amount of mercury oxidized in the flue gas may be substantially higher than that predicted by the model.

[0033] An equilibrium model was used to predict the effects of chlorine and bromine on mercury oxidation. Equilibrium modeling predicts the most stable composition of products at a specified temperature and pressure, thus indicating the dominant direction for the transformation of mercury-containing species.

[0034] FIGURE 9 shows a predicted effect of chlorine and bromine on concentration of oxidized mercury in flue gas resulting from combustion of a typical PRB coal. The concentration of oxidized mercury is shown as a percent of the total mercury in flue gas. Equilibrium modeling predicted that without additives all mercury is present in the elemental form at temperature higher than 700 °F. As temperature decreases, mercury is oxidized by chlorine or bromine released from coal into flue gas during coal combustion.

[0035] Modeling predicts that injection of chlorine or bromine in the amount of 3 ppm results in mercury oxidation at higher temperatures. Modeling also predicts that bromine is a more effective oxidizing agent than is chlorine. The model predicted that a presence of only 0.3 ppm of bromine in flue gas results almost in the same effect as 3 ppm of chlorine.

[0036] The equilibrium calculations predict that chlorine and bromine containing compounds are mercury oxidizing agents. Modeling also predicts that bromine containing compounds are stronger oxidizing agents than are chlorine containing compounds. It is believed that iodine containing compounds also should be strong mercury oxidizing additives.

[0037] For completeness, various aspects of the invention are set out in the following numbered clauses:

1. A method to reduce emissions in flue gas due to combustion of coal in a combustion unit (12), said method comprising:

   a. combusting coal in a primary combustion zone (25) of the combustion unit;
   b. releasing elemental mercury from the combustion into the flue gas;
   c. injecting a halogen-containing additive (36)

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into the flue gas;
d. oxidizing the elemental mercury with a halogen from the halogen-containing additive;
e. adsorbing the oxidized mercury generated by the combustion of the coal with an adsorbent in the flue gas, and
f. collecting the adsorbent with the mercury in a combustion waste treatment system (32).

2. A method as in clause 1 wherein the halogen-containing additive (36) is selected from a group consisting of NH_4Cl, NH_4Br and NH_4I.

3. A method as in clause 1 wherein the coal comprises a coal having a low chlorine content.

4. A method as in clause 3 wherein the coal having the low chlorine content is a Powder River Basin coal or lignite coal.

5. A method as in clause 3 wherein the coal having the low chlorine content has less than 100 parts-per-million (ppm) of chlorine.

6. A method as in clause 1 wherein the combustion waste treatment system includes a particle control device (32).

7. A method as in clause 1 wherein the adsorbent is fly ash, and the oxidized mercury is adsorbed on the fly ash.

8. A method as in clause 1 wherein the adsorbent is activated carbon, and the oxidized mercury is adsorbed on the activated carbon.

9. A method as in clause 1 further comprising heating the halogen-containing additive (36) with flue gas to generate HCl, HBr or HI and oxidizing the elemental mercury with the HCl, HBr or HI.

10. A method as in clause 1 further comprising injecting overfire air (20) downstream of the primary combustion zone to generate excessive carbon fly ash and the adsorbent is the fly ash.

11. A method as in clause 10 wherein the stoichiometric ratio (SR1) in the primary combustion zone is less than 1.1, and the stoichiometric ratio (SR2) at an overfire air injection zone is above 1.0.

12. A method as in clause 11 wherein SR1 is no greater than 0.8 and SR2 is no less than 1.16.

13. A method as in clause 1 further comprising coal reburning downstream of the primary combustion zone to form carbon in fly ash generated during combustion, and the fly ash is the adsorbent.

14. A method as in clause 1 further comprising injecting a nitrogenous reducing agent into the flue gas.

15. A method as in clause 14 further comprising a catalytic surface for NOx and mercury oxidation.

16. A method as in clause 1 wherein the halogen containing additive is injected where the flue gas is in a temperature range of 1600° F to 2300° F.

17. A method as in clause 1 wherein the halogen containing additive is injected where the flue gas is in a temperature range of 1750° F to 1950° F.

18. A method as in clause 1 wherein an amount of halogen injected into the flue gas by the halogen containing additive is in the range of 1 to 200 parts per million.

19. A method as in clause 1 wherein the halogen containing additive is injected in an aqueous solution into the flue gas.

20. A method as in clause 19 wherein the halogen containing additive is injected in the solution further comprising NH_4OH.

21. A method as in clause 19 wherein the halogen containing additive is injected in the solution further comprising urea.

22. A method as in clause 1 wherein the mercury released from combustion is mostly elemental mercury (Hg^0) and further comprising oxidizing the elemental mercury as the flue gases cools.

23. A method as in clause 22 wherein the oxidized mercury is removed from flue gas in a scrubber.

24. A method as in clause 1 further comprising injecting an aqueous solution of the halogen containing additive with a carrier gas.

25. A method as in clause 24 wherein the carrier gas is at least one of air, recycled flue gas and nitrogen gas.

26. A method to reduce mercury in gas emissions from the combustion of coal in a combustion system, said method comprising:

a. combusting the coal in a primary combustion zone of the combustion system, wherein elemental mercury (Hg^0) is released in the flue gas produced by the combustion;
b. staging combustion air supplied to the combustion system by adding a portion of the com-

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bustion air to the primary combustion zone and a second portion of the combustion air to an overfire air zone downstream of the combustion zone;
c. maintaining stoichiometric ratio in the primary combustion zone of no greater than 1.1 so as to form active carbon in the fly ash generated by the combustion of coal;
d. oxidizing the elemental mercury by injection of a halogen containing additive in the flue gas to generate oxidized mercury (Hg^{+2});
e. adsorbing the oxidized mercury in the flue gas by the active carbon in the fly ash, and
f. collecting the fly ash with adsorbed mercury in a combustion waste treatment system.

27. A method as in clause 26 wherein the halogen containing additive is selected from a group consisting of NH_4Cl, NH_4Br and NH_4I.

28. A method as in clause 26 wherein the combustion waste treatment system comprises a particle control device capturing the fly ash with adsorbed mercury and discharging the captured fly ash to a fly ash collection unit.

29. A method as in clause 26 wherein the combustion waste treatment system comprises a particle control device capturing the fly ash after the fly ash cools to a temperature no greater than 400 degrees Fahrenheit.

30. A method as in clause 25 further comprising coal reburning in the combustion system to form carbon in the fly ash generated during combustion.

31. A method as in clause 30 wherein an amount of reburning fuel used during the coal reburning is in a range of about 10 to about 30 percent of a total heat input of fuel used for the combustion.

32. A method as in clause 30 wherein an amount of reburning fuel used during the coal reburning is in a range of about 15 to about 25 percent of a total heat input of fuel used for the combustion.

33. A method as in clause 26 wherein combustion occurs in a low nitrogen oxide (NOx) burner.

34. A system to treat mercury in flue gas emissions from a coal fired furnace comprising:

a primary combustion zone receiving combustion air;
a coal injector adapted to inject coal into the primary combustion zone;
an air injector adapted to introduce combustion oxygen into the primary combustion zone,
a downstream passage of the primary combustion zone for flue gases and fly ash generated during combustion;
an injector in the downstream passage for injecting a halogen containing additive;
a combustion treatment waste system coupled to a flue gas output of the downstream passage and to a discharge for captured particulate waste, and
wherein said primary combustion zone burns the coal, and elemental mercury released in the flue gas reacts with the injected halogen containing additive to oxidize the mercury.

35. A system as in clause 33 wherein halogen containing additive is selected from a group consisting of NH_4Cl, NH_4Br and NH_4I.

36. A system as in clause 34 wherein the downstream passage comprises a duct downstream of the primary combustion zone to cool the flue gas and collect fly ash with the absorbed mercury.

37. A system as in clause 34 further comprising an overfire air burnout zone downstream of the combustion zone and included in the downstream passage, wherein combustion air is injected into the burnout zone.

38. A system as in clause 34 wherein the injector for the halogen containing additive further comprises a nozzle spraying an aqueous solution of halogen-containing additive in the flue gas.

Claims

1. A method to reduce emissions in flue gas due to combustion of coal in a combustion unit (12), said method comprising:

a. combusting coal in a primary combustion zone (26) of the combustion unit;
b. releasing elemental mercury from the combustion into the flue gas;
c. injecting a halogen-containing additive (36) into the flue gas;
d. oxidizing the elemental mercury with a halogen from the halogen-containing additive;
e. adsorbing the oxidized mercury generated by the combustion of the coal with an adsorbent in the flue gas, and
f. collecting the adsorbent with the mercury in a combustion waste treatment system (32).

2. A method as in claim 1 wherein the halogen-containing additive (36) is selected from a group consisting of NH_4Cl, NH_4Br and NH_4I.

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3. A method as in claim 1 wherein the coal comprises a coal having a low chlorine content.

4. A method as in claim 1 wherein the combustion waste treatment system includes a particle control device (32).

5. A method as in claim 1 wherein the adsorbent is fly ash, and the oxidized mercury is adsorbed on the fly ash.

6. A method as in claim 1 wherein the adsorbent is activated carbon, and the oxidized mercury is adsorbed on the activated carbon.

7. A method as in claim 1 further comprising heating the halogen-containing additive (36) with flue gas to generate HCl, HBr or HI and oxidizing the elemental mercury with the HCl, HBr or HI.

8. A method as in claim 1 further comprising injecting overfire air (20) downstream of the primary combustion zone to generate excessive carbon fly ash and the adsorbent is the fly ash.

9. A method to reduce mercury in gas emissions from the combustion of coal in a combustion system, said method comprising:

a. combusting the coal in a primary combustion zone of the combustion system, wherein elemental mercury (Hg^0) is released in the flue gas produced by the combustion;
b. staging combustion air supplied to the combustion system by adding a portion of the combustion air to the primary combustion zone and a second portion of the combustion air to an overfire air zone downstream of the combustion zone;
c. maintaining stoichiometric ratio in the primary combustion zone of no greater than 1.1 so as to form active carbon in the fly ash generated by the combustion of coal;
d. oxidizing the elemental mercury by injection of a halogen containing additive in the flue gas to generate oxidized mercury (Hg^{+2});
e. adsorbing the oxidized mercury in the flue gas by the active carbon in the fly ash, and
f. collecting the fly ash with adsorbed mercury in a combustion waste treatment system.

10. A system to treat mercury in flue gas emissions from a coal fired furnace comprising:

a primary combustion zone receiving combustion air;
a coal injector adapted to inject coal into the primary combustion zone;
an air injector adapted to introduce combustion oxygen into the primary combustion zone;
a downstream passage of the primary combustion zone for flue gases and fly ash generated during combustion;
an injector in the downstream passage for injecting a halogen containing additive;
a combustion treatment waste system coupled to a flue gas output of the downstream passage and to a discharge for captured particulate waste, and
wherein said primary combustion zone burns the coal, and elemental mercury released in the flue gas reacts with the injected halogen containing additive to oxidize the mercury.

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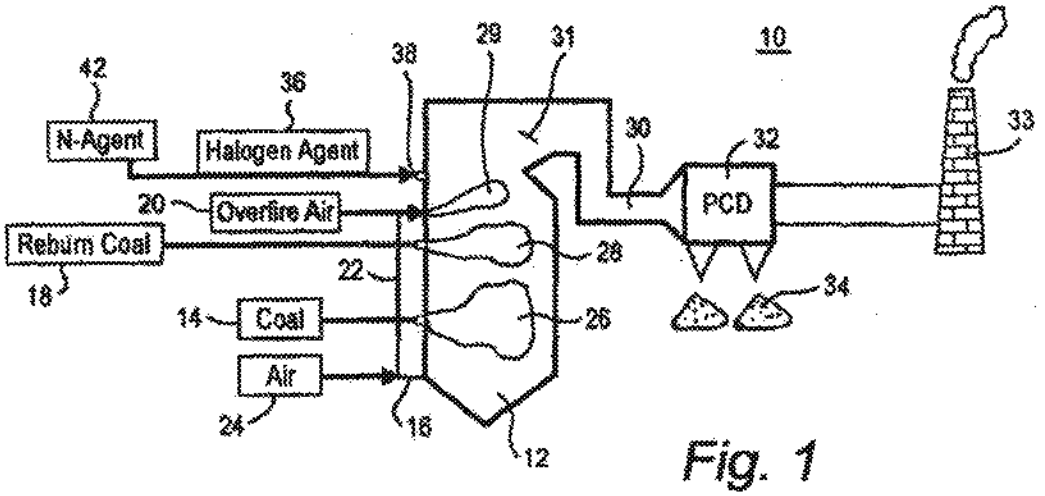


Fig. 1

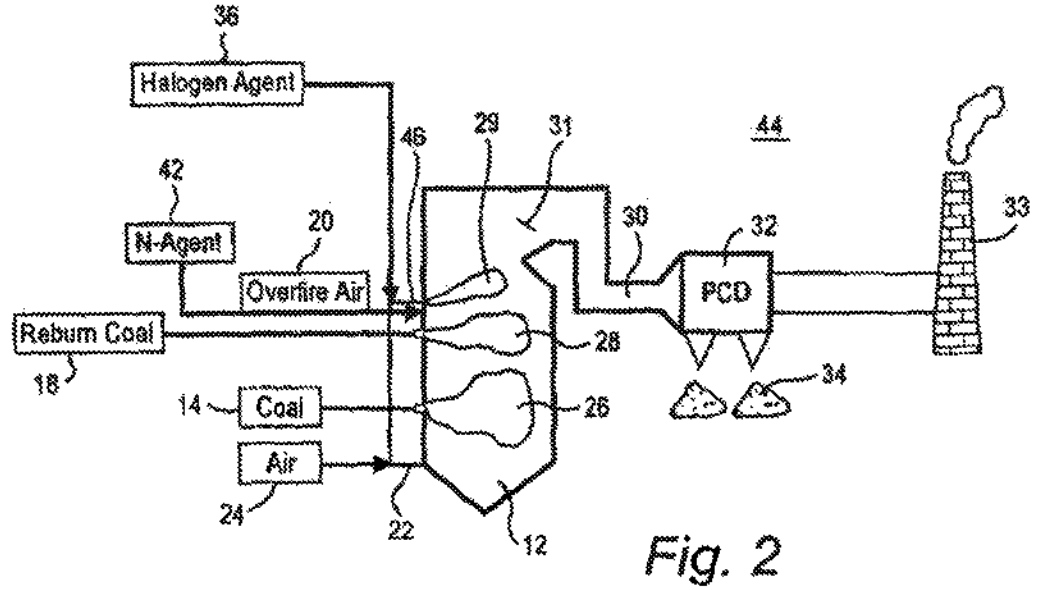


Fig. 2

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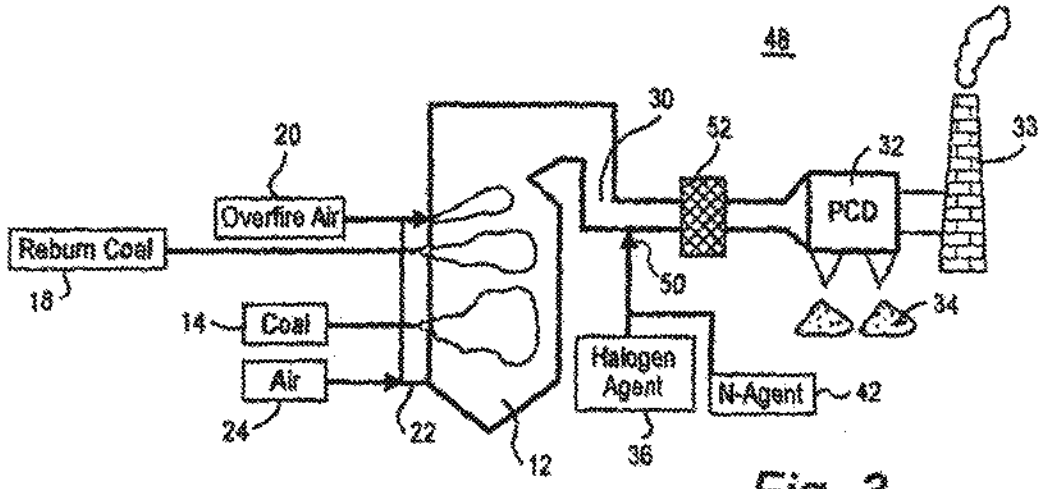


Fig. 3

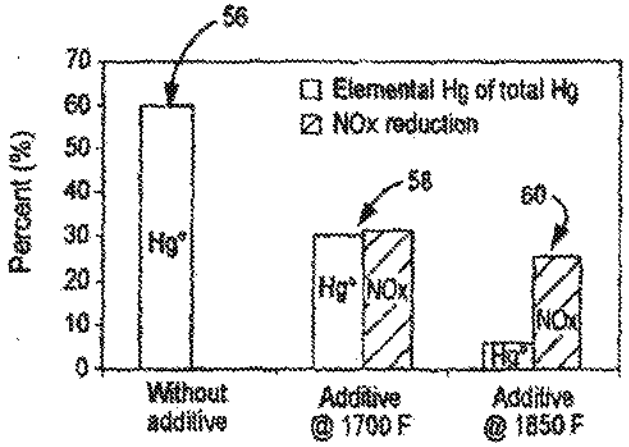


Fig. 4

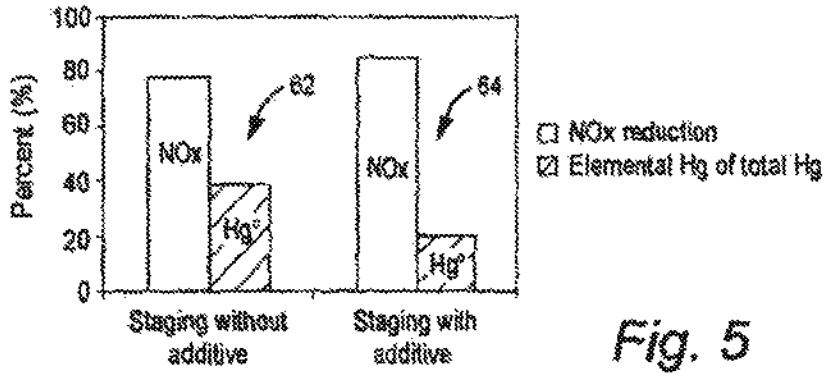


Fig. 5

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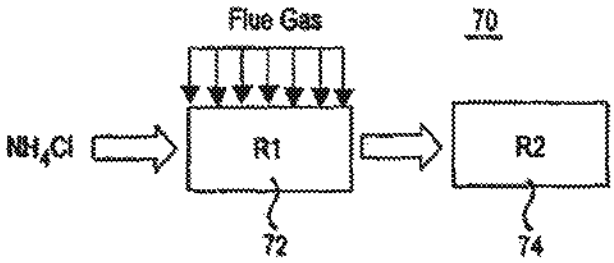


Fig. 6

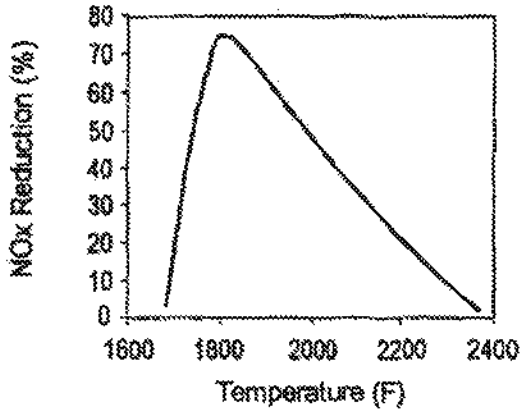


Fig. 7

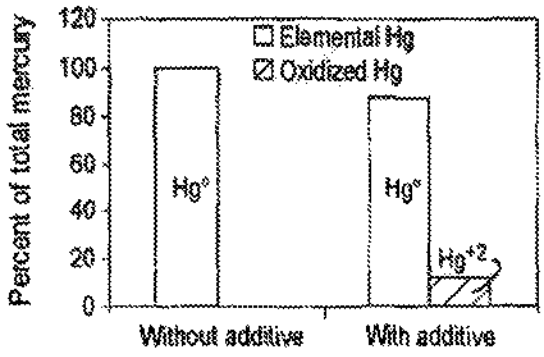


Fig. 8

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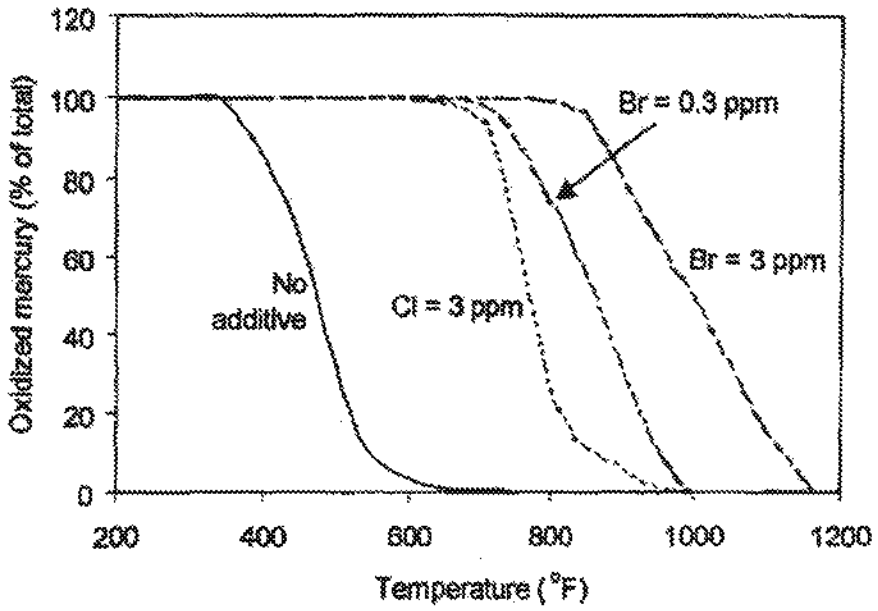


Fig. 9

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 25 8064

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)
Y X	US 2003/143128 A1 (LANIER WILLIAM STEVEN ET AL) 31 July 2003 (2003-07-31) * paragraphs [0014], [0017] - [0021], [0029]; figure 1 *	1-9 10	B01D53/64 B01D53/10
Y	US 1 984 164 A (STOCK ALFRED) 11 December 1934 (1934-12-11) * the whole document *	1-9	
Y	B.HALL, O.LINDQVIST, E.LJUNGSTRÖM: "Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions" ENVIRONMENTAL SCIENCE AND TECHNOLOGY, [Online] vol. 24, no. 1, 25 August 1989 (1989-08-25), - 1990 pages 108-111, XP002320099 USA * the whole document *	1-9	
Y	US 4 729 882 A (IDE ET AL) 8 March 1988 (1988-03-08) * abstract; claim 1 * * column 4, lines 17-40 *	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.7) B01D
Y	US 2002/117094 A1 (TELLER AARON J ET AL) 29 August 2002 (2002-08-29) * abstract * * paragraph [0027] *	1-9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	4 March 2005	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

EPO FORM 1503 03.82 (P04C01)

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 25 8064

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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04-03-2005

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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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No documents available for this priority number.

Espacenet

Bibliographic data: FR2529802 (A1) — 1984-01-13

Absorption compsn. for removing mercury from gas or liq.

Inventor(s): PELOSI JACQUES; SUGIER ANDRE ± (JACQUES PELOSI ET ANDRE SUGIER)

Applicant(s): PRO CATALYSE [FR] ± (PRO CATALYSE STE FSE PRODUITS CA)

Classification: - **international:** ***B01D53/64; B01J20/02; C02F1/28;*** (IPC1-7): B01D53/04; B01J20/16
- **cooperative:** **B01D53/64; B01J20/02; C02F1/281**

Application number: FR19820011821 19820706

Priority number (s): FR19820011821 19820706

Also published as: DE3324091 (A1)

Abstract of FR2529802 (A1)

The compsn. has total pore vol. at least 0.1 (0.2-0.7) cc/g, specific surface 10-250 (30-150) sq.m/g and S proportion 1-90 (5-60) wt.% w.r.t. binder. Opt. the compsn. contains, as auxiliary binder, 0.1-15 wt.%, w.r.t. total wt., of starch, PVA, Me cellulose, micro-polyethylene, epoxy-, polyester- or phenoplast resin. Prodn. comprises (1) shaping a mixt. of (a) hydratable or rehydratable Al2O3, SiO2, SiO2-Al2O3, cement, silicate, or Ca sulphate binder, (2) S, in natural condition, as flower of S, colloidal, in suspension or soln. opt. (c) porosity auxiliary, shrinking or volatilising below 150 deg.C, opt. (d) binder auxiliary and (2) drying below 150 (80-120) deg.C. Gases or liqs. are purified from Hg by contacting with the absorption compsn. The compsn. are stable, resist abrasion and crushing, neither disintegrate nor dissolve in water. The absorption capacity for Hg is 15-200 % w.r.t. initial mixt. Gases treated can contain 10 ng to 10 g Hg and the degree of purifcn. can reach 99.9%.

(19) RÉPUBLIQUE FRANÇAISE

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DE LA PROPRIÉTÉ INDUSTRIELLE

PARIS

(11) N° de publication : **2 529 802**
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(51) Int Cl³ : B 01 D 53/04; B 01 J 20/16.

(12) DEMANDE DE BREVET D'INVENTION A1

(22) Date de dépôt : 6 juillet 1982.

(30) Priorité

(43) Date de la mise à disposition du public de la demande : BOPI « Brevets » n° 2 du 13 janvier 1984.

(60) Références à d'autres documents nationaux apparentés :

(71) Demandeur(s) : *Société française de produits pour catalyse : PRO-CATALYSE SA.* — FR.

(72) Inventeur(s) : Jacques Pekoi et André Sugier.

(73) Titulaire(s) :

(74) Mandataire(s) : Jacques Savine.

(54) Masses d'absorption pour l'élimination du mercure.

(57) La présente invention concerne des masses d'absorption pour l'élimination du mercure présent dans un gaz ou un liquide et leur procédé de fabrication.

Les masses d'absorption sont caractérisées en ce qu'elles sont constituées de soufre et d'un liant choisi parmi : l'alumine, la silice, la silice-alumine, les ciments, le volume poreux total de la masse est supérieur ou égal à 0,10 cm^3/g, sa surface spécifique est comprise entre 10 et 250 m^2/g, la proportion en poids de soufre par rapport au liant est comprise entre 1 et 30 %.

FR 2 529 802 - A1

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2529802

MASSES D'ABSORPTION POUR L'ELIMINATION DU MERCURE

La présente invention concerne des masses d'absorption pour l'élimination du mercure présent dans un gaz ou un liquide et leur procédé de fabrication.

Les gaz naturels renferment, selon leur origine, des teneurs variables de mercure. Ces teneurs sont généralement de l'ordre de 0,1 à 50 microgrammes de mercure par m^3 de gaz. Du fait de la toxicité du mercure et des risques de pollution qui s'ensuivent, il s'avère nécessaire d'extraire le mercure de ces gaz naturels et, plus généralement, des nombreuses atmosphères qui peuvent contenir des traces de mercure.

Il a déjà été proposé de nombreuses masses d'absorption pour éliminer le mercure. Ainsi la demande de brevet français n° 2 310 795 décrit un procédé d'élimination du mercure dans un gaz ou un liquide à l'aide d'une masse solide d'absorption renfermant

a) un support solide choisi parmi le groupe formé par la silice, l'alumine, la silice-alumine, les silicates, les aluminates et les silicoaluminates et,

b) au moins un métal capable de former un alliage avec le mercure, ladite masse ayant une surface spécifique d'au moins $40 m^2/g$ et le métal étant présent dans ladite masse essentiellement sous forme de cristallites de diamètre moyen inférieur à 400 Å, le métal étant choisi parmi l'or, l'argent, le cuivre, le nickel ou certains de leurs mélanges.

De telles masses, bien que satisfaisantes, s'avèrent être d'une préparation assez complexe et nécessitent la mise en oeuvre de métaux peu économiques. Par ailleurs, de telles masses présentent des difficultés lors de leur régénération du fait de la tendance au regroupement des cristallites lors de celle-ci.

La demanderesse a mis au point des masses d'absorption pour l'élimination du mercure présent dans un gaz ou un liquide qui obvient aux inconvénients précités et qui présentent notamment l'avantage de présenter une capacité d'absorption du mercure nettement améliorée, d'être très simple à fabriquer et de posséder une excellente résistance mécanique aussi bien à l'attrition qu'à l'écrasement.

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La présente invention concerne en effet des masses d'absorption pour l'élimination du mercure présent dans un gaz ou un liquide caractérisé en ce qu'elles sont constituées de soufre et d'un liant choisi parmi : l'alumine, la silice, la silice-alumine, les ciments, les silicates, les sulfates de calcium le volume poreux total de la masse est supérieur ou égal à 0,10 cm^3/g, sa surface spécifique est comprise entre 10 et 250 m^2/g ; la proportion en poids de soufre par rapport au liant est comprise entre 1 et 90 % et de préférence entre 5 et 60%.

Les masses d'absorption selon l'invention présentent de préférence un volume poreux total compris entre 0,20 et 0,70cm^3/g, leur surface spécifique est de préférence comprise entre 30 et 150m^2/g et la proportion en poids de soufre par rapport au liant est de préférence comprise entre 5 et 60 %.

Le liant présent dans les masses d'absorption selon l'invention est choisi parmi : l'alumine, la silice, la silice-alumine, les ciments, les silicates de sodium ou de potassium, les sulfates de calcium.

La silice-alumine que l'on peut mettre en oeuvre selon l'invention est de préférence une argile choisie parmi : la kaolinite, la bentonite, l'halloisite et l'attapulgite.

Les ciments que l'on peut mettre en oeuvre selon l'invention sont de préférence choisis parmi : le ciment naturel, le ciment portland, les ciments métallurgiques, les ciments spéciaux, les ciments Ferrari, les ciments de pouzzolanes, les ciments alumineux. Plus particulièrement, on peut mettre en oeuvre les ciments alumineux réfractaires tels que, par exemple, les ciments SECAR ® commercialisés par la Société Lafarge. La composition moyenne de ces ciments est généralement la suivante :

Type de liant	Al_2O_3	CaO	Fe_2O_3	FeO	SiO_2	MgO	K_2O
SECAR 150	50	27	5	1	5	0,2	0,05
SECAR 250	70	26	0,1	0,2	0,2	0,2	0,05
Super SECAR 250	80	19	0,1	-	0,1	0,05	-

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SUITE

Type de liant	Na_2O	SO_3	S	P_2O_5	Mn_2O_3	Cr_2O_3	TiO_2
SECAR 150	0,05	0,05	0,05	0,10	0,02	0,10	3
SECAR 250	0,5	0,03	0,01	0,05	0,005	0,002	0,003
Super SECAR 250	1,0	0,05	0,01	0,05	0,005	0,003	0,003

L'alumine et la silice présentes dans les masses d'absorption de l'invention, sont sous les formes qui proviennent de leur séchage à une température inférieure à 150°C et de préférence comprise entre 80 et 120°C. Ces formes peuvent être variables suivant les matières premières utilisées pour la fabrication des masses ; elles sont largement décrites pour l'alumine dans l'encyclopédie Kirk-Othmer Vol. 2 (1974) ou dans l'ALCOA Paper n° 19 (1972) et pour la silice dans les ouvrages "The colloid Chemistry of silica" de Ralph K. Iler (1955 et 1979).

Lorsque l'alumine est présente comme liant dans les masses d'absorption selon l'invention, celles-ci présentent de préférence une répartition de pore telle que :

- 0,01cm^3/g à 0,15cm^3/g du volume poreux est constitué par des pores dont le diamètre est supérieur à 1 micron,
- 0,15 à 0,65cm^3/g du volume poreux est constitué par des pores dont le diamètre est supérieur à 0,1 micron,

Les masses d'absorption de l'invention contiennent de préférence du soufre tel que le diamètre moyen des particules de soufre est inférieur à 20 microns et de préférence compris entre 0,01 et 10 microns. D'une façon surprenante, la présence de particules de soufre ayant ces dimensions s'avère particulièrement favorable à l'élimination du mercure présent dans les gaz ou les liquides.

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Les masses d'absorption de l'invention peuvent en outre contenir de 0,1 à 15 % en poids par rapport au poids total de la masse d'un composé choisi parmi : l'amidon, l'alcool polyvinylique, la méthylcellulose, le micropolyéthylène, les résines époxy, les résines polyester et les résines phénoliques.

La présente invention concerne également le procédé de fabrication de ces masses d'absorption. Ce procédé est caractérisé en ce qu'il comporte les étapes suivantes :

1°) - Mise en forme d'un mélange comportant

a) un liant choisi parmi : l'alumine hydratée ou réhydratable, la silice, la silice-alumine, les ciments, les silicates et les sulfates de calcium,

b) du soufre à l'état natif, en fleur, colloïdal, en suspension, ou en solution,

c) et, éventuellement, un adjuvant de porosité soit rétractable, soit volatil à une température inférieure à 150°C.

2°) - Séchage de la masse obtenue à une température inférieure à 150°C et de préférence comprise entre 80 et 120°C.

Selon le procédé de l'invention, on opère la mise en forme du mélange par les moyens classiques et, en particulier, par extrusion, pastillage, mise en forme au drageoir tournant, nérumérisation (tel que décrit, par exemple, dans le brevet belge n° 840 770), égouttage dans l'huile (oil-drop), etc..

Selon le procédé de l'invention, la fonction essentielle réalisée par l'alumine hydratée ou l'alumine réhydratable, la silice, la silice-alumine, les ciments, les silicates ou les sulfates de calcium est de servir de liant pour le soufre de façon à obtenir après mise en forme et séchage un produit qui ne se désagrège pas et qui ne se délite pas au contact de l'eau.

Il est toutefois possible, selon une variante du procédé de l'invention lorsque cette fonction de liant n'est pas assurée de façon satisfaisante d'utiliser comme liant, au moins en partie, et de préférence de 0,1 à 15 % en poids, des polymères comme : l'amidon, l'alcool polyvinylique, la méthylcellulose, le micropolyéthylène ou des résines thermodurcissables comme : les résines époxy, les résines polyester et les résines phénoliques.

L'alumine hydratée que l'on peut mettre en oeuvre selon le procédé de l'invention peut être sous forme d'un sol ou d'un gel d'alumine peptisable. L'agent peptisant peut être l'eau, ou un acide faible comme l'acide formique, l'acide acétique, l'acide propionique ou un acide fort comme l'acide chlorhydrique ou l'acide nitrique. La quantité d'agent peptisant doit être suffisante pour convertir le gel en une masse plastique souple.

Les sols d'alumines peuvent notamment être des dispersions ou des suspensions de boehmites ou pseudo-boehmites fines ou ultra-fines qui sont composées de particules ayant des dimensions dans le domaine colloïdal c'est-à-dire inférieur à 2000 Å environ.

Les dispersions ou suspensions aqueuses de boehmites fines ou ultra-fines peuvent être obtenues ainsi qu'il est bien connu de l'homme de l'art par peptisation dans l'eau ou l'eau acidulée de ces produits. Les boehmites fines ou ultra-fines mises en oeuvre selon la présente invention peuvent notamment avoir été obtenues selon le procédé décrit dans les brevets français n° 1 261 182 et 1 381 282 ou dans la demande de brevet européen n° 15 196.

On peut mettre en oeuvre selon le procédé de l'invention, les suspensions ou dispersions aqueuses de boehmite ou de pseudo-boehmite ultra-pures préparées selon le procédé décrit ci-après.

Ce procédé est du type selon lequel on effectue la réaction d'un aluminate alcalin avec de l'anhydride carbonique pour former un précipité d'hydroxycarbonate d'aluminium amorphe, on sépare le précipité obtenu par filtration puis on lave celui-ci (le procédé est notamment décrit dans le brevet américain n° 3 268 295). Ensuite,

a) dans une première étape, on mélange le précipité lavé d'hydroxycarbonate d'aluminium amorphe avec une solution d'un acide, d'une base ou d'un sel ou de leurs mélanges ; ce mélange est effectué en versant la solution sur l'hydroxycarbonate, le pH du milieu ainsi constitué étant inférieur à 11,

b) dans une deuxième étape, on chauffe le milieu réactionnel ainsi constitué à une température inférieure à 90°C pendant un temps d'au moins 5 minutes,

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c) dans une troisième étape, on chauffe le milieu résultant de la deuxième étape à une température comprise entre 90°C et 250°C.

Selon ce procédé, la température de traitement de la deuxième étape est comprise entre 50 et 85°C, la durée du traitement étant comprise entre 5 minutes et 5 heures.

Selon ce procédé, l'acide mis en oeuvre dans la première étape est un acide minéral ou organique fort ou faible soluble dans l'eau et de préférence choisi parmi : l'acide nitrique, l'acide perchlorique, l'acide sulfurique, l'acide chlorhydrique, l'acide iodhydrique, l'acide bromhydrique, les acides formique, acétique, propanoïque, butanoïque, oxalique, maléïque, succinique, glutarique, les acides chloro et bromo-acétiques.

Selon ce procédé, la base mise en oeuvre dans la première étape est une base faible soluble dans l'eau et de préférence choisie parmi : l'ammoniaque, les amines tels que les méthyléthylpropylamines, les amino-alcools tels que les mono, di ou tri éthanol-amines et l'amino-2 propanol, les hydroxydes d'ammonium quaternaire et les produits susceptibles de se décomposer dans les conditions de réaction en donnant une base comme, par exemple, l'hexaméthylène tétramine ou l'urée.

Selon ce procédé, le sel mis en oeuvre dans la première étape est choisi parmi les sels dérivés de l'ammoniac et des amines et ceux comportant le cation aluminium et comportant les anions nitrate, chlorure, formiate, citrate, acétate ou oxalate.

Selon ce procédé, dans la première étape, la concentration en composé d'aluminium exprimée en Al_2O_3 du mélange est comprise entre 20 et 400g/l exprimée en Al_2O_3 et de préférence comprise entre 40 et 200g/l.

Selon ce procédé dans le mélange, selon la première étape, le rapport molaire entre la somme des anions et des cations présents (à l'exclusion de H^+ et OH^-) et l'équivalent exprimé en Al_2O_3 du composé d'aluminium est compris entre 0,01 et 2 et de préférence entre 0,03 et 0,9.

Selon ce procédé, la température de chauffage selon la troisième étape est comprise entre 100 et 160°C, la durée du chauffage étant comprise entre 10 minutes et 30 heures et de préférence entre 30 minutes et 10 heures.

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Les dispersions ou suspensions de boehmite et pseudo-boehmite obtenues selon ce procédé présentent une teneur en alcalins inférieure à 0,005 % exprimée sous forme du rapport pondéral oxyde du métal alcalin/Al_2O_3.

On peut également mettre en oeuvre comme alumine hydratée selon l'invention, les suspensions ou dispersions aqueuses obtenues à partir de pseudo-boehmite, de gels d'alumine amorphe, de gels d'hydroxyde d'aluminium ou d'hydrargillite ultra-fine.

La pseudo-boehmite peut notamment avoir été préparée selon le procédé décrit dans le brevet américain n° 3 630 670 par réaction d'une solution d'un aluminate alcalin avec une solution d'un acide minéral. Elle peut également avoir été préparée tel que décrit dans le brevet français n° 1 357 830 par précipitation à pH 9, à une température faiblement supérieure à l'ambiante à partir de réactifs de concentrations telles que l'on obtient environ 50 g/l d'alumine dans la dispersion.

Les gels d'alumine amorphe peuvent notamment avoir été préparés selon les procédés décrits dans l'article "Alcoa Paper n° 19 (1972) - pages 9 à 12" et notamment par réaction d'aluminate et d'acide, ou d'un sel d'aluminium et d'une base ou d'un aluminate et d'un sel d'aluminium ou par hydrolyse d'alcoolates d'aluminium ou par hydrolyse de sels basiques d'aluminium.

Les gels d'hydroxyde d'aluminium peuvent notamment être ceux qui ont été préparés selon les procédés décrits dans les brevets américains n° 3 268 295 et 3 245 919.

L'hydrargillite ultra-fine peut notamment avoir été préparée selon le procédé décrit dans le brevet français n° 1 371 808, par évolution à une température comprise entre la température ambiante et 60°C de gels d'alumine sous forme de gateau et contenant par rapport à l'alumine comptée en molécules d'Al_2O_3, 0,10 ions acides monovalents.

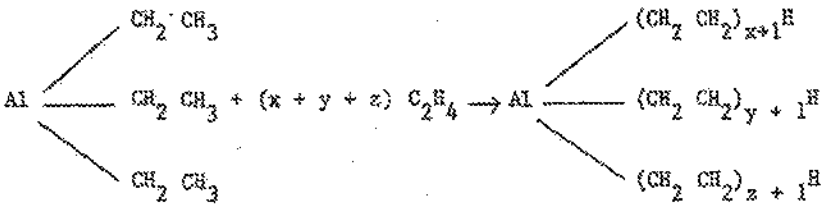
Selon le procédé de l'invention, on peut mettre en oeuvre les alumines hydratées de type boehmite obtenues comme sous-produit dans la fabrication de l'alcool par hydrolyse d'un

alcoolate ou alcoxyde d'aluminium (synthèse de Ziegler). Les réactions de synthèse d'alcools Ziegler sont décrites notamment dans le brevet américain n° 2 892 858. Selon ce procédé, on prépare tout d'abord le triéthylaluminium à partir d'aluminium, d'hydrogène et d'éthylène, la réaction étant réalisée en deux étapes avec recyclage partiel du triéthylaluminium.

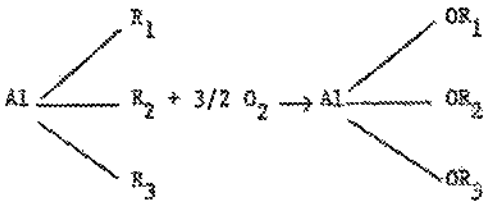
$$Al + 3/2\ H_2 + 2\ Al(C_2H_5)_3 \qquad 3Al(C_2H_5)_2H$$

$$3\ Al(C_2H_5)_2\ H + 3\ C_2H_4 \qquad 3\ Al\ (C_2H_5)_2$$

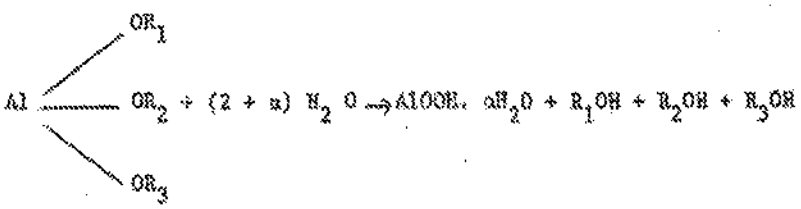
on ajoute de l'éthylène dans l'étape de polymérisation



on oxyde ensuite le produit obtenu en alcoolate d'aluminium.



les alcools étant obtenus par hydrolyse



la pâte d'hydroxyde d'aluminium obtenue peut être éventuellement après séchage et calcination utilisée selon le procédé de l'invention.

L'alumine hydratée obtenue comme sous-produit dans la réaction de Ziegler est notamment décrite dans un bulletin de la Société Conoco du 19 janvier 1971.

On peut également mettre en oeuvre les formes déshydratées ou partiellement déshydratées des alumines hydratées qui sont constituées d'alumines de transition et qui comportent notamment au moins une des phases prises dans le groupe constitué par rhô, chi, êta, gamma, kappa, thêta, delta (à l'exclusion de préférence de l'alumine alpha).

L'alumine que l'on peut mettre en oeuvre selon le procédé de l'invention peut être sous forme d'alumine comprenant une proportion prépondérante d'alumine réhydratable. Une telle alumine présente une structure mal cristallisée et/ou amorphe et par exemple peut être obtenue selon le procédé tel que décrit dans le brevet français n° 1 438 497. (Cette alumine est parfois appelée de façon générique "Alumine Flash").

Au sens de ce procédé, on entend par alumine de structure mal cristallisée, une alumine telle que l'analyse aux rayons X donne un diagramme ne présentant qu'une ou quelques raies diffuses correspondant aux phases cristallines des alumines de transition basse température et comportant essentiellement les phases chi, rho, êta, gamma, pseudogamma et leurs mélanges.

On entend par alumine de structure amorphe, une alumine telle que son analyse aux rayons X ne décèle aucune raie caractéristique d'une phase cristalline quelconque.

L'alumine active réhydratable mise en oeuvre est généralement obtenue par déshydratation rapide des hydroxydes d'aluminium tels que la bayerite, l'hydrargillite ou gibbsite, la nordstrandite ou des oxyhydroxydes d'aluminium tels que la boehmite et le diaspore. Cette déshydratation peut être opérée dans n'importe quel appareillage approprié à l'aide d'un courant de gaz chaud. La température d'entrée des gaz dans l'appareillage varie généralement de 400 à 1200°C environ et le temps de contact de l'hydroxyde ou de l'oxyhydroxyde avec les gaz chauds est généralement compris entre une fraction de seconde et 4 à 5 secondes.

La surface spécifique mesurée par la méthode BET de l'alumine active réhydratable obtenue par déshydratation rapide d'hydroxydes ou d'oxyhydroxydes varie généralement entre environ 50 et 400m^2/g, le diamètre des particules est généralement compris entre 0,1 et 300 microns et de préférence entre 1 et 120 microns. La perte au feu mesurée par calcination à 1000° varie généralement entre 3 et 15%, ce qui correspond à un rapport molaire H_2O/Al_2O_3 compris entre environ 0,17 et 0,85.

Selon un mode de mise en oeuvre particulier, on utilise de préférence une alumine active provenant de la déshydratation rapide de l'hydrate Bayer (hydrargillite) qui est l'hydroxyde d'aluminium industriel facilement accessible et très bon marché ; une telle alumine active est bien connue de l'homme de l'art, son procédé de préparation a notamment été décrit dans le brevet français n° 1 108 011.

La silice que l'on peut mettre en oeuvre selon le procédé de l'invention est toute silice possédant les propriétés de liant désirées et notamment celles commercialisées sous la marque Ludox®.

La silice-alumine et les ciments que l'on peut mettre en oeuvre selon le procédé de l'invention sont ceux qui ont été décrits ci-dessus.

Le soufre mis en oeuvre selon le procédé de l'invention est à l'état natif, en fleur, en suspension, en solution, à l'état colloïdal ou dissout dans un solvant organique tel que le toluène par exemple.

La dimension des particules de soufre doit être telle que leur diamètre moyen est inférieur à 20 microns et de préférence compris entre 0,01 et 10 microns.

Les adjuvants de porosité volatils à une température inférieure à 150°C sont choisis parmi : le naphtalène, le carbonate d'ammonium, l'hydrogénocarbonate d'ammonium, la méthylcellulose, l'éthylcellulose, la carboxyméthylcellulose, les sucres, les gommes, la cellulose microcristalline. Ces adjuvants ont pour fonction de créer de la macroporosité, c'est-à-dire des pores dont le diamètre est supérieur ou égal à 0,1 micron. Ils doivent être éliminables par chauffage à une température inférieure à 150°C.

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Les adjuvants de porosité rétractables à une température inférieure à 150°C sont choisis parmi : les fibres textiles, les fibres de verre, les fibres d'amiante, les fibres d'alumine.

Ces adjuvants ont pour fonction de créer également de la macroporosité, ils améliorent également la résistance mécanique des masses d'absorption qui les contiennent.

Dans le procédé selon l'invention, le mélange peut comporter en outre la mise en oeuvre dans une proportion en poids par rapport au poids total du mélange de 0,1 à 15 % d'un composé choisi parmi : l'amidon, l'alcool polyvinylique, la méthylcellulose, le micropolyéthylène, les résines époxy, les résines polyester et les résines phénoliques. Ces composés, ainsi qu'il a été décrit ci-dessus, ont pour fonction d'améliorer, lorsque ceci est nécessaire, la solidité mécanique des masses lorsque la fonction du liant n'est pas assurée de façon satisfaisante par l'alumine, la silice, la silice-alumine ou les ciments.

Le mélange entre le soufre et le liant est opéré de telle façon dans la masse obtenue, la proportion en poids de soufre par rapport au liant est comprise entre 1 et 90 % et de préférence 5 et 60 %.

La mise en forme du mélange liant, soufre et éventuellement agent porogène est effectuée par les moyens classiques qui ont été rappelés ci-dessus : extrusion, pastillage, drageoir tournant, séchage, égouttage dans l'huile...

On opère de préférence cette mise en forme par extrusion. Cette extrusion peut être réalisée avantageusement en présence de divers agents tensio-actifs anioniques, cationiques et non ioniques, à condition qu'ils ne laissent pas de résidu nuisible dans les masses pour leur utilisation ultérieure. Parmi les agents tensio-actifs convenables, on peut citer les alcools en $C_3 - C_{12}$ les polyéthers d'alcools primaires linéaires, les diméthyl-silicones, les copolymères silicone-polyéther, ainsi que les divers composés polymères connus du type polyoxyéthylène alcoylphénols, polyoxyéthylène esters d'acides gras, polyoxyéthylène alcools, polyoxyéthylène mercaptans, polyoxyéthylène alcoylamines, polyoxyéthylène alcoylamides, etc.. convient particulièrement comme agent tensio-actif un polyéther d'alcool

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primaire linéaire, fourni dans le commerce sous la marque Antarox BL-240. De préférence, l'agent tensio-actif est utilisé dans la proportion approximative de 0,1 à 10,0% en poids par rapport au mélange.

En ce qui concerne la mise en forme par extrusion des compositions de l'invention contenant de l'alumine hydratée, celle-ci peut être réalisée dans les conditions bien connues de l'homme de l'art et qui notamment ont été décrites dans les brevets belges n° 830 652 et 840 770 ainsi que dans les brevets français n° 2 265 452, 2 307 576, 2 364 063, 2 374 956, 2 387 683 et dans le brevet anglais n° 1 094 360.

En ce qui concerne la mise en forme par extrusion des compositions de l'invention contenant de l'alumine réhydratable, celle-ci peut être réalisée dans les conditions bien connues de l'homme de l'art et qui, notamment, ont été décrites dans les brevets français n° 2 351 071, 2 354 815, 2 397 375, 2 398 540 et 2 413 323 ainsi que dans le brevet américain n° 3 404 111.

Les masses d'absorption de l'invention présentent une stabilité très améliorée, une excellente résistance mécanique aussi bien à l'attrition qu'à l'écrasement, une bonne tenue à l'eau : elles ne se désagrègent ou ne se délitent pas à son contact. De plus, les masses de l'invention présentent une capacité d'absorption du mercure considérablement améliorée, généralement cette capacité est supérieure à 15 % et peut atteindre 200 % exprimée en poids de mercure absorbé par rapport au poids de la masse initiale.

Le domaine de température dans lesquelles ces masses peuvent être utilisées est habituellement compris entre - 50°C et 150°C ; les températures optimales peuvent différer selon les gaz à traiter et leur composition de façon à éviter une condensation trop importante de l'eau ou d'autres produits condensables.

Cette captation peut être réalisée à pression atmosphérique ou sous une pression plus basse ou plus élevée, la pression totale pouvant atteindre par exemple 200 bars.

La V.V.H. (volume de charge exprimé à température et pression normale par volume de masse de captation et par heure) pourra varier par exemple de 50 à 50 000 mais on opérera de préférence à

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une V.V.H. comprise entre 200 et 20 000, selon la pression à laquelle on opèrera et selon la teneur en mercure des gaz à traiter et le taux d'épuration que l'on voudra réaliser.

Les gaz traités peuvent renfermer par exemple de 10 nanogrammes à 10 grammes ou plus de mercure par mètre cube.

Le dispositif d'élimination du mercure peut être constitué d'un seul réacteur ou d'au moins deux réacteurs en parallèle mais on utilisera préférentiellement au moins deux réacteurs en série.

L'efficacité des masses de piégeage du mercure est évaluée au moyen de deux appareillages, l'un fonctionnant à la pression atmosphérique, l'autre à 30 bars.

L'appareillage consiste en un tube métallique dont l'inactivité pour la fixation du mercure a été contrôlée, contenant 30ml de la masse de captation à tester et dans lequel on fait passer un débit réglable de gaz.

La détermination de la teneur en mercure est faite au moyen d'un analyseur à mercure COLEMAN basé sur la méthode de HATCH et OTT décrite dans Analytical Chemistry de décembre 1968.

Les essais en phase liquide sont faits à température ambiante avec du pentane contenant 4µg de mercure par litre, injecté à l'aide d'une pompe doseuse.

Les exemples suivants sont destinés à illustrer l'invention et ne doivent en aucune manière en limiter la portée aux modes de réalisation spécifiques qui y sont décrits.

EXEMPLE

A - PREPARATION DES MASSES

MASSE A -

80 Kg de poudre de gel d'alumine hydratée de type boehmite sont soigneusement malaxés à 20 Kg de soufre micronisé.

Le gel d'alumine est obtenu comme sous produit dans la fabrication d'alcools par hydrolyse d'un alcoolate ou d'un alcoxyde d'aluminium, sa surface spécifique est de 150m^2/g, sa teneur en eau est de 20% poids et sa granulométrie est inférieure à 20µ.

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50% du poids du soufre micronisé utilisé a une granulométrie inférieure à 9µ et il n'y a pas de particules de soufre d'un diamètre supérieur à 24µ.

Lors du malaxage, on ajoute 44 litres d'eau, 1,2 litre d'acide chlorhydrique 12N et 5,2kg de naphtaline.

La pâte ainsi obtenue est ensuite extrudée en extrudés de 3mm de diamètre et 4mm de longueur. Après séchage à l'étuve à 80°C, pendant 8 heures, puis à 120°C pendant 3 heures, les extrudés ont une surface spécifique de $50m^2/g$, une résistance à l'écrasement de $1kg/mm^2$ et un volume poreux total de $0,28cm^3/g$, dont $0,09cm^3$ de porosité supérieure à 1 micron.

La teneur en soufre de la masse est de 22 %.

MASSE B -

On mélange soigneusement 80kg de poudre d'alumine active réhydratable, obtenue par déshydratation rapide de bayerite à une température de 800°C, avec 20 kg d'une suspension aqueuse de soufre colloïdal à 60% poids de soufre et 300g de méthylcellulose.

L'alumine a une granulométrie moyenne de 4 microns et une surface spécifique de $300m^2/g$.

50% poids du soufre colloïdal utilisé à une granulométrie inférieure à 4µ et il n'y pas de particules de soufre d'un diamètre supérieur à 15µ.

Le mélange est ensuite dragéifié ; lors de la dragéification, la poudre est humidifiée par pulvérisation de 27 litres d'eau contenant 2,7kg de Na_2O sous forme de NaOH.

Les billes de 2,4 - 4mm obtenues sont mûries 24 heures à 20-30°C puis séchées à 80°C pendant 8h et à 120°C pendant 3h.

La surface spécifique des billes obtenues est de $145m^2/g$. L'écrasement grain à grain est de 7kg et le volume poreux total est de $0,24cm^3/g$ dont $0,04cm^3$ de porosité supérieure à 1 micron.

La teneur en soufre de la masse B est de 21%.

MASSE C -

80Kg de ciment type Secar 250 produit par la Compagnie Lafarge sont mélangés soigneusement à 20Kg de soufre colloïdal identique à celui utilisé pour préparer la masse B.

Le mélange est ensuite dragéifié au drageoir par pulvérisation d'eau.

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Les billes de 2,4 - 4mm obtenues sont ensuite mûries 24 heures à 20-30°C puis séchées à 80°C pendant 9 heures et à 120°C pendant 3 heures.

Les billes ainsi obtenues ont une surface spécifique de $60m^2/g$, une résistance à l'écrasement supérieure à 8kg et un volume poreux total de 0,21cm/g dont $3cm^3$ de porosité supérieure à 1 micron.

La teneur en soufre de la masse C est de 20%.

B - TESTS -

L'efficacité des masses préparée et évaluée en faisant passer un gaz naturel contenant du mercure sur $20cm^3$ de masse de piégeage contenu dans un tube métallique revêtu de 1cm de diamètre dont l'inactivité pour la captation de mercure a été vérifiée.

Le gaz naturel utilisé a une composition en % volume de 84% de méthane et de 0,3% d'hydrocarbures en 3 atomes de carbone ou plus.

L'efficacité initiale des masses est évaluée à température ambiante et à diverses VVH avec un gaz naturel ayant une teneur en mercure de $10mg/m^3$ pour les essais à pression atmosphérique et de $1mg/m^3$ pour les essais sous 30 bars.

L'efficacité est définie pour le rapport :

$$\frac{\text{teneur en Hg à l'entrée - teneur en Hg à la sortie}}{\text{teneur en mercure à l'entrée}} \times 100$$

Les résultats obtenus sont donnés dans le tableau suivant :

MASSE	VVH	P	TAUX D'EPURATION
A	100	1	99,9
	1000	1	99,5
	2000	1	95,2
B	500	1	99,9
	1000	1	99,9
	2000	1	99,4
C	500	1	99,9
	1000	1	99,7
	2000	1	99,1

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Essais sous pression de 30 bars :

MASSE	VVH	P	TAUX D'EPURATION
A	10000	30	99,9
	15000	30	99,5
B	10000	30	99,9
	15000	30	99,9
C	10000	30	99,9
	15000	30	99,7

Dans le but d'évaluer la capacité d'absorption de ces masses, on fait passer un volume de gaz sur ces masses à 30 bars tel qu'à VVH 5000, la quantité de mercure fixée est de 8 % du poids total de ces masses.

L'on fait ensuite un test d'activité pour évaluer l'efficacité de ces masses dans les mêmes conditions que celles définies pour l'essai pour 30 bars de pression.

MASSE	VVH	P	TAUX D'EPURATION
A	10000	30	99,7
	15000	30	99,1
B	10000	30	99,9
	15000	30	99,8
C	10000	30	99,8
	15000	30	99,5

REVENDICATIONS

1) Masses d'absorption pour l'élimination du mercure présent dans un gaz ou un liquide caractérisé en ce qu'elles sont constituées de soufre et d'un liant choisi parmi : l'alumine, la silice, la silice-alumine, les ciments, les silicates, les sulfates de calcium, le volume poreux total de la masse est supérieur ou égal à $0,10cm^3/g$, sa surface spécifique est comprise entre 10 et $250m^2/g$, la proportion en poids de soufre par rapport au liant est comprise entre 1 et 90 %.

2) Masses d'absorption selon la revendication 1 caractérisées en ce que leur volume poreux total est compris entre $0,20cm^3/g$ et $0,70cm^3/g$, leur surface spécifique est comprise entre 30 et $150m^2/g$ et la proportion en poids de soufre par rapport au liant est comprise entre 5 et 60 %.

3) Masses d'absorption selon l'une quelconque des revendications 1 ou 2 caractérisées en ce que le diamètre moyen des particules de soufre est inférieur à 20 microns et de préférence compris entre 0,01 et 10 microns.

4) Masses d'absorption selon l'une quelconque des revendications 1, 2 ou 3 caractérisées en ce que le liant est l'alumine et en ce que la répartition de pore de ces masses est telle que
- $0,01cm^3/g$ à $0,15cm^3/g$ du volume poreux est constitué par des pores dont le diamètre est supérieur à 1 micron,
- 0,15 à $0,65cm^3/g$ du volume poreux est constitué par des pores dont le diamètre est supérieur à 0,1 micron,

5) Masses d'absorption selon l'une quelconque des revendications 1, 2 ou 3 caractérisées en ce que les ciments sont choisis parmi : le ciment naturel, le ciment portland, les ciments métallurgiques, les ciments spéciaux, les ciments Ferrari, les ciments de pouzzolanes, les ciments alumineux.

6) Procédé de fabrication des masses d'absorption selon l'une quelconque des revendications précédentes caractérisé en ce qu'il comporte les étapes suivantes :

1°) Mise en forme d'un mélange comportant

a) un liant choisi parmi : l'alumine hydratée ou réhydratable, la silice, les silices-alumines, les ciments, les silicates, les sulfates de calcium,

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b) du soufre à l'état natif, en fleur, colloïdal, en suspension, ou en solution,

c) et éventuellement un adjuvant de porosité soit rétractable, soit volatif à une température inférieure à 150°C.

2°) Séchage de la masse obtenue à une température inférieure à 150°C et de préférence comprise entre 80 et 120°C.

7) Procédé de fabrication des masses d'absorption selon la revendication 6 caractérisé en ce que la mise en forme est opérée par extrusion, pastillage, mise en forme au dragenir tournant, mérumérisation, égouttage dans l'huile.

8) Procédé selon l'une quelconque des revendications 6 ou 7 caractérisé en ce que le diamètre moyen des particules de soufre est inférieur à 20 microns et de préférence compris entre 0,01 et 10 microns.

9) Procédé selon la revendication 6 caractérisé en ce que le mélange comporte en outre, dans une proportion en poids par rapport au poids total du mélange de 0,1 à 15 %, un composé choisi parmi : l'amidon, l'alcool polyvinylique, la méthylcellulose, le micropolyéthylène, les résines époxy, les résines polyester et les résines phénoliques.

10) Procédé selon la revendication 6 caractérisé en ce que l'adjuvant de porosité est choisi parmi : le naphtalène, le carbonate d'ammonium, l'hydrogénocarbonate d'ammonium, la méthylcellulose, l'éthylcellulose, la carboxyméthylcellulose, les sucres, les gommes, la cellulose microcristalline, les fibres textiles, les fibres de verre, les fibres d'amiante, les fibres d'alumine.

11) Procédé d'élimination du mercure présent dans un gaz ou un liquide caractérisé en ce que l'on met le gaz ou le liquide en contact avec la masse d'absorption selon l'une quelconque des revendications 1 à 5.

Espacenet

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MERCURY VAPOUR SEPARATION

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(54) **Mercury vapour separation**

(54) Mercury vapor in a gas can easily be removed from the gas by contacting the gas with an adsorbent comprising an activated carbon having as supported thereon (1) one or more components included in one of three groups shown below and (2) one or more components included in the remaining two groups shown below.

Group	Component
I	sulfur
II	sulfate and nitrate of Al, V, Fe, Co, Ni, Cu, Zn or NH_4
III	oxide of iodine, oxyacid corresponding to the oxide of iodine, salt of said oxyacid, and bromide and iodide of K, Na or NH_4

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SPECIFICATION

Process for removal of mercury vapor and adsorbent therefor

The present invention relates to a process for the removal of mercury vapor and an adsorbent thereof.

Electrolytic hydrogen is used in process for manufacturing various products such as pharmaceutical and food products, whereby trace amounts of mercury vapor act as catalyst poison and also contaminate such products, thus constituting in some instances the cause of much argument. Mercury vapor contained in natural gas corrodes heat exchanger made of aluminum and other types of equipment in the process of gas liquefaction, and is responsible for serious disasters. Also, mercury vapor contained in incinerator waste gases and waste gases from factories handling mercury is regarded as controversial from the standpoints of air pollution control and working environment preservation.

Therefore, it becomes necessary to remove mercury vapor in these gases by means of some appropriate treatment. As the method of removing mercury vapor in gas, there have been conventionally known the process of washing with chemical solutions and the method of dry adsorbing with use of adsorbents such as activated carbon and ion exchange resins. Nevertheless, the first-mentioned process of washing with chemical solutions suffers from the defects that the efficiency of removal of mercury vapor is poor and that waste solutions are produced, while the last-mentioned dry adsorption method, with its respectively small capacity to adsorb mercury vapor, is far from satisfactory.

The present inventors, in view of such circumstances, conducted extensive research, and as a result, have come to the finding that the adsorbents, which consist of activated carbon having as supported thereon two or more specific components selected from (I) sulfur, (II) specific salt components and (III) specific halogen compounds, adsorb efficiently mercury vapor in gases and also exhibit an outstandingly increased adsorption capacity.

Thus the present invention relates to:

A process for the removal of mercury vapor from a gas containing the same, which comprises contacting the gas with an adsorbent comprising activated carbon having as supported thereon (1) one or more components included in one of the three groups shown below and (2) one or more components included in the remaining two groups shown below:

Group	Component
I	sulfur
II	sulfate and nitrate of Al, V, Fe, Co, Ni, Cu, Zn or NH_4
III	oxide of iodine, oxyacid corresponding to the oxide of iodine, salt of said oxyacid, and bromide and iodide of K, Na or NH_4

and an adsorbent used in the above process.

The adsorbent of the present invention can be prepared by having (1) one or more components included in one of the three groups shown above and (2) one or more components included in the remaining two groups shown above supported on activated carbon.

The activated carbon, which is used in this case, may be any type, so long as in manufactured by a known process from wood charcoal, coal, coke, coconut shells, resins, etc. employed as raw materials and exhibits a specific surface area of 200 to 2000 m^2/g.

Examples of the components of Group II include sulfates such as $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $VOSO_4$, $FeSO_4$, $Fe_2(SO_4)_3$, $CoSO_4$, $NiSO_4$, $CuSO_4$, $ZnSO_4$, etc. and nitrates such as NH_4NO_3, $Al(NO_3)_3$, $VO(NO_3)_2$, $Fe(NO_3)_2$, $Fe(NO_3)_3$, $CO(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, etc.

Examples of the components of Group III include oxides of iodine such as I_2O_5, IO_2, etc., oxyacids corresponding to the oxide of iodine such as HIO_2, HIO_3, etc., salts of said oxyacids such as alkali metal salts (e.g. $NaIO_2$, KIO_2, $NaIO_3$, KIO_3, $NaIO_4$, KIO_4), alkaline earth metal salts (e.g. $Mg(IO_3)_2$, $Ca(IO_3)_2$, $Sr(IO_3)_2$), ammonium salts (e.g. NH_4IO_3, NH_4IO_4), etc., bromide such as KBr, NaBr, NH_4Br, etc., and iodide such as KI, NaI, NH_4I, KI_3, etc.

When sulfur of Group I is used, the amount of sulfur to be supported is 10 to 800 mg per g of activated carbon, preferably 20 to 600 mg. When the component or components of Group II is used, the amount of component or total amount of components of Group II is 5 to 500 mg per g of activated carbon, preferably 10 to 400 mg. When the component or components of Group III is used, the amount

of the component or total amount of components of Group III is 1 to 500 mg per g of activated carbon, preferably 2 to 400 mg, most preferably 10 to 400 mg.

In order to allow activated carbon to support the components selected from Groups I, II and III, in the manufacture of the adsorbent for mercury vapor according to the present invention, there may be mentioned, by way of example, the method which comprises dissolving or suspending these components to be supported together in water or a water-soluble solvent and impregnating or spraying activated carbon with the resultant solution or suspension, followed by heating at 110 to 400°C, if necessary. Also, each of these components may be supported on activated carbon, individually, and the order thereof may be arbitrary.

The heating procedure as described above can be carried out for example in the presence of nitrogen gas, carbon dioxide gas, steam, air, oxygen-containing gas, combustion gas or gas mixtures thereof. As the means of heating, any procedure may be employable, and use is desirably made for example of the method which comprises contacting the above-mentioned gas with activated carbon under heating. As the mode of contacting employable in this case, there may be mentioned the fixed-bed, fluidized bed, slurry and rotary-kiln types and others. The heating time varies with the kind and temperature of the surrounding gases, etc., and is normally not less than 10 minutes, preferably 1/2 to 24 hours.

With reference to the adsorbents for mercury vapor according to the present invention, the adsorbent having component of Group I, component(s) included in Group II and component(s) included in Group III exhibits greater removal efficiency and adsorption capacity for mercury than the one having component(s) included in one of the three groups and component(s) included in one of the remaining two groups.

Further, the adsorbent of the present invention may be an activated carbon having as supported thereon one or more of sulfur compounds in addition to the components included in Group I, II and III. Examples of the sulfur compound include thiocyanates such as NH_4SCN, NaSCN, KSCN, $Mg(SCN)_2$, $Ca(SCN)_2$ and $Sr(SCN)_2$, thiosulfate such as $(NH_4)_2S_2O_3$, $Na_2S_2O_3$, $K_2S_2O_3$, MgS_2O_3, CaS_2O_3 and SrS_2O_3, sulfamates such as $NH_4OSO_2NH_2$, $NaOSO_2NH_2$, $KOSO_2NH_2$, $Mg(OSO_2NH_2)_2$, $Ca(OSO_2NH_2)_2$ and $Sr(OSO_2NH_2)_2$; and sulfides such as $(NH_4)_2S$, Na_2S, K_2S, MgS, CaS and SrS. The total amount of the sulfur compounds is usually 10 to 800 mg per g of activated carbon, preferably 20 to 600 mg.

The process for the removal of mercury vapor of the present invention is carried out by contacting a gas containing mercury vapor with the adsorbent of the present invention. The contacting temperature is not more than 150°C, preferably −10 to 120°C, more preferably 0 to 120°C, and the contacting pressure is not more than 100 mg/cm², preferably 0.1 to 70 kg/cm², while the contacting time at 25°C and at 1 kg/cm² is 1/10 to 30 seconds, preferably 1/5 to 20 seconds. Also, contact between the said adsorbent and the gas containing vaporized mercury can be effected for example by means of the fixed-bed, moving-bed and fluidized-bed operations.

Further, the present inventors have found that an activated carbon having as supported thereon sulfur is desirably prepared by mixing activated carbon with finely powdered sulfur and heating the resultant mixture at 110 to 350°C, preferably 110 to 300°C.

The fine particles of sulfur, which is used in this preparation, may be any of fine pulverized sulfur, if it shows a grain size of not more than 8 mesh, preferably not more than 10 mesh. The amount of sulfur to be supported onto activated carbon is normally 10 to 800 mg per g of activated carbon. In the preparation process, the first step is conducted into practice by mixing activated carbon uniformly with fine particles of sulfur. Such procedure of mixing may be carried out by mixing directly activated carbon with fine particles of sulfur, whereby water or solvent mixtures of water-soluble solvents (e.g., alcohols, etc.) with water may be desirably employed. In the case of the use of water or solvent, examples of the employable procedure include a procedure which comprises firstly suspending fine particles of sulfur in water or solvent and impregnating or spraying activated carbon with the resultant suspension and a procedure which comprises impregnating activated carbon with water or solvent and coating it with fine particles of sulfur. In case of preparing an activated carbon having as supported thereon sulfur and other component or components defined in the present invention, it is preferable to dissolve or suspend in advance in water or solvent as mentioned above the components intended to be supported onto activated carbon. Each amount of the components to be supported is as defined above. The means of mixing may be any of means, such as mixer, sugar-coating machine and agitator, which may be utilized for mixing solids. A mixture of activated carbon and fine particles of sulfur, along with other components, if necessary, is subsequently heated at 110°C to 350°C, preferably 110°C to 300°C. Heating can be effected for example in the presence of nitrogen gas, carbon dioxide gas, steam, combustion gas, air, oxygen-containing gas or gas mixtures thereof. The means of heating may be any of means, whereby, for example, the procedure comprising heating the above gases and contacting it with a mixture of activated carbon and sulfur is desirably employed. As the mode or type of contacting employable in this case, there may be mentioned fixed-bed, moving-bed, fluidized-bed, slurry and rotary-kiln types, and other. The heating time varies with the kinds and temperatures of the surrounding gases, etc., and is normally not less than 30 minutes, preferably 1 to 240 hours, more preferably 1 to 50 hrs. It should be noted that when the above heating temperature is lower than 110°C, sulfur fails to reach the inner surface of activated carbon and therefore, the activated carbon having as supported

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thereon sulfur showing excellent adsorption effect cannot be obtained. Conversely, the increased heating temperature in excess of 350°C causes sulfur vapor to be generated, and is consequently unfavorable. The activated carbon having as supported thereon sulfur as obtained by the above procedure has sulfur supported uniformly on the pore surface of activated carbon, and possesses excellent adsorption capacity for mercury vapor and so forth.

EXAMPLE 1

Activated carbon Ao of 16 to 24 mesh having the BET specific surface area of 1230 m^2/g was evenly sprayed with an aqueous solution or suspension of the given amount of the components, other than sulfur, shown in the following table. When sulfur is used, the given amount of finly powdered sulfur was mixed with the activated carbon. The activated carbon was then heated in an air at 110°C. (Adsorbents (1)—(64))

As controls, activated carbon A_0 was mixed, in the same procedure as described above, with the given amount each of the components alone, and heated at 110°C. (Adsorbents A_1 through A_{16})

Six ml each of the Adsorbents A_0 through A_{16} and (1) through (64) as obtained by the above procedures were packed into a 1.6 cmϕ glass column, respectively, and nitrogen gas of 25°C containing 9 mg/m^3 of mercury vapor was passed through each column at a linear flow rate of 40 cm/sec to conduct the breakthrough adsorption tests for mercury vapor. The results are as shown in Table 1.

TABLE 1–1

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs.	50 hrs.
A_0 (Control)	0	0	0	0	0	0	0
A_1 (,,)	0	0	NH_4I – 150	53	28	3	0
A_2 (,,)	0	0	NaI – 150	59	35	3	0
A_3 (,,)	0	0	KI – 150	78	51	15	0
A_4 (,,)	0	0	KBr – 150	48	35	7	0
A_5 (,,)	0	$Al_2(SO_4)_3$ – 100	0	21	3	0	0
A_6 (,,)	0	$FeSO_4$ – 100	0	66	42	28	7
A_7 (,,)	0	$CuSO_4$ – 100	0	89	61	29	8
A_8 (,,)	0	$CoSO_4$ – 100	0	55	40	23	10
A_9 (,,)	0	NH_4NO_3 – 100	0	33	9	0	0
A_{10} (,,)	0	$Fe(NO_3)_3$ – 100	0	96	84	50	11
A_{11} (,,)	0	$(NH_4)_2SO_4$ – 100	0	19	5	0	0
A_{12} (,,)	S – 100	0	0	68	50	38	24
A_{13} (,,)	S – 200	0	0	51	41	30	25
A_{14} (,,)	0	$ZnSO_4$ – 100	0	35	5	0	0
A_{15} (,,)	0	$Zn(NO_3)_2$ – 100	0	88	74	43	10
A_{16} (,,)	0	0	HI – 100	85	13	0	0

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TABLE 1–2

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs.	50 hrs.
(1) (This invention)	S – 100	0	NH_4I – 10	93	85	59	30
(2) (,,)	S – 100	0	NaI – 10	90	72	48	31
(3) (,,)	S – 100	0	KI – 10	94	78	45	29
(4) (,,)	S – 100	0	KBr – 10	91	71	50	42
(5) (,,)	S – 100	0	NH_4Br – 10	88	73	49	41
(6) (,,)	S – 100	0	KI – 5 KBr – 5	94	85	61	49
(7) (,,)	S – 100	0	NaI – 5 KBr – 5	92	73	47	41
(8) (,,)	S – 100	0	KI – 2	81	65	41	31
(9) (,,)	S – 150	0	KI – 5	83	66	40	33
(10) (,,)	S – 200	0	KI – 5	80	67	43	35
(11) (,,)	S – 100	$Al(SO_4)_3$ – 10	0	88	71	45	32
(12) (,,)	S – 100	$FeSO_4$ – 10	0	95	78	51	23
(13) (,,)	S – 100	$CuSO_4$ – 10	0	95	88	69	48

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TABLE 1–3

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs.	50 hrs.
(14) This (invention)	S – 100	$CoSO_4$ – 10	0	89	75	61	38
(15) (,,)	S – 100	$NiSO_4$ – 10	0	90	75	63	41
(16) (,,)	S – 100	$VOSO_4$ – 10	0	99	70	48	39
(17) (,,)	S – 100	$(NH_4)_2SO_4$ – 10	0	81	61	51	39
(18) (,,)	S – 100	$Fe(NO_3)_2$ – 10	0	93	67	63	44
(19) (,,)	S – 100	$Co(NO_3)_2$ – 10	0	96	75	64	40
(20) (,,)	S – 100	$FeSO_4$ – 5	0	89	75	60	33
(21) (,,)	S – 150	$FeSO_4$ – 5	0	88	76	63	38
(22) (,,)	S – 200	$FeSO_4$ – 5	0	90	78	65	41
(23) (,,)	S – 100	$ZnSO_4$ – 10	0	80	71	43	37
(24) (,,)	S – 100	$FeSO_4$ – 5 $CuSO_4$ – 5	0	96	80	52	41
(25) (,,)	S – 100	$FeSO_4$ – 5 $Fe(NO_3)_3$ – 5	0	91	73	60	43

TABLE 1–4

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs.	50 hrs.
(26) (This invention)	0	$(NH_4)_2SO_4$ – 50	I_2O_5 – 50	100	100	100	85
(27) (")	0	$Al_2(SO_4)_3$ – 50	I_2O_5 – 50	100	100	100	98
(28) (")	0	$Fe_2(SO_4)_3$ – 50	I_2O_5 – 50	100	100	100	93
(29) (")	0	$Fe(NO_3)_3$ – 50	I_2O_5 – 50	100	100	100	96
(30) (")	0	$Co(NO_3)_2$ – 50	I_2O_5 – 50	100	100	100	97
(31) (")	0	$Ni(NO_3)_2$ – 50	HIO_3 – 50	100	100	100	98
(32) (")	S – 50	0	I_2O_5 – 50	100	100	100	95
(33) (")	S – 50	$VOSO_4$ – 50	I_2O_5 – 50	100	100	100	100
(34) (")	S – 50	$FeSO_4$ – 50	I_2O_5 – 50	100	100	100	100
(35) (")	$NaOSO_2NH_2$ – 50	$ZnSO_4$ – 50	I_2O_5 – 50	100	100	100	100
(36) (")	$K_2S_2O_3$ – 50	$Cu(NO)_3$ – 50	HIO_3 – 50	100	100	100	100
(37) (")	K_2S – 50	$FeSO_4$ – 50	I_2O_5 – 50	100	100	100	100
(38) (")	0	$FeSO_4$ – 50	KIO_4 – 50	100	100	100	63
(39) (")	S – 50	$FeSO_4$ – 50	$Mg(IO_3)_2$ – 50	100	100	100	100

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TABLE 1–4

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs.	50 hrs.
(40) (This invention)	0	$(NH_4)_2SO_4$ – 50	NH_4I – 75	100	100	100	75
(41) (,,)	0	$Al_2(SO_4)_3$ – 50	NaI – 75	100	100	100	88
(42) (,,)	0	$VOSO_4$ – 50	KI – 75	100	100	100	95
(43) (,,)	0	$CoSO_4$ – 50	KBr – 50	100	100	100	90
(44) (,,)	0	$FeSO_4$ – 50	NH_4Br – 75	100	100	100	88
(45) (,,)	0	$FeSO_4$ – 50	KI – 75	100	100	100	93
(46) (,,)	0	$CoSO_4$ – 50	NH_4I – 75	100	100	100	89
(47) (,,)	0	$NiSO_4$ – 50	KI – 75	100	100	100	88
(48) (,,)	0	$CuSO_4$ – 50	KIO_3 – 75	100	100	100	83
(49) (,,)	0	$ZnSO_4$ – 50	$NaBrO_3$ – 75	100	100	100	80
(50) (,,)	0	$CuSO_4$ – 50	NH_4Br – 75	100	100	100	95
(51) (,,)	0	$FeSO_4$ – 50	NaI – 75	100	100	100	78
(52) (,,)	0	NH_4NO_3 – 50	KI – 75	100	100	100	73
(53) (,,)	0	$Al(NO_3)_3$ – 50	NH_4I – 75	100	100	100	86
(54) (,,)	0	$Fe(NO_3)_3$ – 50	NaI – 75	100	100	100	81

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TABLE 1–6

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs.	50 hrs.
(55) (This invention)	0	$Fe(NO_3)_3$ – 50	KBr – 75	100	100	100	83
(56) (,,)	0	$Fe(NO_3)_3$ – 50	NaBr – 75	100	100	100	82
(57) (,,)	0	$Co(NO_3)_2$ – 50	NH_4I – 75	100	100	100	91
(58) (,,)	0	$Ni(NO_3)_2$ – 50	NaI – 75	100	100	100	89
(59) (,,)	0	$Cu(NO_3)_2$ – 50	KI – 75	100	100	100	96
(60) (,,)	0	$Zn(NO_3)_2$ – 50	KI – 75	100	100	100	91
(61) (,,)	0	$FeSO_4$ – 100	KI – 400	100	100	100	100
(62) (,,)	0	$FeSO_4$ – 100	KI – 200	100	100	100	100
(63) (,,)	0	$FeSO_4$ – 100	KI – 50	100	100	100	65
(64) (,,)	0	$FeSO_4$ – 100	KI – 10	100	100	100	8

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EXAMPLE 2

A 6 ml portion each of the Adsorbents A_1, A_3, A_5, A_6, A_9, A_{10}, A_{14}, (28), (31), (32), (34), (36), (40), (42), (45), (48), (52), (54), (56), and (59) of Example 1 was packed into a 1.6 cmϕ glass column, respectively, and hydrogen gas of 25°C containing 1 mg/m^3 of Mercury vapor was passed through each column at a linear flow rate of 40 cm/sec to conduct the breakthrough adsorption tests for mercury vapor. The result are shown in Table 2.

TABLE 2

Adsorbent No.	Percent removal of mercury vapor at the elapsed time shown below (%)			
	50 hrs.	100 hrs.	150 hrs.	200 hrs.
A_1 (control)	42	15	6	0
A_3 (,,)	65	35	11	3
A_5 (,,)	42	32	8	0
A_6 (,,)	58	40	13	9
A_9 (,,)	26	15	0	0
A_{10} (,,)	78	43	15	0
A_{14} (,,)	51	23	1	0
(28) (This invention)	100	100	100	98
(31) (,,)	100	100	100	100
(32) (,,)	100	100	100	100
(34) (,,)	100	100	100	100
(36) (,,)	100	100	100	100
(40) (,,)	100	100	100	75
(42) (,,)	100	100	100	100
(45) (,,)	100	100	100	100
(48) (,,)	100	100	100	100
(52) (,,)	100	100	100	83
(54) (,,)	100	100	100	91
(56) (,,)	100	100	100	95
(59) (,,)	100	100	100	100

EXAMPLE 3

A 6 ml portion each of the Adsorbents A_1, A_3, A_5, A_6, A_{10}, A_{14}, (28), (31), (32), (34), (36), (40), (42), (45), (48), (52), (54), (56) and (59) of Example 1 was packed into a 1.6 cm$^\phi$ glass column, respectively, and a gas (N—84.8 vol.%, O_2—14.5 vol.%, H_2O—0.7 vol.%) of 25°C containing 9 mg/m^3 of mercury vapor was passed through each column at a linear flow rate of 40 cm/sec to conduct the breakthrough adsorption tests for mercury vapor. The results are as shown in Table 3.

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TABLE 3

Adsorbent No.	Percent removal of mercury vapor at the elapsed time shown below (%)			
	50 hrs.	100 hrs.	150 hrs.	200 hrs.
A_1 (Control)	68	39	18	8
A_3 (,,)	73	40	24	12
A_8 (,,)	63	39	18	10
A_6 (,,)	63	51	21	15
A_{10} (,,)	32	18	4	0
A_{14} (,,)	60	35	8	3
(28) (This invention)	100	100	100	100
(31) (,,)	100	100	100	100
(32) (,,)	100	100	100	100
(34) (,,)	100	100	100	100
(36) (,,)	100	100	100	100
(40) (,,)	100	100	100	88
(42) (,,)	100	100	100	100
(45) (,,)	100	100	100	100
(48) (,,)	100	100	100	100
(52) (,,)	100	100	100	100
(53) (,,)	100	100	100	100
(56) (,,)	100	100	100	100
(59) (,,)	100	100	100	100

EXAMPLE 4

A 6 ml portion each of the Adsorbents A_3, A_6, A_{12}, (2) through (4) and (12) through (14) of Example 1 was packed into a 1.6 cm^{ϕ} glass column, and methane gas of 70°C containing 9 mg/m^3 of mercury vapor was passed through each column at a linear flow rate of 40 cm/sec to conduct the breakthrough adsorption tests for mercury vapor at 70°C. The results are as shown in Table 4.

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TABLE 4

Adsorbent No.	Percent removal of mercury vapor at the elapsed time shown below (%)						
	5 hrs.	10 hrs.	20 hrs.	50 hrs.	100 hrs.	150 hrs.	200 hrs.
A_3 (Control)	58	59	63	63	35	30	23
A_6 (,,)	20	38	40	40	39	37	37
A_{12} (,,)	55	58	65	68	68	70	70
(2) (This invention)	95	95	96	96	97	96	96
(3) (,,)	96	98	98	98	98	98	99
(4) (,,)	95	96	96	96	96	97	97
(12) (,,)	97	98	98	99	99	100	100
(13) (,,)	98	99	100	100	100	100	100
(14) (,,)	95	97	98	98	98	98	98

EXAMPLE 5

Activated carbon a_0 of 16 to 24 mesh having the BET specific surface area of 1050 m^2/g was sprayed with a solution containing respectively given amount of sulfur (first component), a sulfate or nitrate (second component) and bromide or iodide (third component) (in the case of sulfur, a suspension was used), and subsequently dried at 120°C (Adsorbents (65) through (80).

Six ml each of the Adsorbents a_0 and (65) through (80) was packed into a 1.6 cm^ϕ glass column, respectively, and nitrogen gas of 25°C containing 9 mg/m^3 of mercury vapor was passed through each column at a linear flow rate of 40 cm/sec to conduct the breakthrough adsorption tests for mercury vapor. The results are shown in Table 5.

TABLE 5

Adsorbent No.	The first component or additive; and its amount supported (mg/g)	The second component; and its amount supported (mg/g)	The third component; and its amount supported (mg/g)	Percent removal of mercury vapor at the elapsed time shown below (%)			
				5 hrs.	10 hrs.	20 hrs	50 hrs.
a_0 (Control)	0	0	0	0	0	0	0
(65) (This invention)	S – 150	0	KI – 100	91	70	40	16
(66) (,,)	S – 150	$FeSO_4$ – 100	0	89	65	40	11
(67) (,,)	S – 150	$Zn(NO_3)_2$ – 100	0	68	43	21	7
(68) (,,)	S – 150	0	NH_4I – 100	90	81	54	15
(69) (,,)	S – 75	$FeSO_4$ – 50	KBr – 75	100	100	100	100
(70) (,,)	S – 75	$FeSO_4$ – 50	NaI – 75	100	100	100	100
(71) (,,)	S – 75	$FeSO_4$ – 50	KI – 75	100	100	100	100
(72) (,,)	S – 75	$CuSO_4$ – 50	KI – 75	100	100	100	100
(73) (,,)	S – 75	$Zn(NO_3)_2$ – 50	KI – 75	100	100	100	100
(74) (,,)	S – 50	$VOSO_4$ – 50	NH_4I – 75	100	100	100	100
(75) (,,)	S – 50	$Fe(NO_3)_3$ – 50	KIO_3 – 75	100	100	100	100
(76) (,,)	S – 50	$(NH_4)_2SO_4$ – 50	NH_4Br – 75	100	100	100	100
(77) (,,)	S – 400	$FeSO_4$ – 50	KI – 50	100	100	100	100
(78) (,,)	S – 100	$FeSO_4$ – 50	KI – 50	100	100	100	100
(79) (,,)	S – 50	$FeSO_4$ – 50	KI – 50	100	100	100	100
(80) (,,)	S – 10	$FeSO_4$ – 50	KI – 50	100	100	100	99

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EXAMPLE 6

From activated carbon A of 16 to 24 mesh having the BET surface area of 1100 m^2/g, there was prepared the activated carbon having as supported thereon 100 mg/g of sulfur by the following procedure:

(1) Activated carbon having as supported thereon sulfur B_0 through B_3:

10.0 g of finely powdered sulfur of not more than 50 mesh was uniformly suspended in 90 ml of water, and the suspension was sprayed evenly onto 100 g of activated carbon A.

Part of the activated carbon thus treated was sampled and heated in air for 1 hour at different temperatures of 90°C, 120°C, 150°C and 200°C, respectively.

(2) Activated carbon having as supported thereon sulfur C_0 through C_2:

90 ml of water was sprayed evenly on 100 g of activated carbon A, and 10.0 g of finely powdered sulfur was sprayed evenly over the wet activated carbon with stirring to coat the particle-surface of the activated carbon with sulfur.

Part of the activated carbon thus treated was sampled and heated in nitrogen gas for 1/2 hour at different temperature of 120°C and 250°C, respectively.

(3) Activated carbon having as supported thereon sulfur D:

90 ml of water was sprayed evenly on 100 g of activated carbon A, and 10.0 g of finely powdered sulfur was sprayed evenly over the wet activated carbon with stirring to coat the particle-surface of the activated carbon with sulfur.

Part of the activated carbon thus treated was sampled and heated in heavy-oil combustion waste gas at 150°C for 1 hour.

(4) Activated carbon having as supported thereon sulfur E_0.

10.0 g of finely powdered sulfur of not more than 50 mesh was dissolved in 120 ml of carbon disulfide, and the solution was sprayed evenly on 100 g of activated carbon A.

Part of the activated carbon thus treated was sampled and heated in nitrogen gas at a temperature of 80°C for 1/2 hour.

(5) Activated carbon having as supported thereon sulfur F_0:

15 g of activated carbon A was packed into a 2.0 cm^ϕ quartz glass tube, which was then heated at 140°C. Air of 140°C containing 1.0 vol.% of H_2S was passed through the packed layer at a linear flow rate of 15 cm/sec (at 25°C) for 15 hours to have 1.5 g of sulfur supported on the whole activated carbon.

The amount of the sulfur supported was found to decrease in the order of the gas-inlet side, middle and gas-outlet side in the packed layer of activated carbon, with the found amounts as sulfur of 14 g/100 g of activated carbon, 10 g/100 g of activated carbon and 6 g/100 g of activated carbon respectively. The middle layer is referred to as "F_0".

6 ml each of the activated carbon samples A, B_0 through B_3, C_0 through C_2, D, E_0 and F_0 as obtained by the above procedures were packed into a 1.6 cm^ϕ glass column, respectively, and air of 25°C containing 2.0 mg/m^3 of mercury vapor was passed through each column at a linear flow rate of 20 cm/sec to conduct the breakthrough adsorption tests for mercury vapor. The results are as shown in Table 6.

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TABLE 6

Sulfur-supporting method	Sample No.	Heating temp. °C	Observed conditions of sulfur supported	Removal of mercury vapor at the elapsed time shown below (%)			
				2 hr.	5 hr.	10 hr.	20 hr.
Sulfur is suspended in water, and the suspension is sprayed on activated carbon, which is heated.	B_0 (Control)	90	Sulfur particles are adhered to external surface	10	4	0	0
	B_1 (This invention)	120	Sulfur is settled and adhered evenly inside pores.	100	70	50	30
	B_2 (,,)	150	,,	100	80	63	43
	B_3 (,,)	200	,,	100	100	65	45
Activated carbon is wetted on the surface with water, then coated with powdered sulfur and heated.	C_0 (Control)	80	Sulfur particles are adhered to external surface.	13	5	0	0
	C_1 (This invention)	120	Sulfur is settled and adhered evenly inside pores.	100	65	43	31
	C_2 (,,)	250	,,	100	78	61	42
	D (This invention)	150	,,	100	83	75	60
Sulfur is dissolved in carbon disulfide, and the solution is sprayed on activated carbon, which is heated.	E_0 (Control)	80	Sulfur is settled and adhered almost evenly inside pores.	70	51	32	21
A gas containing H_2S and O_2 is contacted with activated carbon.	F_0 (Control)	140	The same as above, but the amount of sulfur supported varies among particles of activated carbon.	95	65	48	29
Not treated	A (Control)	–	–	5	0	0	0

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EXAMPLE 7

From activated carbon G of 10 to 24 mesh having the BET surface area of 950 m^2/g, there was prepared the activated carbon having as supported thereon a mixture of sulfur and other components.

(1) Activated carbon H having as supported thereon S—KI

45 ml of an aqueous solution of 1.0 g of KI was evenly sprayed on 100 g of activated carbon G with stirring to allow KI to adhere to the activated carbon. 5 g of sulfur of not more than 20 mesh was poured onto the activated carbon, and stirring was continued for about 10 minutes to coat the surface of the activated carbon with sulfur. The activated carbon as obtained by the above procedure was heated in air at 130°C for 2 hours.

(2) Activated carbon I having as supported thereon S—KI-$FeSO_4$

45 ml of an aqueous solution containing 1.0 g of KI and 2.0 g of $FeSO_4$ was evenly sprayed on 100 g of activated carbon G with stirring to allow KI and $FeSO_4$ to adhere to the activated carbon. 3 g of sulfur of not more than 20 mesh was poured onto the activated carbon, and stirring was continued for about 10 minutes to coat the surface of the activated carbon with sulfur. The activated carbon as obtained by the above procedure was heated in air at 150°C for 2 hours.

(3) Activated carbon J having as supported thereon S—KBr-$Fe(NO_3)_3$:

48 ml of aqueous ethanol (5 ml of ethanol with the remaining 43 ml of water. Sulfur contained in the state of suspension) containing 1.0 g of KBr, 2.0 g of $Fe(NO_3)_3$ and 3.0 g of sulfur of not more than 100 mesh was evenly sprayed on 100 g of activated carbon G with stirring, and then heated in an atmosphere of nitrogen gas at 115°C for 1 hour, whereby each of the activated carbon samples was found to have sulfur settled and adhered almost uniformly inside pores of the activated carbon.

25 ml each of the activated carbon samples H, I and J as obtained by the above procedures was packed into a 4 cm^{ϕ} glass tube, and nitrogen gas of 25°C containing 5.0 mg/m^3 of mercury vapor was passed through each tube at a linear flow rate of 60 cm/sec to conduct the breakthrough adsorption tests for mercury vapor. The results are as shown in Table 7.

TABLE 7

Sample No.	Component supported	Percent removal of mercury vapor at the elapsed time shown below			
		1 hr.	5 hrs.	10 hrs.	20 hrs.
H	S–KI	100	95	71	35
I	S–KI–$FeSO_4$	100	100	93	65
J	S–KBr–$Fe(NO_3)_3$	100	100	90	52

CLAIMS

1. A process for the removal of mercury vapor from a gas containing the same, which comprises contacting the gas with an adsorbent comprising an activated carbon having as supported thereon (1) one or more components included in one of the three groups shown below and (2) one or more components included in the remaining two groups shown below.

Group	Component
I	sulfur
II	sulfate and nitrate of Al, V, Fe, Co, Ni, Cu, Zn or NH_4
III	oxide of iodine, oxyacid corresponding to the oxide of iodine, salt of said oxyacid, and bromide and iodide of K, Na or NH_4

2. A process as claimed in Claim 1, wherein the one or more components included in one of the

three groups are sulfur included in Group I, and the one or more components included in the remaining two groups are one or more components included in Group II.

3. A process as claimed in Claim 1, wherein the one or more components included in one of the three groups are sulfur included in Group I, and the one or more components included in the remaining two groups are one or more components included in Group III.

4. A process as claimed in Claim 1, wherein the one or more components included in the other two groups are one or more components included in one of the remaining two components and one or more components included in the other of the remaining two components.

5. A process as claimed in Claim 1, wherein each of the components is supported on the activated carbon so that the amount of sulfur, when used, is in the range of from 10 to 800 mg per g of activated carbon, the total amounts of the components included in Group II, when used, is in the range of from 5 to 500 mg per g of activated carbon, and the total amounts of the components included in Group III, when used, is in the range of from 1 to 500 mg per g of activated carbon.

6. A process as claimed in Claim 1, wherein the activated carbon is one having as supported thereon sulfur and potassium iodide.

7. A process as claimed in Claim 1, wherein the activated carbon is one having as supported thereon sulfur and ferrous sulfate.

8. A process as claimed in Claim 1, wherein the activated carbon is one having as supported thereon sulfur, potassium iodide and ferrous sulfate.

9. An adsorbent for the removal of mercury vapor, which comprises an activated carbon having as supported thereon (1) one or more components included in one of the three groups shown below and (2) one or more components included in the remaining two groups shown below.

Sample	Component
I	sulfur
II	sulfate and nitrate of Al, V, Fe, Co, Ni, Cu, Zn or NH_4
III	oxide of iodine, oxyacid corresponding to the oxide of iodine, salt of said oxyacid, and bromide and iodide of K, Na or NH_4

10. An adsorbent as claimed in Claim 9, wherein the one or more components included in one of the three groups are sulfur included in Group I, and the one or more components included in the remaining two groups are one or more components included in Group II.

11. An adsorbent as claimed in Claim 9, wherein the one or more components included in one of the three groups are sulfur included in Group I, and the one or more components included in the remaining two groups are one or more components included in Group III.

12. An adsorbent as claimed in Claim 9, wherein the one or more components included in the other two groups are one or more components included in one of the remaining two components and one or more components included in the other of the remaining two components.

13. An adsorbent as claimed in Claim 9, wherein each of the components is supported on the activated carbon so that the amount of sulfur, when used, is in the range of from 10 to 800 mg per g of activated carbon, the total amounts of the components included in Group II, when used, is in the range of from 5 to 500 mg per g of activated carbon, and the total amounts of the components included in Group III, when used, is in the range of from 1 to 500 mg per g of activated carbon.

14. An adsorbent as claimed in Claim 9, wherein the activated carbon is one having as supported thereon sulfur and potassium iodide.

15. An adsorbent as claimed in Claim 9, wherein the activated carbon is one having as supported thereon sulfur and ferrous sulfate.

16. An adsorbent as claimed in Claim 9, wherein the activated carbon is one having as supported thereon sulfur, potassium iodide and ferrous sulfate.

17. A process for producing an activated carbon having sulfur as supported thereon, which comprises mixing activated carbon with finely powdered sulfur and heating the resultant mixture at 110 to 350°C for not less than 30 minutes.

18. A process as claimed in Claim 17, wherein the resultant mixture is heated at 110 to 300°C.

19. A process as claimed in Claim 1, substantially as hereinbefore described with reference to any of the Examples.

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20. An adsorbent as claimed in Claim 9, substantially as hereinbefore described with reference to any of the Examples.

21. A process as claimed in Claim 17, substantially as hereinbefore described with reference to any of the Examples.

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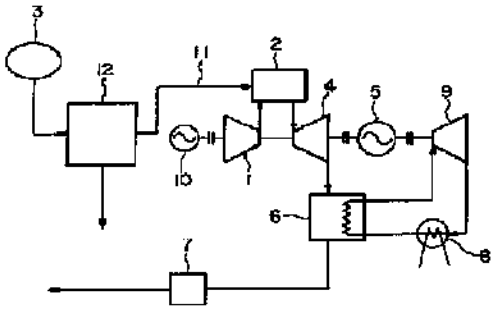
(54) **COMBINED CYCLE GENERATING PLANT**

(57) Abstract:

PROBLEM TO BE SOLVED: To use a low quality heavy fuel oil and the like without any reduction in plant operation efficiency by arranging a magnetic separating device, which removes a metal component or a sulfur component contained in fuel obtained from petroleum, in a fuel supply pipe path to a combustor or in a combustion gas supply pipe path to a gas turbine.

SOLUTION: Air compressed by means of a compressor 1 is fed to a combustor 2 so as to be burnt with petroleum fuel supplied from a fuel source 3 to the combustor 2, and burnt gas generated here is fed to a gas turbine 4 so as to actuate the gas turbine 4, and then, power generation is carried out by means of a generator 5. Exhaust gas discharged from the gas turbine 4 is fed to an exhaust heat collecting boiler 6 so as to generate steam, by which the steam turbine 9 is operated. In this kind of fuel direct burning type combined cycle generating plant, a magnetic separating device 12 is arranged in the middle of a fuel supply pipe path 11 through which petroleum fuel is fed from the fuel source 3 to the combustor 2. By means of the magnetic separating device, metals in the fuel are eliminated and purged, so that reliability of the operation can be improved.

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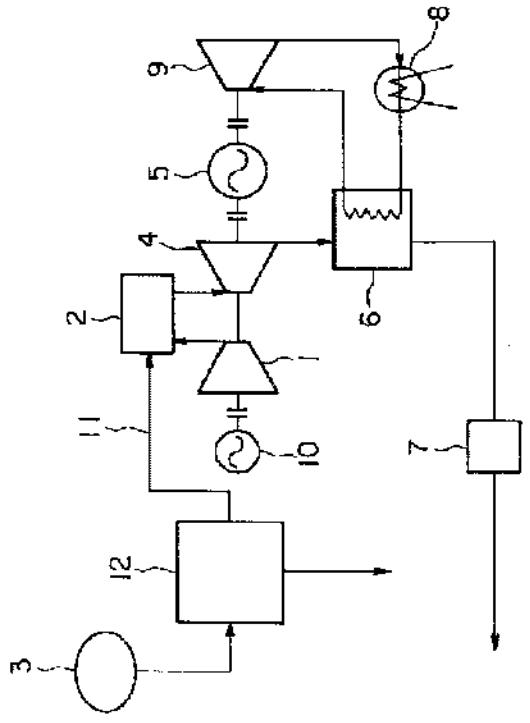
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(54)【発明の名称】　コンバインドサイクル発電プラント

(57)【要約】
【課題】　低質な重油等の石油燃料の使用をも十分可能としたコンバインドサイクル発電プラントを得ること。
【解決手段】　石油を原料とする燃料を使用するコンバインドサイクル発電プラントにおいて、燃焼器２への燃料供給管路１１またはガスタービンへの燃焼ガス供給管路１６に、石油を原料とする燃料中に含まれる金属分や硫黄分を除去する磁気分離装置１２を設けた。



【特許請求の範囲】
【請求項１】石油を原料とする燃料を使用するコンバインドサイクル発電プラントにおいて、燃焼器への燃料供給管路またはガスタービンへの燃焼ガス供給管路に、石油を原料とする燃料中に含まれる金属分や硫黄分を除去する磁気分離装置を設けたことを特徴とする、コンバインドサイクル発電プラント。
【請求項２】互いに除去可能な金属や金属錯体の種類を異にする複数の磁気分離装置が複数段にわたって設けられていることを特徴とする、請求項１記載のコンバインドサイクル発電プラント。
【請求項３】磁気分離装置の上流側に、燃料中の金属類を強磁性体化および大粒径化する反応処理槽が配設されていることを特徴とする、請求項１記載のコンバインドサイクル発電プラント。
【請求項４】磁気分離装置とともに遠心分離装置が併設されていることを特徴とする、請求項１記載のコンバインドサイクル発電プラント。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、石油、重油等の石油を原料とする燃料（以下石油燃料という）を直焚きするようにしたコンバインドサイクル発電プラントに関する。
【０００２】
【従来の技術】図６は従来のコンバインドサイクル発電プラントの概略系統を示す図であり、圧縮機１で圧縮された空気は燃焼器２に送給され、燃料源３から上記燃焼器２に直接供給された石油燃料とともに燃焼される。そして、上記燃焼器２で発生した高温高圧の燃焼ガスがガスタービン４に送られ、ガスタービン４を作動させ同軸上に連結された発電機５が回転駆動され発電が行われる。
【０００３】上記ガスタービン４から排出された排ガスは排熱回収ボイラ６を通り電気集塵器７で除塵された後大気中に排出される。一方、上記排熱回収ボイラ６には復水ポンプ８によって給水が供給されており、そこで前記ガスタービン４からの排ガスと熱交換して蒸気が発生され、その蒸気が蒸気タービン９に供給される。蒸気タービン９に供給された蒸気はそこで仕事を行い、蒸気タービン９を駆動するとともに、仕事を行った蒸気は復水器８に導入され復水が行われる。なお、図中符号１０は起動機である。
【０００４】
【発明が解決しようとする課題】ところが、このような燃料直焚き式のコンバインドサイクル発電プラントにおいては、燃焼ガスが直接ガスタービン４に送り込まれるため、燃料中に含まれる金属類（バナジウム、ナトリウム等）が燃焼されてできる酸化物や塩が、同様に燃料中に含まれる硫黄分と反応してガスタービン４のブレードを腐食させたり、ブレードへの付着により発電効率を著しく低下させる等の問題がある。
【０００５】従来は燃料に酸化マグネシウム等の腐食防止剤を添加し腐食防止を施していたが、この防止剤もブレードに付着し、さらに発電効率を低下させる原因となる。そしてこれらの付着物はさらにガスタービン４のみならず排熱回収ボイラ６のフインチューブへも付着し、その性能を大幅に劣化させる。したがって、このような発電効率の低下や信頼性の低下を防ぐため、数十時間から数百時間毎にコンバインドサイクル発電プラントを停止させ、ガスタービン４や排熱回収ボイラ６を洗浄する必要があり、このためにプラントの運転効率が低下するという不都合がある。
【０００６】すなわち、石油やその精製過程で残される残さ重油や油中に存在する金属類は、ナフテン環や芳香族環と複雑に重合し合い、化学的に安定で強固な形態をなしている。このため、これらの金属類を化学的に分離除去することはできず、特に低質の重油や残さ油は燃料直焚きのコンバインドサイクル発電プラントの燃料として不適当とされ、あまり使用されていなかった。
【０００７】一方、近年の石油や天然ガス資源の枯渇問題等により、燃料の種類の多様化が進められようとしており、低質な重油や残さ油の燃料化が望まれている。
【０００８】本発明はこのような点に鑑み、プラントの運転効率の低下をもたらすことなく、低質な重油等の石油燃料の使用をも十分可能としたコンバインドサイクル発電プラントを得ることを目的とする。
【０００９】
【課題を解決するための手段】第１の発明は、石油を原料とする燃料を使用するコンバインドサイクル発電プラントにおいて、燃焼器への燃料供給管路またはガスタービンへの燃焼ガス供給管路に、石油燃料中に含まれる金属分や硫黄分を除去する磁気分離装置を設けたことを特徴とする。
【００１０】第２の発明は、互いに除去可能な金属や金属錯体の種類を異にする複数の磁気分離装置が複数段にわたって設けられていることを特徴とする。
【００１１】また、第３の発明は、磁気分離装置の上流側に、燃料中の金属類を強磁性体化および大粒径化する反応処理槽が設けられていることを特徴とする。
【００１２】第４の発明は、磁気分離装置とともに遠心分離装置が併設されていることを特徴とする。
【００１３】
【発明の実施の形態】以下、図１乃至図５を参照して本発明の実施の形態について説明する。なお、図中図６と同一部分には同一符号を付しその詳細な説明は省略する。
【００１４】図１は本発明のコンバインドサイクル発電プラントの一実施の形態の概略系統を示す図であって、燃料源３から石油燃料を燃焼器２に供給する燃料供給管

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路１１にはその途中に磁気分離装置１２が設けられている。

【００１５】しかして、石油燃料は燃焼器２へ供給される前に、上記磁気分離装置１２で金属類が除去され清浄化される。そして分離された金属類は排液とともに排出される。したがって、ガスタービン４に供給される燃焼ガスの中にはガスタービン４のブレードの腐食や付着による効率低下を引き起こす金属の酸化物や塩がなくなり、ガスタービン４や排熱回収ボイラ６の信頼性や運用効率を向上させることができる。

$$Fm = V \times \mu o \times M \times \nabla H$$

【００１８】

【数１】

$$M = \frac{9(xp - xf)}{(3 + xp)(3 + xf)} \times H \qquad \cdots (2)$$

ここで、各パラメータは以下の通りである。

Ｆｍ：分散質に働く磁気力

Ｖ　：分散質の体積

μｏ：真空の透磁率

Ｍ　：分散質と分散媒の相対磁比

Ｈ　：外部磁界

▽Ｈ：外部磁界の傾き

ｘｐ：分散質の体積磁化率

ｘｆ：分散媒の体積磁化率

このようにして分離した分散質に働く磁気力Ｆｍを利用して、分散媒からの分離を行うことができる。磁気分離では、磁気力Ｆｍを大きくしてより分離性能を上げるため、超電導率電磁石を用いて外部磁界Ｈを大きくすることにより、分散質が強磁性体のみならず常磁性体や反磁性体であっても分離が可能である。

【００１９】上記磁気分離装置としては、例えば線径数１０～１００μｍ程度のステンレス強磁性細線に外部磁界を垂直に印加する方法等がある。

【００２０】ところで、上記外部磁界の傾き▽Ｈを大きくするためには、磁性体の細いフィラメント状のメッシュを分散媒中に入れたり、酸化鉄などの強磁性体を添加して分散質と結合させ、分散質を強磁性体化させるなどの手法があり、従来法である化学的分離法や遠心分離法では除去不可能な燃料中の金属類を除去することができる。

【００２１】図２は、本発明の他の実施の形態を示す図であり、燃料供給管路１１には多段の磁気分離装置１２ａ，１２ｂ，１２ｃが設けられている。

【００２２】磁気分離装置によって分離可能な金属類は、（１），（２）式からも明らかなように、印加する外部磁界強度Ｈ、メッシュ状フィラメントを使って作る磁界の傾斜度▽Ｈによって変化する。そのため、図２に示すように磁気分離システムを多段化し、印加する磁界Ｈ、および磁界傾斜▽Ｈを各段の磁気分離装置１２ａ，

【００１６】上記磁気分離装置１２は、溶媒（以下分散媒）中に分散する微粒子（以下分散質）を磁気力によって選別或はろ過する技術であり、従来化学的性質が似ている物質同士や化学的に安定で強固な結合をしている物質の分解や分離が化学的には難しいもの、また溶液中に錯体をなして溶け込み、遠心分離では分離が不可能であった金属や金属化合物・金属錯体を、磁気的な性質の違いを利用して分離するものである。

【００１７】上記分散媒に分散する分散質を選別する磁気力は下記の（１），（２）式で表わされる。

…（１）

１２ｂ，１２ｃ毎に変化させることにより、効率よく金属類の除去ができるばかりでなく、除去可能な金属や金属錯体の種類が限定されることから、各磁気分離装置からの排液中に含まれる金属が限定され、特定金属の回収を容易に行うことができる。

【００２３】図３は本発明のさらに他の実施の形態を示す図であり、磁気分離装置１２の上流側に燃料中の金属類を強磁性体化および大粒径化させることにより分離性能を向上させる反応処理槽１３が設けられている。上記反応処理槽１３には添加剤源１４から添加剤が供給されるようにしてあり、その反応処理槽１３内で燃料に対して添加剤が混入されさらに反応が行われる。これにより、燃料中の金属類が強磁性化および大粒径化され、分散媒からの分離性能・速度が向上される。

【００２４】図４は本発明のさらに他の実施の形態を示す図であり、磁気分離装置１２の上流側に遠心分離機１５が設けられている。しかして、上記遠心分離機１５においては磁気分離で原理的に分離機能がない油水分離や汚泥除去等が行われる。このように分離機能の違うものをハイブリッド化して使用することで、より広範囲に不要分の燃料中よりの除去が可能となる。さらに装置を多段化・ハイブリッド化して分離機能を分けることにより、排出される排液中には特定の金属類のみが含まれ、バナジウム等のレアーメタルなど付加価値の高い金属類については、その回収を効率よく行うことができる。

【００２５】なお、上記各実施の形態においては、燃料供給管路１１に磁気分離装置１２を設けたものを示したが、図５に示すように、磁気分離のもつ分離機能を燃焼ガスに対して適用するため、ガスタービン４に燃焼ガスを供給する燃焼ガス供給管路１６に磁気分離装置１２を設けてもよい。

【００２６】すなわち、磁気分離装置はその分離原理により、分離機能は被分離対象物が必ずしも液体である必要がないことから、これを燃焼ガスに適用したものである。しかして、液体状態では分離が難しい金属錯体なども磁気分離装置を用いることにより、燃焼後の酸化物として燃焼ガスから除去することができる。

【００２７】

【発明の効果】以上説明したように、本発明は燃料供給

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管路または燃焼ガス供給管路に磁気分離装置を設けたので、低質の石油燃料直焚きのコンバインドサイクル発電プラントの問題点であったガスタービンへの金属酸化物や塩の付着による効率低下やブレードの腐食および排熱回収ボイラの性能劣化を防ぐことができる。したがって、従来補助運転的に使用されていた石油や重油等の直炊きコンバインドサイクル発電プラントが運転効率や信頼性の向上により液化天然ガスを使用するものと同様に主機としての役割を担うことができる。さらに、ＬＮＧに比べ低価格である重油等を燃料とすることができ発電コストを大幅に下げることもできる等の効果を奏する。

【図面の簡単な説明】

【図１】本発明のコンバインドサイクル発電プラントの概略系統図。

【図２】本発明のコンバインドサイクル発電プラントの他の実施の形態を示す図。

【図３】本発明のコンバインドサイクル発電プラントのさらに他の実施の形態を示す図。

【図４】本発明の他の実施の形態を示す図。

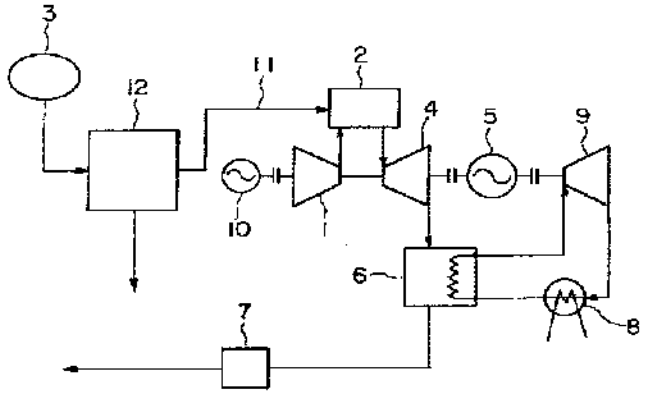
【図５】本発明のさらに他の実施の形態を示す図。

【図６】従来のコンバインドサイクル発電プラントの概略系統図。

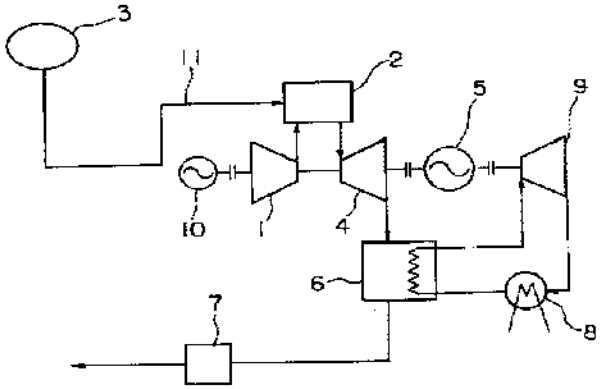
【符号の説明】

1　圧縮機
2　燃焼器
4　ガスタービン
5　発電機
6　排熱回収ボイラ
9　蒸気タービン
11　燃料供給管路
12　磁気分離装置
13　反応処理槽
15　遠心分離機

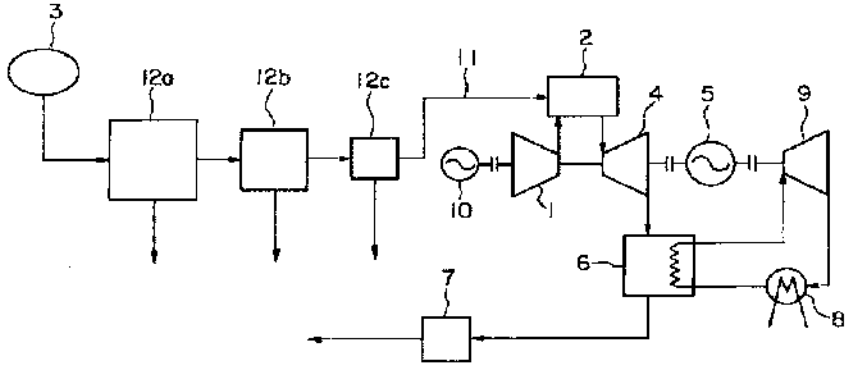
【図１】



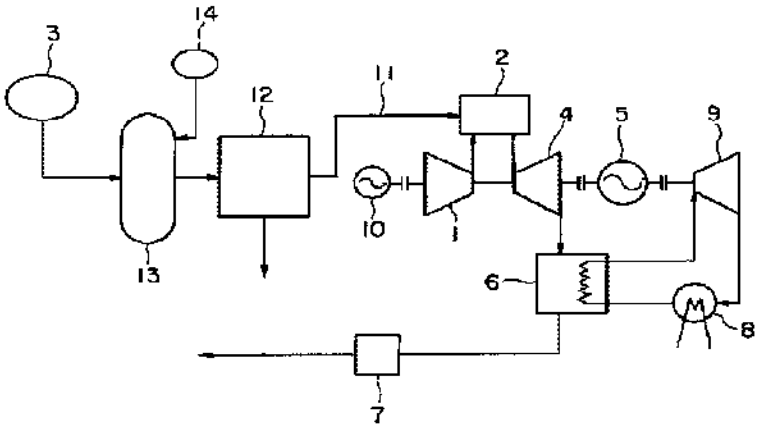
【図６】



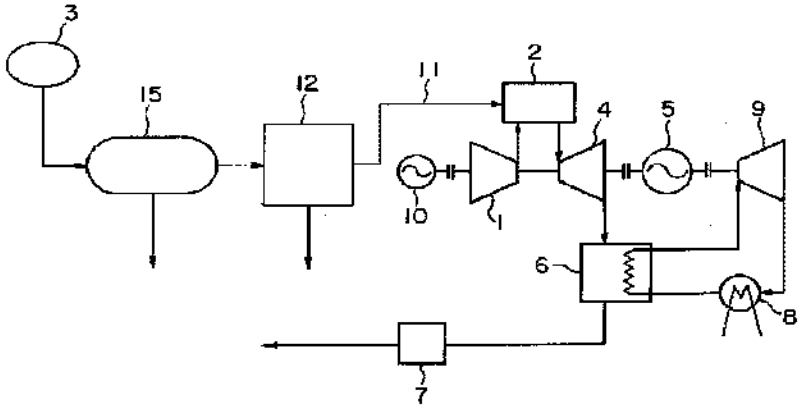
【図２】



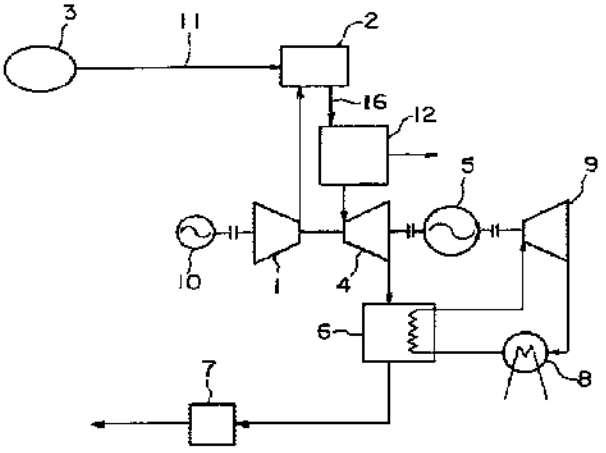
【図３】


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【図４】


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【図５】


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フロントページの続き

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Removal of mercury from a gas. Yokota, Noriyuki; Tokuda, Shingo; Ito, Yoshiro; Takatomi, Hiroshi. (Osaka Soda Co., Ltd.). Jpn. Tokkyo Koho (1974), 3 pp. CODEN: JAXXAD JP 49043197 19741119 Showa. Patent written in Japanese. Application: JP 70-124108 19701229. CAN 82:144527 AN 1975:144527 CAPLUS (Copyright 2005 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
JP 49043197	B4	19741119	JP 1970-124108	19701229

Priority Application		
JP 1970-124108	A	19701229

Abstract

Hg can be removed from a gas by treating with an absorbent comprising a metal (Li, Na, K, Ca, Mg, Zn, Al, Fe, Ni, Co) iodide or a compd. of the general formula R4NI (where R = H or a C1-4 alkyl) and an inorg. reducing agent on a carrier such as zeolite or silica gel. The reducing agent may be a hydrazonium salt, phosphorous acid salt, thiosulfuric acid, sulfurous acid salt, or stannous compds. Hg is present in H in alkali salt electrolysis. In an example, when a gas contg. Hg 1000-40,000 ±g/m3 is passed over a packed layer of the absorbent at a space velocity of 200-4000 hr-1, the amt. of Hg in the exit gas is reduced to <10 μg/m3.

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昭49-43197
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(全3頁)

1

(54)ガス中の水銀除去方法

(21)特　願　昭45-124108
(22)出　願　昭45(1970)12月29日
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発明の詳細な説明

本発明はガス中に含まれる微量の水銀を除去する方法に関する。

例えば水銀法アルカリ塩電解で得られる水素ガス中には水銀を含み、これは微量でも有機化合物の接触還元等に水素を使用する際、触媒毒となるため、あらかじめ実質的に除去しておくことが要求される。このような場合、水銀の除去方法としては水素を液体アンモニアの真空蒸発により−40℃に冷却してある竪型の管型冷却器に送り冷却し、水銀を微粒子に凝縮して除く深冷凝縮法、或いは水銀蒸気を含むガスを3～5kg/cm²の圧力の下に−30℃以下に冷却して除去する方法があるが、いずれも気体冷却のため膨大な冷凍設備を必要とする。

さらにモレキュラーシーブ又は活性炭により選択的に吸着させる方法、あるいは水銀を含むガスを活性炭または酸化アルミニウム上で硫化水銀と硫黄の混合物と接触せしめる方法があるが、前者は比較的能率の悪い欠点があり又後者は微量な水

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銀分が完全には吸着されない欠点がある。

又化学的方法として塩素水と水銀含有水素ガスを接触させて、水銀塩化物として除去する方法が知られているが操作時の調節が難かしく余分の塩素によりガスを再汚染する欠点がある。

又オゾン処理による除去方法も考案されているが後処理の静電分離、又は機械的ろ過に難点がある。さらにヨウ素を活性炭に吸着せしめた担体で除去方法があるが、ヨウ素が逸散する為に連続使用の点に難点があつた。

本発明者らは以上の問題点を解決するために検討をかさねた結果、水銀との反応性に富んだ遊離ヨウ素を含有しないヨウ素化合物および還元剤を利用してきわめて効果的にガス中の水銀を除去することに成功したものである。すなわち本発明はガス中の水銀を除去するに当り遊離ヨウ素を含有しないリチウム、ナトリウム、カリウム、カルシウム、マグネシウム、亜鉛、アルミニウム、鉄、ニッケル、コバルトより選ばれた金属ヨウ化物、あるいは一般式R_4NI（但しRはHまたはC_1～C_6のアルキル基）で示される化合物を炭素系担体、ゼオライト、シリカゲルのいづれかに吸着させた吸着剤担体に無機還元剤を1種または2種以上共存せしめて水銀を含むガスを接触させることを特徴とするガス中の水銀除去方法である。

このようなヨウ素化合物としてはヨウ化リチウム、ヨウ化ナトリウム、ヨウ化カリウム、ヨウ化カルシウム、ヨウ化マグネシウム、ヨウ化亜鉛、ヨウ化アルミニウム、ヨウ化鉄、ヨウ化ニッケル、ヨウ化コバルト、ヨウ化テトラエチルアンモニウムなどが挙げられる。また共存させる無機還元剤としてはヒドラジニウム塩、ヒドロキシルアンモニウム塩、亜リン酸及びその塩、チオ硫酸、次亜硫酸、亜硫酸及びその塩、第1銅化合物などが挙げられる。

また本発明に用いられる吸着剤担体の粒度は約6～100メッシュが適当である。

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本発明方法を実施するためにはあらかじめ該ヨウ素化合物を水に溶解させて、吸着剤担体の充填層に流下させることにより充分担体表面にヨウ素化合物を吸着せしめるか、あるいは該ヨウ素化合物を溶解させたアルコール溶液に吸着剤担体に加えて充分接触後、アルコールを蒸散せしめて担体表面にヨウ素化合物を吸着せしめる。さらに無機還元剤を共存させるために、その水溶液を同様にして担体表面に吸着させた後水銀を含むガスを通ずればよい。本発明方法は水素以外のガス、たとえば空気、窒素、炭酸ガスなどにも適用しうるものである。またガスの種類によつて耐用性が劣化を来したり、あるいはガス中の水銀の形態は通常水銀蒸気であるがガスの種類によつてそのごく一部が塩化水銀のごとき水銀化合物になつていることもあり、本発明法のごとく還元剤を共存せしめることにより効果的に水銀を除去しうるものである。

なおヨウ素化合物の吸着量はヨウ素分として吸着剤担体の重量の2～25重量%程度、無機還元剤の吸着量は担体重量の0.1～5重量%程度が適当である。

このようにして水銀含量約1000～40000 μg/m³（μgはmgの1000分の1）のガスを空間速度200～40001/Hrで充填層に流通せしめると、排ガス中の水銀は10 μg/m³以下に減少する。

ガス中におけるヨウ素化合物と水銀との反応機構は明らかではないが、最終的には吸着もしくは担持せしめたヨウ素化合物が水銀と反応してこれを捕捉するものと思われる。

又還元剤を共存させることによる反応機構は明らかではないが最終的には担体に存在するヨウ素化合物が水銀と反応してこれを捕捉すると同時に共存せしめた還元剤により耐用性がよくなりさらに亜硫酸水銀の如き水銀化合物も還元されてより効果的に水銀を除去しうるものと思われる。

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なお還元剤としては種々知られているが本発明方法に用いられる還元剤はこれらのうちで特に還元力にとみ、又耐用性を助長することが大で、実用化に適しているものである。

参考例　1

6～20メッシュの活性炭40gを内径20%のガラス管に充填し水銀含量12000 μg/m³の水素ガスを空間速度1500 l/Hrで流通せしめたところ排出ガス中の水銀濃度は1時間後で150 μg/m³、20時間後で3200 μg/m³、90時間後で11700 μg/m³であつた。

参考例　2

20～30メッシュのゼオライト30gを内径20%のガラス管に充填し水銀含量9700 μg/m³の水素ガスを空間速度1000 l/Hrで流通せしめたところ排出ガス中の水銀濃度は1時間後で9600 μg/m³であつた。

実施例　1

10～40メッシュの活性炭40gを内径20%のガラス管に充填しあらかじめヨウ化ナトリウム10gを溶解しているエタノール150 mlを流下せしめて担体に充分吸着せしめたのち風乾し、溶媒を充分除去する。さらに硫酸第一錫2gを含む水溶液50 mlを流下せしめて硫酸第一錫を共存せしめた後、水銀含量250 μg/m³の塩酸ガスを空間速度1500 l/Hrで流通せしめたところ排出ガス中の水銀濃度は10時間後で2 μg/m³、90時間後で3 μg/m³、250時間後で5 μg/m³、500時間後で9 μg/m³であつた。

実施例　2～4

実施例1と同様の方法でヨウ素化合物、担体および還元剤の種類をかえた実験結果を下表に示す。

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実施例	ヨウ素化合物	溶媒	担体 種類	担体 重量	担体 ヨウ素化合物含有量	還元剤 種類	還元剤 共存量	対象ガス 種類	対象ガス 流量空間速度	ガス中の水銀濃度（μg/Nm³） 入口	ガス中の水銀濃度（μg/Nm³） 出口 10時間後	ガス中の水銀濃度（μg/Nm³） 出口 250時間後	ガス中の水銀濃度（μg/Nm³） 出口 500時間後
例				g	重量%		重量%		1／Hr				
2.	ヨウ化亜鉛	水	活性炭	40	約 4.5	塩化第一錫	約2.0	H_2	1500	14600	2	4	9
3.	ヨウ化アルミニウム	水	活性炭	40	約10.0	塩酸ヒドロキシルアミン＋塩化第一錫	約2.0	H_2	1500	15000	3	4	10
4.	ヨウ化テトラエチルアンモニウム	水	ゼオライト	50	約 5.5	塩酸ヒドラジン	約1.5	H_2	600	9700	4	5	10

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◎特許請求の範囲

1　ガス中の水銀を除去するにあたり遊離ヨウ素を含有しないリチウム、ナトリウム、カリウム、カルシウム、マグネシウム、亜鉛、アルミニウム、鉄、ニッケル、コバルトより選ばれた金属ヨウ化物、あるいは一般式R_4NI（但しRはHまたはC_1～C_4のアルキル基）で示される化合物を炭素系担体、ゼオライト、シリカゲルのいづれかに吸着させた吸着剤担体に無機還元剤を1種または2種以上共存せしめて、水銀を含むガスを接触させることを特徴とするガス中の水銀除去方法。

◎引用文献

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米国特許　3194629

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JP 49053590 – Derwent Patent Family & English Abstract

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DIALOG(R)File 351: Derwent WPI
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0000681273
WPI Acc no: 1974-86196V/197450

Activated carbon contg. halides for mercury extn. - from air or gases, with excellent adsorptivity

Patent Assignee: NIPPON SODA CO (NIPS)

Patent Family (2 patents, 1 countries)							
Patent Number	**Kind**	**Date**	**Application Number**	**Kind**	**Date**	**Update**	**Type**
JP 49053590	A	19740524	JP 197297142	A	19720929	197450	B
JP 1980033375	B	19800830				198039	E

Priority Applications (no., kind, date): JP 197297142 A 19720929
Alerting Abstract JP A
Activated carbon contg. halides of Group III-VIII metals has excellent adsorptive capacity for Hg and is useful for removal of Hg from air or gases. The activated carbon is prepd. by immersing ordinary activated carbon in a soln. of the halides in water or an org. solvent. Thus, 50 parts activated carbon (20-50 mesh) was immersed in 200 parts aq. 10% FeCl3 soln. for 30 min and dried at 105-100 degrees after removing excess soln. Then, the activated carbon was packed in a glass tube and air contg. 10 mg Hg/m3 was passed through the tube at 1.1 l./min. Even after 10 hr, the activated carbon actively adsorbed Hg and the air from the tube contained <0.005 mg Hg/m3.

Title Terms /Index Terms/Additional Words: ACTIVATE; CARBON; CONTAIN; MERCURY; EXTRACT; AIR; GAS; ADSORB

Class Codes

International Patent Classification					
IPC	**Class Level**	**Scope**	**Position**	**Status**	**Version Date**
B01D-0053/34	A	I		R	20060101
B01D-0053/64	A	I	F	R	20060101
B01J-0020/20	A	I	L	R	20060101
C01B-0031/08	A	I	L	R	20060101
B01D-0053/34	C	I		R	20060101
B01D-0053/46	C	I	F	R	20060101
B01J-0020/20	C	I	L	R	20060101
C01B-0031/00	C	I	L	R	20060101

Japan National Classification FI Terms			
FI Term	**Facet**	**Rank**	**Type**
B01D-053/34 136 A			
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Japan National Classification F Terms		
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4D002		
4G046		
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4G146	AA16	
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4G066	AA37	B
4G146	AC02	B
4G066	AC07	A
4G146	AC28	B
4D002	BA04	
4G066	BA20	
4G146	BA31	
4D002	CA07	
4D002	CA08	
4D002	CA09	
4D002	CA11	
4G066	CA47	
4G146	CB11	
4G146	CB12	
4G146	CB34	
4G066	DA03	
4D002	DA41	
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Current JP FI-Terms: B01D-53/34 136 A B01J-20/20 D C01B-31/08 Z B01J-20/20 D (BCM)
Current JP F-Terms: 4D002 4G046 4G066 4G146 4G066AA05B 4G146AA06 4G146AA16 4D002AA29 4G066AA37B 4G146AC02B 4G066AC07A 4G146AC28B 4D002BA04 4G066BA20 4G146BA31 4D002CA07 4D002CA08 4D002CA09 4D002CA11 4G066CA47 4G146CB11 4G146CB12 4G146CB34 4G066DA03 4D002DA41 4D002DA70 4D002GA02 4D002GB02 4G046HA08 4G046HB02 4G046HC14

Publication No. JP 1980033375 B (Update 198039 E)
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公開特許公報

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特許願(A)

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特許庁長官 三宅幸夫 殿

1. 発明の名称
活性炭

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5. 添付書類の目録
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(エ) 審査請求書 1通



明細書

1. 発明の名称
活性炭

2. 特許請求の範囲
活性炭に遷移律表の3族より8族までの金属元素のハロゲン化物を担持したことを特徴とする活性炭。

3. 発明の詳細な説明
本発明は、ガス中に存在する水銀に適用する新規な水銀吸着用の活性炭及びその製造方法に係わるものである。

大気中に含まれる水銀は従来から労働衛生的立場より許容値（0.1 mg/m³）以下に管理することが必要であつたが、昨今の公害規制の強化に伴つて、環境衛生的立場からも次第に厳しい管理が必要とされるようになつてきている。同様に、又化学工業製品の原料となる各種の気体、例えば天然ガスなどに含まれる水銀に対しても厳しい規制と管理が必要になつている。

この様な大気中の水銀又は各種気体中の水銀の除去に関しては従来既にいくつかの方法が提案されている。例えば、高濃度の水銀に対しては、冷却して凝縮させる方法、又低濃度の水銀に対しては、硫化物を含む溶液に吸収させる方法や活性炭などの吸着剤に吸着させる方法などが夫々提案されている。

これらの方法のうち、吸着剤を用いる方法は操作が簡単で、ある程度大容量のガスにも適用でき、又除去下限も割合い低いなどの利点を有しているようであるが、なお吸着剤として吸着能力の高い優れたものを必要とする。しかしながら、現在この様な条件に適するものが見当らず、一部に使用されている活性炭もその性能特に細孔（ポア）が極かく工業的な使用に対しては不適当である。

本発明者らは大気中、あるいは各種の製品気体中の水銀を除去するために、上記の優れた特長をもつ吸着法を採用することとし、それに適する優れた吸着剤を得ることを目的として鋭多

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くの実験研究を行なった結果、吸着剤として活性炭に、周期律表の第3族から第8族までの金属元素のハロゲン化物、特に2価もしくは3価の鉄の塩化物が、各種気体中の水銀の吸着除去に著しく優れた機能をもつことを見出し、更に種々検討の結果、本発明を完成したものである。

本発明に云う周期律表第3族より8族までの金属元素のハロゲン化物とは、例えば、アルミニウム、アンチモン（3価、5価）、インジウム、クロム、コバルト、すず（2価、4価）、チタニウム（3価、4価）、鉄（2価、3価）、銅、ニッケル、パナジウム、マンガンなどの各金属のあらゆる塩化物、臭化物、沃化物及び弗化物である。又、これらの金属元素のハロゲン化物を担持させるための活性炭は、一般の活性炭でよいが、特にヤシガラ炭が適当であり、又その形状は普通粒状が用いられるが、勿論粉末も使用できる。

本発明の吸着剤の製造法は上記の如き周期律表の第3族より第8族までの金属元素の塩化物、臭化物、沃化物又は弗化物の1種又は2種以上の混合物を水溶液又は適宜の不活性なる有機溶媒の溶液、例えばエタノール、メタノール、プロパノール等のアルコール類、アセトン、メチルエチルケトン等のケトン類、その他の極性有機溶媒の溶液とし、この溶液を浸漬、噴霧、その他の方法を用いて活性炭に含浸させ、乾燥させるものである。この場合、溶液中の金属元素のハロゲン化物の濃度は活性炭にこれらの化合物が均一に含浸される程度のものであればよく、一般には0.1～40%、好ましくは1～30%が適当である。又、浸漬の場合、浸漬する時間は均一含浸に必要な時間でよく、又、減圧下で含浸する場合には更に短時間ですむ。更に乾燥温度及びその時間は含浸した化合物が熱分解を起さない程度であればよく、一般には常圧下、50～110℃で、3～10時間が適当であるが、減圧状態下では更に低温、短時間の乾燥が可能である。活性炭中のハロゲン化物の量は特に限定されず少量でも効果があるが通常0.01%～40%（重量）、好ましくは0.1%～20%程度が採用される。

本発明の活性炭は吸着剤成はその主成分として利用され、一般のガス用吸着剤と同様に、各種の気－固接触による吸着方式の何んといずれをも採用することが可能である。例えば、固定床方式、移動床方式、流動床方式、気体輸送方式などの各種の方式にて被処理気体と接触せしめることができるが、勿論、本発明はその使用法によって制限されることはない。

本発明の活性炭からなる吸着剤の性能をその吸着剤である活性炭と比較してみると表1の通りである。これより本発明の吸着剤は通常の活性炭に比較して著しく高い吸着性能を有していることが認められる。尚この場合の試験方法は実施例1に示した方法と同じである。

表1

空気中水銀濃度	吸着までの時間	
	本発明の活性炭（下記実施例）	通常の活性炭
約10mg/m³ 約25℃	2日経過以上 340分	1時以下 〃

この様な本発明の活性炭からなる吸着剤における著しい性能向上の機構は必ずしも明らかではないが、この様な効果は活性炭以外の多孔性吸着剤、例えば活性アルミナ、シリカ、ゼオライト、オイルコークス、パーライト、けいそう土などには見られないことであることから、活性炭独特のものとみられ、活性炭表面の水銀吸着のための活性点又はミクロやマクロな細孔が、これらの第3族から第8族迄の金属元素のハロゲン化物によって影響され、水銀吸着速度が増加すると共に、吸着量も増加したことによるものと考えられる。

本発明の方法を更に詳細な実施例で示すと以下の様になるが、本発明は以下の実施例により制限されることはない。

実施例1

ヤシガラ活性炭（20～50メッシュ）50部を秤取し、塩化第二鉄の10%溶液200部中に浸漬し、充分に攪拌をはかり約30分後にとりだし、過剰の溶液を減圧濾過して乾燥器に

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入れ、105～110℃にて10時間乾燥させた。

かくして得られた活性炭である吸着剤の重量は5.7部であり、17部の増量を認めた。次にこのものを内径6mmのガラス管中に充填し（充填長さ20cm，充填重量350mg）約30mgの水銀を入れた二口の500mlの三角フラスコに取付け（他の口は解放）、カラムの他端を水銀蒸気計（ベックマン製、モーラ型）に連結したのち、先端にエアーポンプをとりつけて流量1.1l/minで作動させた。従ってフラスコ内を通る空気は水銀蒸気（約10mg/m³）を伴ってカラムに入り、カラム内の吸着剤層を通る間に水銀は吸着され、水銀の減少したガスは水銀蒸気計を通して外に排出された。ここで蒸気計のペンはガス中の残存水銀量を示し、これをレコーダーで記録することにより、カラムに含まれる吸着剤の水銀吸着挙動を知り得た。この記録図よりその条件における活性炭の吸着剤の破過時間を読みとり、これを吸着剤の性能の尺度とした。その結果、本実施例の活性炭は20時間の通気によっても破過に至らなかった。そして、カラムを通過してできた空気中の水銀濃度は、カラムが破過に達する迄は0.005mg/m³（5γ/l）以下であった。一方活性炭の場合は、1秒以下の通気によって破過に達した。そしてカラムを通過してできた空気中の水銀濃度は0.005mg/m³以上であった。

実施例2

実施例1に準じヤシガラ活性炭（20～50メッシュ）に、表2に示す第3族から第8族迄の種々の金属元素のハロゲン化物の溶液を含浸させ、乾燥させた。

かくして得られた吸着剤につき実施例1と同様な試験方法により吸着能力の測定を行なった。又、金属水銀を入れた三角フラスコは恒温槽中に入れて加熱し、通気用空気中の水銀濃度を高くして（約250mg/m³）同様に試験を行なった。得られた結果は表2の通りである。

表2

担持物	破過迄の時間	
	1通気中Hgが10mg/m³の場合	3通気中Hgが250mg/m³の場合
塩化アルミニウム $AlCl_3 \cdot 6H_2O$	10時間以上	130分
塩化マンガン $MnCl_2$	〃	100
塩化クロム $CrCl_3$	〃	150
塩化第一すず $SnCl_2$	20時間以上	190
塩化第二すず $SnCl_4$	19時間以上	210
塩化第一鉄 $FeCl_2$	20時間以上	340
塩化第二鉄 $FeCl_3 \cdot 6H_2O$	〃	320
塩化銅 $CuCl_2$	10時間以上	50
塩化ニッケル $NiCl_2$	〃	195
塩化マンガン $MnCl_2 \cdot 4H_2O$	〃	80
臭化アルミニウム $AlBr_3$	〃	105
臭化すず $SnBr_2$	〃	120
臭化第二鉄 $FeBr_3$	〃	310
臭化ニッケル $NiBr_2$	〃	170
よう化アルミニウム AlI_3	〃	250
よう化コバルト CoI_2	〃	230
よう化すず SnI_2	〃	270
よう化鉄 FeI_2	〃	380
よう化ニッケル NiI_2	〃	130
硫化鉄 FeS	5時間以上	50
硫化すず SnS	〃	45
弗化アルミニウム AlF_3	〃	70
なし（活性炭のみ）	1秒以内	1秒以内

実施例3

実施例1で作成した活性炭（吸着剤）を径6mmのガラス管に20cmの長さに充填（約350mg）し、これに水素ガス（Hg約12mg/m³を含む）を流量1.1l/minで通じ、実施例1と同様な装置によりカラムを通って出てきた水素ガス中の水銀の分析を行なった。その結果、20時間の通気によっても本実施例の吸着剤は破過に至らなかったが、一方通常の活性炭単独の場合は1秒以内に破過に達した。尚カラムを通過した水素ガス中の水銀の濃度は、本実施例の吸着剤の場合は0.005mg/m³（5γ/l）であったが、通常の活性炭単独の場合は時間が短かく、不安定で0.005mg/m³以下までは低下しなかった。

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JP 49066592 – Derwent Patent Family & English Abstract

4/9/2
DIALOG(R)File 351: Derwent WPI
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WPI Acc no: 1975-06408W/197504

Carbon adsorbent for removing mercury vapour from air - carrying at least one chloride of alkali or transition metal

Patent Assignee: SUMITOMO CHEM CO LTD (SUMO)

Patent Family (1 patents, 1 countries)							
Patent Number	**Kind**	**Date**	**Application Number**	**Kind**	**Date**	**Update**	**Type**
JP 49066592	A	19740627	JP 1972110054	A	19721101	197504	B

Priority Applications (no., kind, date): JP 1972110054 A 19691027

Alerting Abstract JP A
An activated C carrying >=1 chlorides of Li, Na, K, Mg, Ba, Zn, Al, Sn, Mn, Fe, Co, Ni, and NH4 is used as a collector for Hg vapour. In an example, activated C 4-6 mesh) was soaked in aq. 10% BaCl2 for 10 min, and dried at 100 degrees for 10 hr to yield a collector for Hg vapour. Air (5 l./min) contg. 31 mg H/m3 was passed through a column (diam. 2, height 0, packed height 10 cm) packed with the activated C. After 5 hr, the air from the column contained 0.0003 mg Hg/m3, as compared to 0.42 mg/m3 for an untreated activated C after passing air (37 mg Hg/m3) for 1 hr.

Title Terms /Index Terms/Additional Words: CARBON; ADSORB; REMOVE; MERCURY; VAPOUR; AIR ; CARRY; ONE; CHLORIDE; ALKALI; TRANSITION; METAL

Class Codes

International Patent Classification					
IPC	**Class Level**	**Scope**	**Position**	**Status**	**Version Date**
B01D-0053/64	A	I	L	R	20060101
C25B-0001/36	A	I	F	R	20060101

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⑲ 日本国特許庁

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6518 4A

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特 許 願 ㊞

昭和47年11月1日

特許庁長官 三 宅 幸 夫 殿

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水素選択吸着剤

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明細書

1. 発明の名称
水素選択吸着剤

2. 特許請求の範囲
Li, Na, K, Mg, Be, Zn, Al, Sn, Mn, Fe, Co, Ni, MoO_3 の酸化物の中から選ばれた少なくとも3ノ種の酸化物を担持した活性炭を有効成分としてなる水素選択吸着剤。

3. 発明の詳細な説明
本発明は水素選択吸着剤に関する。更に詳細には Li, Na, K, Mg, Be, Zn, Al, Sn, Mn, Fe, Co, Ni, MoO_3 の酸化物の中から選ばれた少なくとも3ノ種の酸化物を担持した活性炭を有効成分としてなる水素選択吸着剤に関する。

ガス中の水素選択の操作は製造上また水素精製の点から水素を選択するプロセスにおいては極めて重要である。

従来、ガス中の水素選択除去方法としては、水素含有ガスを圧縮、冷却して、水蒸気の分圧を下げ、凝縮分離させる方法(特公昭37-3741号公報)、特殊な吸着剤、例えばモレキュラーシーブス(ジャーナル・オブ・アプライド・ケミストリー、7巻、Oct. 283頁)、WO_3 ガスを吸着させた活性炭(特公昭47-23004号公報)、$CaCl_2$ を担持せしめた活性炭(特公昭47-22334号公報)、Ag あるいは Cu のような重金属を担持せしめた活性炭(米国特許第3,173,787号明細書)、Ag を担持せしめたアルミナ(米国特許第3,237,774号明細書)などを用いる方法や、溶液を吸収剤液、例えば炭酸水素ソーダ溶液(米国特許第3,647,337号明細書)や過マンガン酸カリー硫酸溶液(特公昭47-23944号公報)などで洗浄する方法などが提案されている。

本発明者らは、水素選択吸着方法としては、吸収剤溶液洗浄法よりも乾式法が適当であると考え水素選択吸着能の大なる吸着剤を見出すべく鋭意研究の結果、上記吸着物を担持させた活性炭が著しく優れた水素選択吸着能を有することを見出し、本発明に至ったものである。すな

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わち、高価な貴金属を使用したり、有害な SO_2 を使用しないで低廉で無害な触媒剤を活性炭に含浸させた等れた水蒸気吸着を有する水蒸気吸着剤である。上記塩化物の中から選ばれた少なくとも一種の塩化物を担持させることにより水蒸気に対する親和力が増大するために水蒸気を著しく吸着するものと考えられる。

すなわち、本発明は、Li, Na, K, Mg, Ca, Sr, Al, Sn, Mn, Fe, Co, Ni, NH_3 の塩化物の中から選ばれた少なくとも一種の塩化物を担持せしめた活性炭を有効成分とする水蒸気の吸着剤を提供するものである。

原料活性炭の種類、粒径、形状等は特に限定されるものではない。

活性炭と上記塩化物の担持は上記塩化物の中から選ばれた少なくとも一種の塩化物の水溶液中へ活性炭を浸漬する等の方法により容易に出来る。担持に用いる塩化物の水溶液は約1重量%～飽和濃度であり、担持時間は一般に数分以上、望ましくは、1分以上である。

塩化物を担持させた活性炭は通常100℃で1～6時間乾燥処理すればよい。

このようにして得られた水蒸気吸着剤は未処理の活性炭に比し 10^3 倍以上の水蒸気吸着能を有し、ガス中の水蒸気濃度を数10 ppm 以下にすることが可能である。

また、活性炭製造時に賦活のために塩化亜鉛等が使用されているが、この場合でも脱塩処理後使用すれば全く支障ない。従って、本発明にいう上記塩化物の活性炭への担持は、活性炭製造中の塩化亜鉛等の残存処理を意味するものではない。

上記吸着剤を用い、水蒸気吸着を行なうに当り、ガス中に含まれるミストや水分を出来るだけ除去しておくのが吸着剤の寿命を延ばし、効率を維持する上から好ましい。例えば、水蒸気発生装置工場より発生する含水蒸気ガスから本発明の水蒸気吸着剤により、水蒸気を除去する場合には、含水蒸気含有ガスを先ず水洗塔を通し、ミストを除去し、ブライン冷却により水蒸気濃度を約1/3～1/10とし、更にミストセパレーターでミストを除去し、次いで本発明の水蒸気吸着剤と接触させる方法によって行うのが好ましい。

本発明の水蒸気吸着剤は一般の気ガス中の水蒸の除去の他、特に水銀整流装置工場より発生する水素中の水蒸の除去に極めて有効である。

以下本発明を実施例により説明するが本発明は実施例によって限定されるものではない。

実施例1

6～14メッシュの粒状活性炭を1%の塩化バリウム、塩化亜鉛、塩化アルミニウム、塩化第二鉄、塩化アンモニウム、塩化マグネシウム、塩化マンガンのそれぞれの水溶液中に1分間浸漬したのち100℃で1時間乾燥し水蒸気吸着剤を作成した。この吸着剤を内径3cmの管中で充填し、水蒸気を含有する空気を3.5 l/分の速度で通した。

上記水蒸気含有空気の吸着前後通過時間のガス中の水蒸気量を吸光光度法で測定した。その結果を第1表に示す。

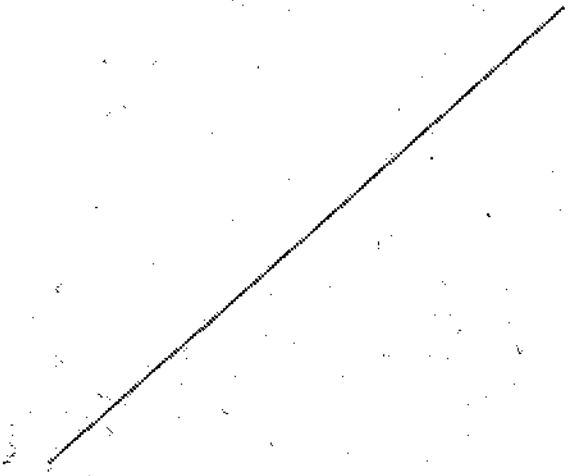
第 1 表

実験番号	活性炭に担持された塩化物	通気時間（時間）	水蒸気量（mg/l）	
			通過前	通過後
1	塩化バリウム	3	31	0.0003
		10	34	0.0038
		20	34	0.0095
		30	32	0.010
		70	35	0.16
2	塩化亜鉛	10	28	0.0094
		30	32	0.016
		50	29	0.063
		70	28	0.078
		100	27	0.23
3	塩化アルミニウム	3	30	0.027
		10	30	0.0049
		15	30	0.0031
4	塩化第二鉄	10	41	0.0034
		30	33	0.041
		45	29	0.080
		70	31	0.11
5	塩化アンモニウム	4	43	0.0038
		8	43	0.0038
		12	43	0.0093
6	塩化マグネシウム	3	28	0.030
		6	28	0.013
7	塩化マンガン	3	32	0.019
		6	32	0.019

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実施例2

ノクーノSメッシュの粒状活性炭をノ%の塩化コバルト、塩化鉛、塩化リチウム、塩化カルシウム、塩化ニッケル、塩化ナトリウムのそれぞれの水溶液に/0分間浸漬した後、/00℃で/0時間乾燥して水銀蒸気捕集剤を製造した。この捕集剤を用いて実施例/と同様にして水銀吸着能力を調べた。その結果を第2表に示す。



第 2 表

実験No.	活性炭に担持された塩化物	通気時間（時間）	水銀濃度（%/m³）	
			通気前	通気後
8	塩化コバルト	5	34	0.0068
		10	33	0.0031
		15	30	0.0039
9	塩化鉛	2	38	0.016
		4	38	0.014
		6	38	0.013
10	塩化リチウム	2	35	0.020
		4	37	0.023
		6	37	0.023
11	塩化カリウム	10	36	0.023
		20	40	0.030
		30	38	0.029
12	塩化ニッケル	4	41	0.0092
		8	36	0.0086
		12	38	0.0089
13	塩化ナトリウム	4	33	0.0028
		8	33	0.0038
		12	34	0.0008
		16	36	0.0044

比較例

未処理の活性炭を用いて実施例/と同様にして水銀吸着能力を調べた。結果を第3表に示す。

第 3 表

実験No.	通気時間（時間）	水銀濃度（%/m³）	
		通気前	通気後
14	1	37	0.43
	2	37	1.1

実施例/～2および比較例より本発明の水銀蒸気捕集剤は未処理の活性炭に比し、著しく水銀蒸気吸着能が優れていることが明らかである。

5. 添付書類の目録

(1) 明 細 書　　1 通 (7 頁)
(2) 委 任 状　　1 通

6. 前記以外の発明者，特許出願人または代理人

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Page 1158

Bibliographic Information

Removal of mercury contained in gas. Yokota, Noriyuki; Tokuda, Shingo; Ito, Yoshiro; Matsushita, Hiroshi. (Osaka Soda Co., Ltd., Japan). Jpn. Tokkyo Koho (1975), 3 pp. CODEN: JAXXAD JP 50006438 19750313 Showa. Patent written in Japanese. Application: JP 70-124107 19701229. CAN 83:168162 AN 1975:568162 CAPLUS (Copyright 2005 ACS on SciFinder (R))

Patent Family Information

Patent No.	Kind	Date	Application No.	Date
JP 50006438	B4	19750313	JP 1970-124107	19701229

Priority Application		
JP 1970-124107	A	19701229

Abstract

An I-contg. compd. and/or I mixt. is adsorbed on an anion exchange resin. The resulting compd. is used to remove Hg from a gas by contact. Thus, a 500 ml aq. soln. contg. 43 g NaI was introduced into a 20 mm-diam. glass column packed with 50 g 15-50 mesh anion exchange resin having the functional group NMe3+ Cl-. The amt. of I adsorbed on the resin was 17 wt.%. H contg. 7500 mg Hg/m3 was passed through the column at 800 l./hr and the Hg concns. after 10, 90, and 250 hr were 2, 4, and 10 mg Hg/m3.

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B 01 D 53/00
C 25 B 1/36

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特許公報

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昭50-6438
④公告 昭和50年(1975) 3月13日
発明の数 1
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1

⑤ガス中の水銀除去方法

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（公害防止関連技術）

発明の詳細な説明

本発明はガス中に含まれる微量の水銀を除去する方法に関する。

例えば水銀法アルカリ塩電解で得られる水素ガス中には水銀を含み、これは微量でも有機化合物の接触還元等に水素を使用する際、触媒毒となるため、あらかじめ実質的に除去しておくことが要求される。

このような場合、水銀の除去方法としては水素を液体アンモニアの真空蒸発により−80℃に冷却してある垂直の管型冷却器に送り冷却し、水銀を微粒子に凝縮して除く深冷凝縮法、あるいは水銀蒸気を含むガスを3～5kg/cm²の圧力の下に−30℃以下に冷却して除去する方法があるが、いずれも気体冷却のため膨大な冷凍設備を必要とする。さらにモレキュラーシーブ又は活性炭により選択的に吸着させる方法、あるいは水銀を含むガスを活性炭または酸化アルミニウム上で硫化水銀と硫黄の混合物と接触させる方法があるが前者は比較的能率の悪い欠点があり、又後者は微量な水銀分が完全には吸着されない欠点がある。又化学的方法として塩素水と水銀含有水素ガスを接触させて、水銀塩化物として除去する方法が知られているが操作時の調節が難かしく余分の塩素によりガスを再汚染する欠点がある。又オゾン処理による除去方法も考案されているが後処理の静電分離又は機械的ろ過に難点がある。

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本発明は以上の難点を解決するものであつて水銀との反応性に富むヨウ素化合物単独あるいはこれとヨウ素を利用し、加うるにそれらの特異な吸着性を示す陰イオン交換樹脂を併用して、容易にかつ有効にガス中の水銀を除去する方法を提供するものである。

すなわち本発明は、ヨウ素化合物、又はこれらとヨウ素の混合物を吸着せしめた陰イオン交換樹脂に水銀を含むガスを接触せしめることを特徴とするガス中の水銀除去方法である。

このようなヨウ素化合物としては、ヨウ化アルミニウム、ヨウ化亜鉛、ヨウ化カリウム、ヨウ化アンモニウム、ヨウ化カルシウム、ヨウ化コバルト、ヨウ化ストロンチウム、ヨウ化鉄(II)、ヨウ化ナトリウム、ヨウ化ニッケル、ヨウ化マグネシウム、ヨウ化リチウム、ヨウ化テトラエチルアンモニウム、ヨウ化メチレン、α-ヨードナフタリン、O-ヨードフエノール、ヨードベンゼンなどが上げられる。

又本発明に用いられる陰イオン交換樹脂としては、その母体に、$-N(CH_3)_3^+X^-$, $-N(CH_3)_2(C_2H_4OH)^+X^-$, $-N(R)_2$ $-NHR$, $-NH_2$ と$-N(CH_3)_2$, (XはCl⁻, OH⁻などの陰イオンを表わし、RはCH₃, C₂H₅などのアルキル基を表わす)の如き交換基を有するものが適当である。

本発明に用いる陰イオン交換樹脂は水溶媒系、非水溶媒系のいずれにおいても吸着能を有するものが用いられる。

本発明方法を実施するためには、あらかじめ上記ヨウ素化合物、又はこれらとヨウ素の混合物を

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水又は有機溶媒に溶解させて、陰イオン交換樹脂の充填層に通下させることにより充分樹脂にヨウ素化合物、又はこれらとヨウ素の混合物を吸着させて被水銀を含むガスを通ずればよい。本来陰イオン交換樹脂には水溶媒系においてヨウ素イオンとして吸着されるものであるが、エタノールの如き有機溶媒には前記ヨウ素化合物のうち例えばヨウ化ナトリウム、ヨウ化メチレンなどはよく溶解し、陰イオン交換樹脂に吸着される、このような場合を含めて、本発明方法におけるヨウ素化合物とはヨウ素イオンになりえて陰イオン交換樹脂にイオン吸着されるものである。

本発明方法は水素以外のガス、たとえば空気、窒素、炭酸ガスなどにも適用しうる。

なおヨウ素分の陰イオン交換樹脂に対する吸着量は樹脂重量の5～95%が適当である。

ここで云うヨウ素分とは、例えばヨウ化カリウムのみを含む溶液、あるいはヨウ素とヨウ化カリウムとの混合溶液中で陰イオン交換樹脂にそれらを吸着せしめた場合、吸着された全ヨウ素を意味するものである。又実施例において重量当りに対し吸着されたヨウ素分が大きい値を示している場合があるが、これは単にヨウ素イオンの吸着量が大きいのみでなく、例えばヨウ素とヨウ化カリウムの混合溶液中では、下記に示す反応式の如きポリヨウ素イオンが生成し、よく吸着されるものである。

$$nI+I^{+} \rightarrow I_{n}^{-} \quad (n:3,5\text{など})$$

このようにして、水銀約1,000～40,000 μg／m³（μgは㎎の1,000分の1）を含むガスを空間速度200～4,000 l／Hr で充填層に流通せしめると排出ガス中の水銀濃度は10 μg／m³以下に減少する。

ヨウ素化合物、又はこれらとヨウ素の混合物を吸着した陰イオン交換樹脂とガス中における水銀との反応機構は明らかではないが、最終的には陰イオン交換樹脂上に吸着されたヨウ素分が水銀と反応してこれを補捉するものと思われる。

本発明に使用する、ヨウ素イオンを吸着した陰イオン交換樹脂はきわめてその製法が簡単であり、かつヨウ素分としてきわめて多く吸着するために水銀に対する吸着能もすぐれ、長時間の連続使用に耐えうるものである。

以下示す比較例および実施例において水銀濃度の測定方法は次の如くである。すなわち充填層の通過前のガス中の水銀濃度（100～10,000 μg／m³）の分析は、北川式ガス検知管（ヨウ化第一銅を吸着せしめたシリカゲル粉を入れたガラス管に被検ガスを流し、そのシリカゲル粉の変色域の長さにより水銀濃度を測定する）により行つた。また充填層通過後のガス中の微量水銀濃度（1～10 μg／m³）の分析は、震盪一週マンガン酸カリ混合水溶液中に被検ガスを導き、水銀分を吸収せしめ、その吸収液に還元剤を加えて空気でバブリングを行い、水銀を金属蒸気として気化せしめ253.7 mμの紫外線での吸光光度を測定した。

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比較例　1

粒度15～50メッシュの－N（CH_3）$_3^{+}$ Cl^{-}基を有する陰イオン交換樹脂（商品名DIAION・SA11A・三菱化成社製）50 gを内径20 m／mのガラス管に充填し、水銀12,000 μg／m³の水素ガスを空間速度4601／Hrで流通せしめたところ排出ガス中の水銀濃度を1時間後に測定したところ12,000 μg／m³であつた。

実施例　1

粒度15～50メッシュの－N（CH_3）$_3^{+}$ Cl^{-}基を有する陰イオン交換樹脂（商品名DIAION・SA11A・三菱化成社製）50 gを内径20 m／mのガラス管に充填し、ヨウ化ナトリウム43 gを溶解した水溶液500 m/lを流下せしめて陰イオン交換樹脂に充分吸着せしめたところ、樹脂重量当りのヨウ素分の吸着量は約17%であつた。このヨウ化ナトリウム吸着陰イオン交換樹脂に水銀含量7,500 μg／m³の水素ガスを空間速度8001／Hrで流通せしめたところ排出ガス中の水銀濃度は10時間後で2 μg／m³，90時間後で4 μg／m³，250時間後で10 μg／m³であつた。

実施例　2

粒度15～50メッシュの－N（CH_3）$_2$（C_2H_4OH）$^{+}$ Cl^{-}基を有する陰イオン交換樹脂（商品名DIAION・SA21A三菱化成社製）50 gを内径20 m／mのガラス管に充填し、ヨウ化カリウム90 gとヨウ素60 gを溶解した水溶液1,200 m/lを流下せしめて陰イオン交換樹脂に充分吸着せしめたところ樹脂重量当りのヨウ素分の吸着量は約90%であつた。

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このヨウ素分を吸着した陰イオン交換樹脂に水銀含量5,500 μg／m³の水素空間速度1,500 l／Hrで流通せしめたところ排出ガス中の水銀濃度は10時間後で3 μg／m³，90時間後で5 μg／m³，250時間後で9 μg／m³であつた。

実施例　3

粒度15～40メッシュの－N（CH_3）$_2$（C_2H_4OH）$^+$Cl$^-$基を有する陰イオン交換樹脂（商品名DIAION・SA21A三菱化成社製）50 gを内径20 m／mのガラス管に充填し，ヨウ化コバルト50 gとヨウ化テトラエチルアンモニウム10 gを溶解した水溶液500 mlを流下せしめて陰イオン交換樹脂に充分吸着せしめたところ樹脂重量当りのヨウ素分の吸着量は約15 %であつた。このヨウ素分を吸着した陰イオン交換樹脂に水銀含量6,000 μg／m³の水素を空間速度700 l／Hrで流通せしめたところ排出ガス中の水銀濃度は10時間後で4 μg／m³，90時間後で5 μg／m³，250時間後で9 μg／m³であつた。

実施例　4

粒度15～50メッシュの－N（CH_3）$_2$基

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を有する陰イオン交換樹脂（商品名Dewex-3 ダウケミカル社製）50 gを内径20 m／mのガラス管に充填し、ヨウ化ナトリウム60 gとヨウ素40 gを溶解したエタノール1,000 mlを流下せしめて陰イオン交換樹脂に充分吸着せしめたところ樹脂重量当りのヨウ素分の吸着量は約60 %であつた。このヨウ素分を吸着した陰イオン交換樹脂に水銀含量400 μg／m³の塩素ガスを空間速度350 l／Hrで流通せしめたところ排出ガス中の水銀濃度は10時間後で4 μg／m³，90時間後で7 μg／m³，250時間後で10 μg／m³であつた。

㊀特許請求の範囲

1　ヨウ素化合物、又はこれらとヨウ素の混合物を吸着せしめた陰イオン交換樹脂に水銀を含むガスを接触せしめることを特徴とするガス中の水銀除去方法。

㊁引用文献

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JP 51003386 – Derwent Patent Family & English Abstract

4/9/1
DIALOG(R)File 351: Derwent WPI
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WPI Acc no: 1976-15461X/197609

Heavy metal adsorption agent - comprising hydrohalogenic acid salt of amino deriv activated carbon
Patent Assignee: TOKUYAMA SODA KK (TOKU)

Patent Family (2 patents, 1 countries)

Patent Number	Kind	Date	Application Number	Kind	Date	Update	Type
JP 51003386	A	19760112	JP 197473430	A	19740628	197609	B
JP 1979008474	B	19790416				197919	E

Priority Applications (no., kind, date): JP 197473430 A 19740628
Alerting Abstract JP A
An agent for adsorbing heavy metal and exhibiting a low break-through value and large adsorption capacity, esp. an agent for adsorbing mercury which exhibits long stable adsorption activity is prepd. The agent comprises a hydrogen halide salt of cpd. (I) having >=1 of -NH2, -NH- and N-, gps. and activated carbon. (I) may be inorganic amino cpds., aliphatic amines, alicyclic amines, heterocyclic amines, aromatic amines, amino acids, amides or hydrazides.

Title Terms /Index Terms/Additional Words: HEAVY; METAL; ADSORB; AGENT; COMPRISE; HYDROHALOGENATION; ACID; SALT; AMINO; DERIVATIVE; ACTIVATE; CARBON

Class Codes

International Patent Classification

IPC	Class Level	Scope	Position	Status	Version Date
B01D-0015/00	A	I		R	20060101
B01D-0053/64	A	I	L	R	20060101
B01J-0020/20	A	I	L	R	20060101
B01J-0020/22	A	I	L	R	20060101
C02F-0001/28	A	I	L	R	20060101
C09K-0003/00	A	I	F	R	20060101
B01D-0015/00	C	I		R	20060101
B01D-0053/46	C	I	L	R	20060101
B01J-0020/20	C	I	L	R	20060101
B01J-0020/22	C	I	L	R	20060101
C02F-0001/28	C	I	L	R	20060101
C09K-0003/00	C	I	F	R	20060101

Japan National Classification FI Terms			
FI Term	**Facet**	**Rank**	**Type**
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4D024		
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4G066		
4H016		
4G066	AA05	B
4D024	AA09	
4D624	AA09	
4D002	AA28	
4D002	AA29	
4G066	AA33	B
4G066	AA34	B
4G066	AA51	B
4G066	AB07	B
4G066	AB10	B
4G066	AB12	B
4G066	AB13	B
4G066	AB15	B
4D024	AB16	
4D624	AB16	
4D024	AB18	
4D624	AB18	
4H016	AE00	
4H016	AE02	
4H016	AE03	
4H016	AE04	
4D024	BA01	
4D624	BA01	
4D024	BA02	
4D624	BA02	
4D002	BA04	

4D024	BA16
4D624	BA16
4G066	BA20
4D024	BB01
4D624	BB01
4D024	BB08
4D624	BB08
4D024	CA01
4D624	CA01
4D002	CA07
4G066	CA46
4G066	CA47
4G066	DA03
4D002	DA31
4D002	DA32
4D002	DA41
4D002	DA61
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Current JP FI-Terms: B01D-53/34 136 A B01J-20/20 D B01J-20/22 B C02F-1/28 B C09K-3/00 106 C09K-3/00 108 C09K-3/00 108 B C09K-3/00 108 C C09K-3/00 108 D
Current JP F-Terms: 4D002 4D024 4D624 4G066 4H016 4G066AA05B 4D024AA09 4D624AA09 4D002AA28 4D002AA29 4G066AA33B 4G066AA34B 4G066AA51B 4G066AB07B 4G066AB10B 4G066AB12B 4G066AB13B 4G066AB15B 4D024AB16

4D624AB16 4D024AB18 4D624AB18 4H016AE00 4H016AE02 4H016AE03 4H016AE04
4D024BA01 4D624BA01 4D024BA02 4D624BA02 4D002BA04 4D024BA16 4D624BA16
4G066BA20 4D024BB01 4D624BB01 4D024BB08 4D624BB08 4D024CA01 4D624CA01
4D002CA07 4G066CA46 4G066CA47 4G066DA03 4D002DA31 4D002DA32 4D002DA41
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⑲ 日本国特許庁

公開特許公報

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1. 発明の名称
2. 発明者
3. 特許出願人
4. 添付書類の目録
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明 細 書

1. 発明の名称

2. 特許請求の範囲

$-NH_2$, $-NH-$, および $>N-$ で表わされる基の内、少なくとも一種を有する化合物のハロゲン化水素酸塩と活性炭とよりなる吸着剤。

3. 発明の詳細な説明

本発明は新規な吸着剤の提供に係る。詳しくは、極めて高い吸着容量を有する吸着剤であって、$-NH_2$, $-NH-$, および $>N-$ で表わされる基の内、少なくとも一種を有する化合物のハロゲン化水素酸塩と活性炭とよりなる吸着剤である。

従来水溶の吸着剤として、活性炭を用いる試はなされているが、吸着容量が低く、また無機物又は微量の水溶を極めて低濃度まで除去することはできなかつた。また、活性炭に金属、塩化アンモニウム等の塩化物を添加して、活性炭の吸着能を向上させる試みもなされている。このような試みによつては、また本発明の目的とする効果は達成しない。

即ち、本発明の目的は、高い吸着能をもち、しかも吸着容量の大きい吸着剤を得ることであり、また、廃棄物にわたつて安定した吸着性能を示す吸着剤を提供するにある。

更に本発明の目的は、室温又は微化性雰囲気中にあつても安定で、吸着性能の低下しない水溶吸着剤を提供するにある。

本発明は、上述の目的及び以下に述べる種々の作用効果を達成するために、$-NH_2$, $-NH-$, および $>N-$ で表わされる基(但し、$-NC$ 等のごく一部で示した結合手は水素以外の原子と結合しているものとする)の内少なくとも一種を有する化合物のハロゲン化水素酸塩と活性炭とよりなる吸着剤であつて、例えば、繊維状の等方性石炭系のピッチ(例えばコールタールピッチ)を原料として繊維状の活性炭を製造する際に、上記の化合物のハロゲン化水素酸塩を含浸させ、

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[illegible]

の水準し、5 ppbの水銀イオンを含む水溶液を5ml／hrで通液することにより、水銀濃度1 ppb以下にまで低下させることができるのである。しかも、このような低い濃度にまで水銀を除去する能力の持続性が極めて大きく、例えば1 ppb以下にまで除去する能力は、本樹脂で4000倍にも及ぶことができるのである。

従来から無機の除去に対しては、架橋キレートとともに用いられることが知られており、例えば、塩素及び硫黄原子を同一分子中に有するキレート樹脂が用いられている。これらのキレート樹脂は、極めて十分な水銀除去を有するものもあるがその製法に難点があったり、経時的劣化が大きく、高価となる等の欠点があり、更に、イオン性の水銀に対しては十分であっても、金属との錯塩の錯形成力が小さいものも多い。また酸性及びアルミナ等の担体表面にキレートの層を付着させた担体吸着剤による後の水銀除去の検討なども報告されている。これらもすでに述べた如く、経時的劣化が大きいという欠点がある。

このような経時的な劣化の原因を鋭意研究したところ、従来知られているキレート化合物のほとんどは、窒素原子を持つ化合物であり、これが保存又は使用中に何等かの影響を受けるのではないかという疑問を得た。かくして、更にこの窒素原子を含む基について、検討を重ねた結果、これをハロゲン化水素酸の塩とすることにより、単に経時的な劣化を防止するのみならず、除去効果を向上し、しかも高濃度の水銀溶液を飛躍的に増大させ得ることを見出した。それは本発明は、$-NH_2$、$-NH-$、及び$-N<$で表わされる原子団を有する化合物、具体的には一級アミン類、二級アミン類、三級アミン類、ヒドラジド類、アミノ酸類等よりなる化合物の塩酸塩、臭化水素酸塩等のハロゲン化水素酸塩と活性炭とよりなる水銀除去剤である。本発明者等においては、上記$-NH_2$、$-NH-$、及び$-N<$で表わされる原子団を少なくとも一個を有する化合物のハロゲン化水素酸塩であればよく。該化合物が更に、例えば硫黄、酸素、その他の原子又は原子団を有せずついてもさしつかえない。従って、$N-S$型、$N-O$型等のキレート化剤であっても、それがハロゲン化水素酸と塩を形成する能力があれば本発明の目的に使用することができる。このようにハロゲン化水素酸と塩を形成すると、窒素原子及びイオン性の水銀に対する吸着能力が向上し更に吸着剤の安定性が向上するという効果は、誠に驚くべきことである。

本発明において、ハロゲン化水素酸の塩の形成させ方は、特に限定とはならない。一般に化学者が通常行っているアミン類のハロゲン化水素酸塩を形成させる方法で十分であり、特に当業者者にとって、これ以上の説明は必要としないであろう。

本発明に使用する$-NH_2$、$-NH-$、及び$-N<$で表わされる原子団の内少なくとも一個を有する化合物を例示すると、例えば、メトラジン、ヒドロキシルアミン、モノメトラジンホルメート等の脂肪族アミノ化合物（但し、アミノ酢酸は本発明には含まれない）；メチルアミン、ジメチルアミン、トリメチルアミン、エチルアミン、ジエチルアミン、トリエチルアミン、エタノールアミン、ジエタノールアミン、トリエタノールアミン、プロピルアミン、ブチルアミン、エチレンジアミン、N・メチルエチレンジアミン、N,N－ジメチルエチレンジアミン、N,N'－ジメチルエチレンジアミン、N,N,N'－トリメチルエチレンジアミン、N,N,N',N'－テトラメチルエチレンジアミン、ジエチレントリアミン、トリエチレンテトラミン、テトラエチレンペンタミン、ペンタエチレンヘキサミン、ポリエチレンイミン、グアニジン、エチレンジアミン尿素縮合物、イミノ二酢酸、メチルヒドラジン、ジメチルヒドラジン、テトラメチルヒドラジン等の脂肪族アミン類；ピロリジン、ピペリジン、ピペラジン、ピペラジン、テトラハイドロイミダゾール、ジアミノヘキタルアミン、モルホリン等

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以上をまとめると本発明のヘテロ化水素吸着剤とは成分と吸着方法は、次のようになる。例えば、共に液体であれば、プレンダーを用いてドライブレンドしてもよいし、また、水その他の液体媒体の存在下に混合してもよい。また、前記混合物のヘテロ化水素吸着剤が水その他の溶媒に可溶であれば（多くの場合水可溶である）、これらの水等の溶媒中に吸着剤を溶解して、水その他の溶媒を蒸発乾燥する方法も採用しうる。また活性炭は粉末状であっても、粒、塊状であってもよいし、更に吸着の効果に関する限度によっては、成型した後、前記化合物のヘテロ化水素と混合するとがましい場合がある。勿論、前記化合物を先に活性炭と混合した後、ヘテロ化水素吸着とすることもできる。本発明によるがましい吸着剤の態様は、活性炭その他合物のヘテロ化水素吸着が表面に担持した状態のものである。また本発明にあっては、前記化合物のヘテロ化水素吸着と活性炭との混合比率に関係とはならず、当該技術者が必要に応じて、適宜決定すればよいが、一般に前記化合物のヘテロ化水素吸着の含有量（例えば0.1％重量）から、飽和吸着量、これを活性炭に十分含ませた後、乾燥することにより得られる程度の含有量合で十分である。勿論、前記化合物のヘテロ化水素吸着の割合が更に多く、例えば、50％の割合を混合物とすることもできるが、一般にこれらの吸着は表面であるから、活性炭中の吸着活性点の数パーセントにこれらの吸着が吸着した状態で使用するのが有利となる。

以下実施例及び比較例を示す。

実施例　1

二酸化ヒドラジンの1％重量水溶液に、10～20メッシュの活性炭（クラレケミカル製；商品名「クラレコール10／30」）100gを浸漬し、よく水溶液含浸して吸着剤を製造した。

この吸着剤を、ほぼ2mの層子管に2mの長さにおさめて充填し（容積約2.3ml）、管の一端より水素を流おさせた空気をSV／min.の速さで送入させた。後者より出るガスは、これを冷却手段分析計（東芝ーベックマン製）にかけて、残存する水素の濃度を定量した。ここで用いた水素含有空気は、空気と水素ボンベとをバブルさせて得たもので、1s.v／分前後の水素を含んでいた。

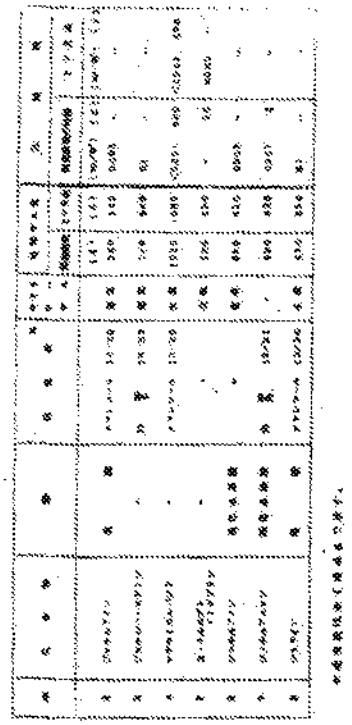
実験の分析結果から見ると、吸着剤が充填に用いている間は、出口ガスの水素濃度は0.001vol／分以下に保たれるが、吸着剤の能力が飽えるに従い、水素濃度は次第に上昇する。本例の吸着剤では、出口水素濃度が0.001vol／分を越えるまでに通過、容積で10000倍の水素含有空気を処理することが出来た。

更に、本例の吸着塔（水洗浄）を室温中そのまま2ヶ月及び4ヶ月保存した後の吸着容量はそれぞれ10302及び10005cmであって吸着能力は変りなかった。

比較例　1

実施例1において、二酸化ヒドラジンの代りに

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以上

実施例 9

実施例5と同様にして製造した改質触媒100gを、反応器3mの縦型管に充填し、水素濃度5 ppm、炭化水素濃度2%の多環芳香族をSV/hrの速さで通液した。通油する液中の水素濃度は水素電極式検出器で測定し、濃度が0.02 ppmを越えるまでに通液した4000倍の液を処理することが出来た。

実施例 10

実施例5に於けるジエチレントリアミン代りにオキサンを用いた以外は実施例5と同様にして製造した改質触媒を実施例5と同様な条件に充填し、硫黄濃度40 ppmを含む 水素添を通下した結果、触媒下部より流出する液中の硫黄濃度（真度法）は0.8ppm以下であった。

同様に重質油について測定した脱硫反応率は0.05 ppm以下であった。

特許出願人

東洋曹達株式会社

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Espacenet

Bibliographic data: JPS544868 (A) — 1979-01-13

CLEANING METHOD FOR AIR

Inventor(s): SEKI MICHIHARU; SAKURAI HIROSHI

Applicant(s): HITACHI LTD

Classification: - International: *B01D53/02; B01D53/04; B01D53/34; B01D53/50; B01D53/60; B01D53/74; B01D53/81;* (IPC1-7): B01D53/02; B01D53/04; B01D53/34

- cooperative:

Application number: JP19770069843 19770615

Priority number(s): JP19770069843 19770615

Abstract of JPS544868 (A)

PURPOSE:To remove the harmful substances in air, especially NO2, with a high removing rate and a long life, by contacting the air containing NOx and SOx to the active carbon on which at least one kind out of NH4I, NH4Br and NH4Cl has been supported.

⑲日本国特許庁　　⑪特許出願公開

公開特許公報　　昭54—4868

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	104	13(9) F 2		審査請求　未請求
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（全5頁）

⑤4空気浄化法

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⑦2出願　昭52(1977)6月15日

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明　細　書

発明の名称　空気浄化法

特許請求の範囲

1．ヨウ化アンモニウム、臭化アンモニウム、塩化アンモニウムの少なくとも一種を担持した炭素系物質に窒素酸化物、硫黄酸化物の少なくとも一種を含有する空気を接触して、空気中の有害物質を除去することを特徴とする空気浄化法。

発明の詳細な説明

本発明は、汚染された空気中の窒素酸化物、硫黄酸化物等を除去する空気浄化法に関するものである。

近年、産業文明の発展にともない、工場、自動車などからの排煙、排気などによつて大気が汚染され、有害ガスの濃度は、ますます増大しつつある。

一方、ビルなどの建物の内部の空気は、たばこや事務機械などから出る有害ガスなどによつて、大気よりもさらに汚染されている場合が多い。大気汚染物質の中には、二酸化硫黄、一酸化炭素、炭化水素、窒素酸化物、オキシダント、鉛、粉じんなどがある。

本発明は、これらの汚染物質のうち、窒素酸化物及び又は硫黄酸化物を対象としたものであるが、窒素酸化物及び硫黄酸化物は、それ自身、人体および動植物に対して有害であり、これらを除去することは重要なことである。特に窒素酸化物については大気中の炭化水素と光化学反応を起して、オゾンやPAN(Peroxy acetyl nitrate)などの過酸化物を二次的に生成するので、この窒素酸化物の除去は重要な意味をもつている。なお、常温での空気中の窒素酸化物成分は、主にNOおよびNO₂であるが、このNO₂は、低温で燃料などを燃焼したときに生じたもの、および高温燃焼で発生したNOが、空気中の酸素とさらに結合して生成したものであり、この酸化反応は低温ほど進行しやすく、常温での空気中の全窒素酸化物中にしめるNO₂の割合は大である。さらに、NO₂の毒性はNOの5倍、あるいは10倍ともいわれており、窒素酸化物の中でもNO₂を除去

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することは重要な意味をもつている。

この有害な空気中の窒素酸化物及び硫黄酸化物を除去する方法として、従来一般に行なわれている方法は、活性炭を吸着剤として用いる方法である。この方法は簡便という利点はあるが、除去の機構が単純な吸着のために寿命が短かいという欠点をもつている。

本発明は、この欠点を改良するためになされたものであり、具体的には、ヨウ化アンモニウム、臭化アンモニウム、あるいは塩化アンモニウムを添着した活性炭を用いるものであり、これによつてNO_2の除去率と寿命を著しく増大することができる。われわれは、さきに、本発明のごときハロゲン化アンモニウムを添着した活性炭に前記窒素酸化物等を含む排ガスとアンモニアとを接触させて、排ガス中の窒素酸化物を除去する方法を見出した（特公、昭50—4622）。このように、この技術では排ガスにアンモニアを同時に添加することが排ガス中窒素酸化物除去に必要であるが、本発明は、窒素酸化物硫黄酸化物の少なくとも一

分解されることによつて、除去される。しかし、排ガス中の窒素酸化物濃度が150～400ppmと高いためにアンモニアを供給しなければ、除去率、および寿命を維持することはできない。

$$NO+NH_3+\frac{1}{4}O_2 \rightarrow N_2+\frac{3}{2}H_2O \quad (1)$$

$$NO_2+\frac{4}{3}NH_3 \rightarrow \frac{7}{6}N_2+2H_2O \quad (2)$$

このように、窒素酸化物の除去機構が、本発明では触媒への吸着であり、一方先の特公昭50—4622の場合は、触媒上での分解反応である。ここで除去機構が異なる結果として、活性炭に添着するハロゲン化アンモニウムの種類の違いによる除去性能が本願の室温脱硝と、先の特許発明の場合とで異にしていることは興味深いことである。つまり、本願ではヨウ素が最も効果が大で、つぎが、塩素、臭素の順であるのに対して、先の特許発明の場合は臭素が最も効果大で、つぎが塩素、ヨウ素の順である。

つぎに、これらのハロゲン化アンモニウム添着活性炭を用いた空気中窒素酸化物除去特性を実施例によつて説明する。

種を含む空気を、アンモニアと共存させることなしに、ハロゲン化アンモニウム添着活性炭と接触させることによつて、空気中の窒素酸化物を除去するものである。

本発明において、アンモニアを共存させることなしに除去できる理由は、反応が前記特公昭50—4622の場合と本質的にことなるためであり、これは反応温度、および窒素酸化物の濃度の違いが関与している。すなわち、本発明では、対象にしている温度が室温で、比較的低温のために、NO_2が活性炭に添着されたハロゲン化アンモニウムと結合することによつて除去され、しかも、NO_2濃度が0.003～0.2ppmと低いために、活性炭に添着された比較的少ない量のハロゲン化アンモニウムであつても除去率と寿命を十分維持することができる。一方、先の特公、昭50—4622では対象のガスがボイラー排ガスのために温度が130℃付近と比較的高いので、触媒上でハロゲン化アンモニウムから遊離されたアンモニアと窒素酸化物とが反応し、下式(1)、(2)のように窒素に

以下、本発明を実施例を参照して詳細に説明する。

1．NH_4I添着活性炭を用いたNO_2除去活性炭として、ヤシガラを水蒸気賦活した破砕状活性炭の4～8メッシュ（4.76～2.39㎜）の粒度のものを用い、この活性炭にその充填容積に対して$\frac{1}{2}$の容積のNH_4I水溶液を含浸し、130℃、2時間、乾燥器中で乾燥してNH_4I添着活性炭を作つた。活性炭に対するNH_4Iの添着量は5重量％である。

このNH_4I添着活性炭の1.5ccを内径13㎜の反応管に装填し、相対湿度55％の水蒸気とNO_2濃度1.0ppmを含む空気を反応管に流入し、温度18℃、SV（空間速度）100,000h^{-1}の条件で行なつたNO_2除去率の経時変化の結果を第1図の曲線1に示す。

比較のために上記と同様の条件下で行なつた上記活性炭のみの場合のNO_2除去率の経時変化の結果を第1図の曲線2に示す。

この結果から、明らかに本発明によるハロゲ

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ン化アンモニウム添着活性炭が、活性炭のみの場合にくらべて、すぐれたNO₂除去性能をもつていることがわかる。なお本実験はNO₂濃度が実際の環境濃度（環境基準はNO₂濃度の一時間値の一日平均が0.02ppm以下）にくらべ著しく高い加速寿命実験である。

2．NH_4Br添着活性炭を用いたNO₂除去

NH_4Br添着活性炭の製作、およびこれを用いたNO₂の除去率の経時変化実験を、前1項のNH_4Iの場合と同様な方法で行ない、実施例1のヨウ化アンモニウムに比較すれば若干劣るが、活性炭のみの曲線2に比較して著しくすぐれた結果（第1図の曲線3）をえた。

3．NH_4Cl添着活性炭を用いたNO₂除去NH_4Cl添着活性炭の製作、およびNO₂除去率の経時変化実験を、前記1項のNH_4Iの場合と同様な方法で行ない、ヨウ化アンモニウムには若干劣るが臭化アンモニウムよりもより優れた結果（第1図の4）をえた。

4．上述1～3項はハロゲン化アンモニウム添着

(7)

ついて主に述べたが、NOについても一部はNO₂と同様に本発明の実施に用いた触媒で吸着除去され、その吸着能は活性炭に較べて大であることが実験で確かめられている。

前記の説明では窒素酸化物の除去方法についてのみ述べたが、本発明では窒素酸化物の他硫黄酸化物或いは前記二者の混入されたものについても除去が可能なものであり、次に硫黄酸化物の除去方法についても説明する。

5．NH_4I添着活性炭を用いたSO₂除去活性炭として、ヤシガラを水蒸気賦活した破砕状活性炭の4～8メッシュ（4.76～2.39㎜）の粒度のものを用い、この活性炭に、その充填容積に対して$\frac{1}{2}$の容積のNH_4I水溶液を含浸し、130℃、2時間、乾燥器中で乾燥してNH_4I添着活性炭を作つた。活性炭に対するNH_4I添着量は5重量%である。

このNH_4I添着活性炭の1.5ccを内径13㎜の反応管に装填し、相対湿度55%の水蒸気とSO₂濃度5.0ppmを含む空気を反応管

(9)

活性炭の製作法として、ハロゲン化アンモニウム水溶液を活性炭に含浸し、後乾燥する方法を行なつたが、活性炭にハロゲン、あるいはハロゲン化水素を吸着後、さらにアンモニアを接触させて処理したものもハロゲン化アンモニウム添着活性炭と同様のNO₂除去性能をうることがわかつた。

さて、以上の実施例の測定条件はNO₂の濃度1.0ppmと実際の環境基準濃度0.02ppm以下にくらべて著るしく高い。したがつて第1図に示した寿命は実際には著るしく延長される。

第2図にNO₂濃度1.0ppm、0.1ppm（他の空間速度等の諸条件は前記実施例と同じ）で実施した場合のNO₂除去率を示す。これによると環境基準濃度の数倍程度のガス濃度では極めて可使用時間を長くすることができることが明らかである。

第2図において曲線5は1.0ppm、曲線6は0.1ppmの場合を表わす。

また、実施例では窒素酸化物としてNO₂に

(8)

に流入し、温度20℃、SV（空間速度）100,000h^{-1}の条件で行なつたSO₂除去率の経時変化の結果を第3図の7に示す。

比較のために上記と同様の条件下で行なつた上記活性炭のみの場合のSO₂除去率の経時変化の結果を第3図の曲線8に示す。この結果から明らかに本発明によるハロゲン化アンモニウム添着活性炭が活性炭のみの場合にくらべて、すぐれたSO₂除去性能をもつていることがわかる。なお、本実験はSO₂の濃度が、実際の環境濃度（環境基準は0.04ppm）にくらべ著しく高い加速寿命実験である。

6．NH_4Br添着活性炭を用いたSO₂除去

NH_4Br添着活性炭の製作、およびこれを用いたときのSO₂除去率の経時変化実験について、前記実施例第1項と同様の方法で実施し、ヨウ化アンモニウムの場合には若干劣るが、活性炭のみの場合に比較して著るしく優れた結果（第3図の曲線9）を得た。

7．NH_4Cl添着活性炭を用いたSO₂除去。

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NH_4Cl添着活性炭の製作、およびSO_2除去率の経時変化実験を、前1項のNH_4Iの場合と同様な方法で行ない、臭化アンモニウムより若干劣るが活性炭のみのものよりもより優れた結果〔第3図の曲線10〕をえた。

8．上述の実施例5～7ではハロゲン化アンモニウム添着活性炭製作法として、ハロゲン化アンモニウム水溶液を活性炭に含浸し、後乾燥する方法を行なつたが、活性炭にハロゲン、あるいはハロゲン化水素を吸着後さらに、これにアンモニアを接触させて処理したものも、ハロゲン化アンモニウム添着活性炭の場合と同様のSO_2除去性能をうることがわかつた。

なお、以上の実施例では窒素酸化物と硫黄酸化物が単独のもので示したが、混合されて空気中に含まれている場合でも勿論除去しうるものであり、室内空気浄化法としては装置等も簡単なもので済み、極めて有効なものである。

以上説明したように本発明のハロゲン化アンモニウム添着活性炭を空気中の窒素酸化物並びに硫

(11)

黄酸化物の除去用フイルタに用いることにより、従来用いられている活性炭フイルタにくらべて著しく除去性能を高めることができ、その効果は大である。

図面の簡単な説明

第1図は、本発明のハロゲン化アンモニウム添着活性炭のNO_2除去率の経時変化を示すものであり、1はヨウ化アンモニウム添着活性炭、2は、活性炭のみ、3は臭化アンモニウム添着活性炭、4は塩化アンモニウム添着活性炭をフイルタとして用いた場合の特性である。なお、流通ガス組成は、NO_2 1.0 ppm、H_2O相対湿度で55%を含む空気であり、実験条件は、温度18℃、SV 100,000h^{-1}である。

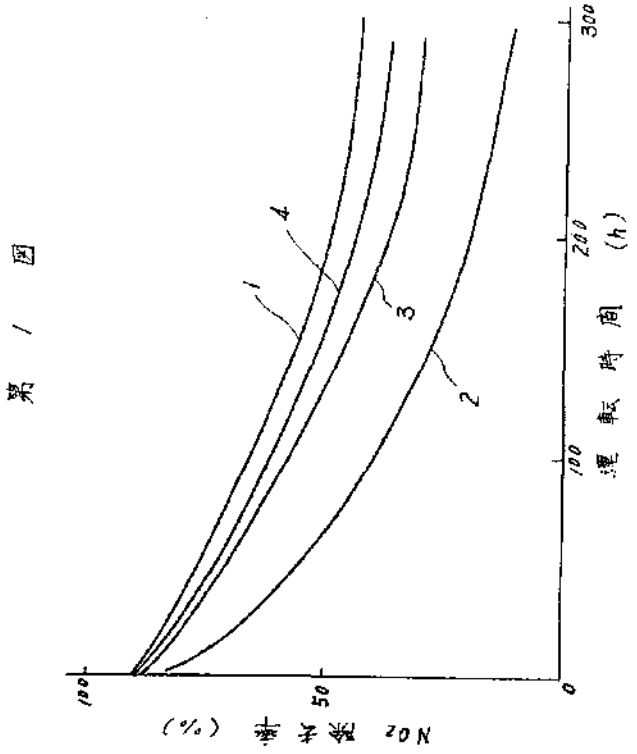
第2図は、第1図1（NO_2濃度1 ppmの場合）と同一条件のデータにNO_2濃度が0.1 ppmの場合のNO_2除去率の経時変化を示したものである。

第3図は本発明のハロゲン化アンモニウム添着活性炭の二酸化硫黄除去率の経時変化を示す図で

(12)

ある。

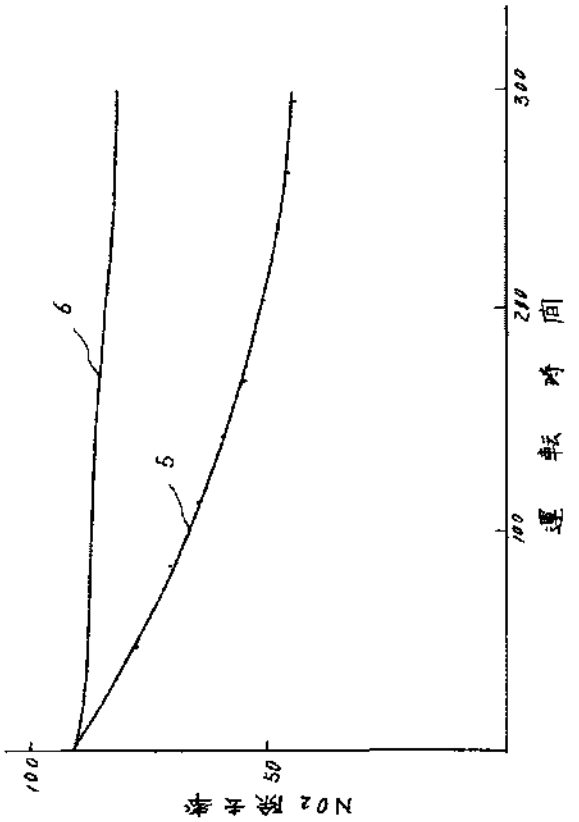
代理人　弁理士　~~青木朗~~



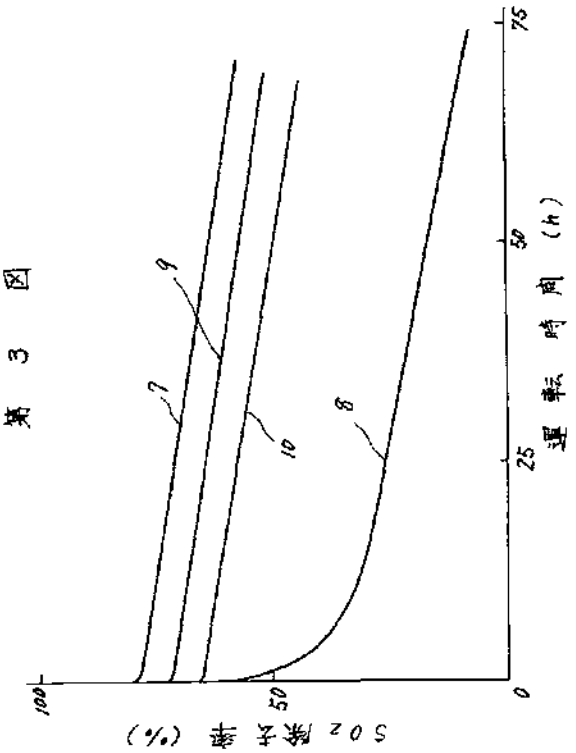
(13)

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第 2 図



第 3 図



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Mercury sepn. from air contg. dust and aerosols

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Inventor: BELOZEROV, I M KALKORIN, B N Kurakin, V I

Publication info: 198603 (First update). 198603 (Last update).
ProQuest document link

Alerting

First section
Mercury is removed from air contg. dusts and aerosols by passage through a layer of activated carbon, then through activated carbon modified with an interhalogen cpd. such as monochloroiodide. The process will reduce Hg concn. to below the max. permitted level of 0.01 mg/m3, and the sorbent will last 300 hr. before requiring replacement.

Air contg. Hg 0.54 mg/g3 and total contaminants of dust and alkaline aerosols 0.15 mg/g3 was passed at 65 l/min. through 10 mm. activated, 30 mm activated carbon impregnated with 15.3% ICl, and 10mm activated carbon. Breakthrough was after 1270 hr. compared to 826 hr. on use of 50 mm impregnated activated carbon alone.

USE/ADVANTAGE
The combined sorbent will remove mercury from air contg. other impurities unlike the previous process in which only one layer of treated carbon was used, and breakthrough time is half as long again as the previous value. Bul.24/30.6.85

Publication number: SU 1163892 A (30 June 1985)

Application number: SU 3584931 A (28 January 1983)

Priority number: SU 3584931 A (28 January 1983)

IPC classification: Version 8:B01D 53/02 (main)

IPC version 8:

Class code	Level	Value	Position	Status	Version
B01D 53/02	A	I	F	B	20060101

Chemical fragment codes unlinked: 2211-U 1669-U

Keyword concept 1: 0: 2211-H-USE

Derwent chemical class: J01: Separation - including evaporation, crystallisation, solvent extraction, chromatography, dialysis, osmosis including drying gases and/or vapours, and separation of solids from gases, liquids and other solids. Isotope separation, filter materials (including molecular sieves for separation), and centrifuges (except where used for analysis)

CPI manual code: J01-E03C

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Includes: 1 patents; 1 countries

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Publication number	Kind	Publication date	Application number	Kind	Application date	Update code	Type
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SU 1163892 A:

Assignee: BELOZEROV I M (BELOStandardized Individual)

Inventor: BELOZEROV I M KURAKIN V I KALKORIN B N

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Class code	Level	Value	Position	Status	Version	Action	Source	Office
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IPC (versions 1-7):

Class code	Rank	Version	Type
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Number of drawings: 0

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СОЮЗ СОВЕТСКИХ СОЦИАЛИСТИЧЕСКИХ РЕСПУБЛИК

(19) SU (11) 1163892 A

(51) B 01 D 53/02

ГОСУДАРСТВЕННЫЙ КОМИТЕТ СССР ПО ДЕЛАМ ИЗОБРЕТЕНИЙ И ОТКРЫТИЙ

ОПИСАНИЕ ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

(21) 3584931/23-26
(22) 28.01.83
(46) 30.06.85. Бюл. № 24
(72) И.И. Белозеров, В.И. Куракин, В.Н. Ласкорин, В.Д. Мазавенко, А.И. Новиков, А.И. Оворнин, А.Д. Рябцев, А.П. Скворцов и В.А. Усольцев
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(56) Патент США № 4139354, кл. B 01 D 53/04, 1979.
Патент США № 3662523, кл. B 01 D 53/04, 1972.

(54)(57) СПОСОБ ОЧИСТКИ ВОЗДУХА ОТ РТУТИ путем пропускания через слой активированного угля, модифицированного нейтральным соединением, о т л и ч а ю щ и й с я тем, что, с целью повышения степени очистки воздуха от ртути, содержащего одновременно пыль в аэрозоли, предварительно и дополнительно газ пропускают через слой активированного угля.

SU (11) 1163892 A

Изобретение относится к очистке газов от ртути и может быть использовано в химической и электротехнической промышленности, приборостроении, цветной металлургии и других областях техники, связанных с применением ртути в технологических процессах.

Целью изобретения является повышение степени очистки воздуха от ртути, содержащего одновременно пыль и аэрозоли.

Пример. В колонку из стекла Ø 37 мм насыпают активный уголь марки КАД до образования слоя толщиной 10 мм, затем насыпают импрегнированный однохлористым иодом (содержание 15,3 вес.%), активированный уголь до образования слоя толщиной 30 мм, сверху помещают сетчатую перегородку и вновь насыпают слой активного угля марки КШД толщиной 10 мм (общая толщина фильтрующего слоя 50 мм, количество однохлористого иода, содержащегося в системе, 2,68 г).

Во вторую колонку (как в прототипе) насыпают импрегнированный однохлористым иодом активный уголь (содержание однохлористого иода в активном угле 9,7 вес.%) до образования слоя толщиной 50 мм (количество однохлористого иода, содержащегося в системе, 2,68 г.).

Далее через колонки сверху вниз пропускают воздух, содержащий 0,54 мг/г³ ртути, пыль и щелочные аэрозоли в суммарном количестве 0,15 мг/м³, причем расход воздуха через первую колонку составляет 65 л/мин, а через вторую колонку – 60 л/мин. В процессе проведения опыта верхний слой активного угля в первой колонке периодически заменяют на новый через 300 ч работы. На выходе из колонок постоянно контролируют содержание ртути в очищенных воздушных потоках. Ртуть в очищаемом воздушном потоке, в концентрации, превышающей ПДК (0,01 мг/м³), появляется на выходе из первой колонки через 1270 ч, на выходе из второй колонки – через 826 ч.

Составитель Н. Строганова
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WO 01/62368 A1

(54) Title: ADSORPTION POWDER FOR REMOVING MERCURY FROM HIGH TEMPERATURE, HIGH MOISTURE GAS STREAMS

(57) Abstract: There is disclosed an adsorption powder effective for capturing mercury from a high temperature, high moisture gas stream comprising: about 1-97% carbon; about 1-97% calcium hydroxide; about 1-97% cupric chloride impregnated carbon, and about 1-60% carbon impregnated with KI3. Additionally, a method of removing mercury from high temperature, high moisture gas streams is disclosed.

ADSORPTION POWDER FOR REMOVING MERCURY FROM HIGH TEMPERATURE, HIGH MOISTURE GAS STREAMS

BACKGROUND OF THE INVENTION

The present invention relates generally to removal of pollutants from high temperature, high moisture gas streams such as those found in devices designed to treat contaminated soil and in hazardous material incinerators. More particularly, the invention relates to the capture of mercury and other metals, dioxins, furans and other organic compounds from high temperature, high moisture gas streams using an adsorption powder containing cupric chloride.

Strict standards exist for particulate and total mercury emissions by coal-fired power plants, petroleum refineries, chemical refineries, coal fired furnaces, trash burning facilities, incinerators, metallurgical operations, thermal treatment units and other particulate and mercury emitting facilities. These same restrictions apply to mercury vapor, which can enter the atmosphere as a result of low temperature thermal desorption (LTTD) treatment of contaminated soils.

These stringent standards exist in order to protect the environment and the community. When mercury-containing gases are released, the gases disperse and mercury is deposited over a wide area. The dispersed mercury can accumulate in the soil or water supplies, where it may be incorporated into the food chain. Mercury is extremely harmful to aquatic life and ultimately to the humans who consume mercury-contaminated plants and animals. It is necessary, therefore, to have a safe and effective method of eliminating mercury from the environment.

The problem of the capture and treatment of mercury vapor, typically in the context of coal-fired power plants and waste incinerators, has been previously considered. For example, U.S. Patent No. 3,193, 987 discloses passing mercury-containing vapor over activated carbon impregnated with a metal which forms an amalgam with mercury. U.S. Patent No. 4,094,777 discloses passing a mercury-containing vapor over an adsorption mass consisting essentially of a support, sulfided

copper and sulfided silver. U.S. Patent No. 3,876,393 discloses passing mercury-containing vapors over activated carbon that has been impregnated with sulfuric acid. Selenium has also been used in the removal of mercury from a vapor. U.S. Patent No. 3,786,619 discloses passing a mercury-containing gas over a mass containing as an active component, selenium, selenium sulfide or other selenium compounds. Electrostatic precipitators and various filters have traditionally been used for mercury removal, although complex apparatus have also been disclosed. (See e.g., U.S. Patent Nos. 5,409,522 and 5,607,496.)

The problem of recapturing mercury from power plant gas streams is analogous to the need for recapturing mercury from incinerators that treat contaminated soils. A process currently in use at soil treatment facilities is known as low temperature thermal desorption (LTTD). LTTD is the main process by which contaminated soils are treated to remove mercury and other contaminants. In this process, contaminated soils are fed into a heating furnace, most commonly a rotary kiln/drum, where the soil is heated by conduction. The heating volatizes the soil components and when a thermal oxidizer is added, the components are oxidized to manageable gases, such as CO_2, Cl_2, NO_x and SO_x, where x is 1-3.

The hot gas stream is subsequently cooled. The stream may be quenched with water, which cools the stream and concurrently increases the moisture content. Although water quenching is a highly effective cooling method, this treatment increases the difficulty of removing mercury from the gas stream. The gas stream is further treated to reduce and remove metals, HCl, NO_x and SO_x using acid scrubbers, carbon beds, condensation units and through the addition of adsorption powders.

When adsorption powders are injected into the gas stream, mercury and other metals bind to moieties present in the powder, precipitating them from the gas stream. The powder-bound mercury is ultimately collected in a bag house for appropriate disposal, while the clean gas stream is exhausted to the outside atmosphere. The problem with standard LTTD methods is that some metals, such as mercury, are not removed from the stream at high efficiency and will move with

the gas stream, ultimately into the environment. Other methods require the use of complex machinery and expensive adsorption beds. LTTD and other methods also suffer from the limitation that mercury removal from high moisture gas streams is much more difficult than mercury removal from dry streams.

Available adsorption powders remove organics, metals and other contaminants, but they do not effectively remove mercury. For example, one available powder (Sorbalite ™) consisting of carbon, calcium hydroxide and sulfur removes HCl from a gas stream, but removes only about 55-65% of the mercury. Another powder (WUELFRAsorb-C ™) consisting of alcohol saturated lime and activated carbon is also inefficient at removing mercury.

Some powders include sulfur or iodine impregnated carbon. At temperatures of 75°C or less, sulfur or iodine impregnated carbon based powders show a 95% mercury removal efficiency, however, powders formulated with sulfur impregnated carbon require a dry or low moisture gas stream to show this level of removal.

Finally, the mercury removal efficiency of the powders described and other available powders is known to be very temperature dependent, placing an additional limitation on powder formulations.

A pending application describing a process from the same inventors involved the use of solid fine cupric chloride that is not impregnated on carbon. This was found to be more difficult to handle because of the grinding process required to pulverize the cupric chloride which is generally provided in rock sizes. The grinding process requires a great amount of attention due to the dust production and associated heath hazards. Additionally, the powder is very corrosive and results in breakdown of the machinery used in the process.

Accordingly, there is a need in the industry for an adsorption powder that effectively removes metals and other organic compounds, in general, and mercury, in particular, from high temperature, high moisture gas streams generated by the incineration of contaminated soils, treatment of hazardous materials, combustion of coal and other mercury liberating sources. The powder must be inexpensive and

easy to use. Ideally, such an adsorption powder can be employed at treatment facilities already in place and can take advantage of equipment already in position, without requiring retooling or reconfiguring existing equipment.

SUMMARY OF THE INVENTION

There is disclosed an adsorption powder and method for removing mercury and other metals and contaminants from a high temperature, high moisture gas stream comprising: about 1-97% carbon; about 1-97% calcium hydroxide; about 1-97% cupric chloride impregnated carbon and about 1-60% KI_3 impregnated carbon. A method for removing mercury and other metals, dioxins, furans and other organic compounds from high temperature, high moisture gas streams using the claimed powder is also disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

The instant invention will be more fully understood in the following detailed description, it being understood, however, that the invention is not confined to the precise disclosure. Changes and modifications may be made that do not affect the spirit of the invention, nor exceed the scope thereof, as expressed in the appended claims. Accordingly, the instant invention will now be described with particular reference to the accompanying drawings.

Figure 1 is a schematic diagram illustrating the design of an LTTD facility in which the claimed adsorption powder can be used to remove mercury from gas streams.

DETAILED DESCRIPTION OF THE INVENTION

There is disclosed an adsorption powder for removing mercury and other metals from a gas stream comprising:

a) about 1-97% carbon;

b) about 1-97% calcium hydroxide;

c) about 1-97% cupric chloride impregnated carbon; and

d) about 1-60% KI_3 impregnated carbon.

The powder more particularly comprises about 10-70% carbon, about 20-80% calcium hydroxide, about 1-50% cupric chloride impregnated carbon and about 1-50% KI_3 impregnated carbon. A preferred adsorption powder comprises about 20-60% carbon, about 30-70% calcium hydroxide, about 1-30% cupric chloride impregnated carbon and about -30% KI_3 impregnated carbon.

In a more preferred embodiment, the adsorption powder comprises about 25-45% carbon, about 40-60% calcium hydroxide, about 1-15% cupric chloride impregnated carbon and about 1-15% KI_3 impregnated carbon. The most preferred embodiment comprises about 40% carbon, about 40% calcium hydroxide, about 10% cupric chloride impregnated carbon and about 10% KI_3 impregnated carbon.

The use of the KI_3 impregnated carbon has been found to be optional as the powder lacking this component performed equally as well as one containing the KI_3 impregnated carbon.

Thus, in another embodiment of the invention, , the adsorption powder comprises about 10-70% carbon, about 20-80% calcium hydroxide and about 1-50% cupric chloride impregnated carbon.

There is also disclosed a process for removing mercury from a gas stream using the adsorption powder of the invention comprising the steps of:

a) placing a solid phase mercury-containing contaminated soil feed into a rotary kiln/drum;

b) heating said kiln/drum containing said soil feed to form gaseous and solid components of the sample;

c) transferring the gaseous component of said soil feed to an exhaust cleaning unit/afterburner and the solid component of clean soil to a soil cooling unit;

d) heating the gaseous component of said contaminated soil feed in said exhaust cleaning unit/afterburner;

e) cooling the gaseous component of said contaminated soil feed;

f) adding the adsorption powder of Claim 1 to the gaseous component;

g) transferring the powder-containing gaseous component to a baghouse; and

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h) releasing the substantially mercury-free gaseous component of said sample to the atmosphere.

An adsorption powder for the removal of mercury and other metals, dioxins, furans and other organic compounds must be efficient under a range of conditions. Currently available powders do not function well at high temperatures and in high moisture environments, conditions that are favorable to mercury removal.

High temperatures are necessary for effective removal of contaminants from soil. Temperatures of about 1800°F are necessary to volatize organics, metals and other impurities from the contaminated soil. Mercury that is trapped in contaminated soil, however, is most efficiently adsorbed on carbon at about 300-500°F. The most practical method of cooling a gas stream exiting an 1800°F oven is to inject water into the gas stream. Water injection cools the gas stream to a temperature favorable to mercury removal, but also increases the moisture content of the sample, which decreases the efficiency of available mercury adsorption powders. The mercury absorbing properties of available powders suffer dramatically in a high moisture environment. The adsorption powder of the invention, however, operates effectively even in a higher moisture environment.

Experiments with carbon sources showed that coal carbon was superior to wood carbon for mercury adsorption. Many available adsorption powders use wood carbon as a component, rather than coal carbon. Cupric chloride was observed to significantly enhance the adsorption of mercury from a gas stream and is the key to the instant invention. Cupric chloride supplies chlorine and activated copper to the elemental mercury in the exhaust stream. Elemental mercury reacts with the chlorine to form mercury chloride and the activated copper to form a stable mercury amalgam. Both forms of mercury are easily captured from the exhaust gas stream. KI_3 impregnated carbon was also found to increase mercury adsorption when it was included in the powder.

Figure 1 shows a schematic diagram of the actual process and equipment used to carry out the invention. Prescreened contaminated feed soil ready to be processed 2 is placed within soil cleaning unit 4. The contaminated soil is heated to about 900°F or a temperature that will completely volatize the contaminates from the soil and generate a gas stream, as well as a clean/remediated solid soil component. Preferably, soil cleaning unit 4 is a rotary kiln. The gas stream is then passed out

of soil cleaning unit **4** to dust remover **6**, while any solid fraction of the feed soil is transferred to clean soil cooling unit **8**, where the soil is cooled and prepared for reuse. Dust remover **6** is preferably a multi-tube dust collector.

After dust remover **6** removes any particulate matter from the gas stream sample, the gas stream is passed into the Exhaust Cleaning Unit **10.** The Exhaust Cleaning Unit heats the volatilized contaminates to a temperature of about 1800°F for a minimum of two seconds retention time, which assures complete destruction of any remaining organic or other contaminants. From the Exhaust Cleaning Unit **10,** the gas stream then passes through cooling chamber **12** wherein a water pump (not shown) injects water into the cooling chamber **12** to lower the temperature of the sample to about 360°F. This cooling process consequentially increases the moisture content of the sample.

The high temperature, high moisture gas stream is then contacted to the adsorption powder of the invention, which is stored in adsorbent storage silo **14** and injected into the gas stream. This powder formulation is effective in removing metals, particularly mercury, and other contaminants.

After the gas stream has been contacted to the adsorption powder, the powder/gas stream mixture continues on to baghouse **16**. The carbon component of the adsorption powder collects on the walls of bags and acts as a particulate filter for the gases leaving the baghouse. Baghouse **16** collects the particulate mercury-containing fraction of the adsorption powder mixture, which is transported to a suitable bulk storage facility **20** and subsequently removed. The gaseous fraction is released to the outside atmosphere through vent **18**, while the remaining dust particulate fraction is handled in a similar manner to the particulate mercury fraction of the adsorption powder mixture **20.**

EXAMPLE 1

A series of field tests were performed employing a preferred adsorption powder formulation. Three soil samples containing about 4.2 mg/kg of mercury were prepared by screening to 1 inch. The coarse material was discarded, and the remaining soil was fed into a soil cleaning unit and heated to about 900°F. The cleaned soil was transferred to a soil cooling unit and prepared for reuse. The exhaust stream was sent to a dust remover and the precipitated material was sent to the soil cooling unit. The exhaust stream was then fed into an exhaust cleaning unit, which was heated to

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about 1850°F. The exhaust gas was then cooled to about 360°F by quenching with water, and subsequently an adsorption powder comprising 40% coal carbon, 10% KI_3 impregnated carbon, 40% calcium hydroxide and 10% cupric chloride impregnated carbon was added. The exhaust stream/adsorption powder mixture was fed into a baghouse, where the mercury-bound particulate was separated from the mercury-free exhaust gas. The particulate material was removed from the baghouse for analysis and disposal, while gas analyzers on the exhaust stack recorded mercury emission levels. The results of the three, two hour runs are reported in the following table.

	Run 1	Run 2	Run 3	Average
LTTD Mercury Input (lbs/hr)	0.193	0.199	0.199	0.197
Clean Soil Mercury Output (lbs/hr)	0.0020	0.0020	0.0020	0.0020
Mercury Emission Rate (lbs/hr)	0.0012	0.0006	0.0007	0.0008
Mercury Removal Efficiency[1]	99.4%	99.7%	99.6%	99.6%

[1] *Removal Efficiency (%) = (Mass input - Stack Output- Clean Soil Output)/(Mass Input - Clean Soil Output)*

The average mercury removal efficiency of 99.6% exceeds the current mercury control efficiency specification of 96.5% efficiency, set by NJDEP air permit legislation. Mercury emissions were determined by EPA method 29-060.

Although the adsorption powder and method described and claimed are presented in the context of mercury removal from a gas stream, it should be appreciated that the powder and method are also useful for removing organics, metals and other contaminants from a gas stream.

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WHAT IS CLAIMED IS:

1. An adsorption powder for removing mercury and other metals, dioxins, furans and other organic compounds from a gas stream comprising:

a) about 1-97% carbon;

b) about 1-97% calcium hydroxide;

c) about 1-97% cupric chloride; and

d) about 1-60% KI_3 impregnated carbon.

2. The adsorption powder of claim 1 wherein the adsorption powder comprises about 10-70% carbon, about 20-80% calcium hydroxide, about 1-50% cupric chloride impregnated carbon and about 1-50% KI_3 impregnated carbon.

3. The adsorption powder of claim 1 wherein the adsorption powder comprises about 20-60% carbon, about 30-70% calcium hydroxide, about 1-30% cupric chloride impregnated carbon and about -30% KI_3 impregnated carbon.

4. The adsorption powder of claim 1 wherein the adsorption powder comprises about 25-45% carbon, about 40-60% calcium hydroxide, about 1-15% cupric chloride impregnated carbon and about 1-15% KI_3 impregnated carbon.

5. The adsorption powder of claim 1 wherein the adsorption powder comprises about 30% carbon, about 50% calcium hydroxide, about 10% cupric chloride impregnated carbon and about 10% KI_3 impregnated carbon.

6. The adsorption powder of claim 1 wherein the adsorption powder comprises about 10-70% carbon, about 20-80% calcium hydroxide, about 1-50% cupric chloride impregnated carbon.

7. The adsorption powder of claim 1 wherein the carbon is coal carbon.

8. A method for removing mercury and other metals, dioxins, furans and other organic compounds from a gas stream using the adsorption powder of claim 1 comprising the steps of:

a) placing a solid phase mercury-containing contaminated soil feed into a rotary kiln/drum;

b) heating said kiln/drum containing said soil feed to form gaseous and solid components of the sample;

c) transferring the gaseous component of said soil feed to an exhaust cleaning unit/afterburner and the solid component of clean soil to a soil cooling unit;

d) heating the gaseous component of said contaminated soil feed in said exhaust cleaning unit/afterburner;

e) cooling the gaseous component of said contaminated soil feed;

f) adding the adsorption powder of Claim 1 to the gaseous component;

g) transferring the powder-containing gaseous component to a baghouse; and

h) releasing the substantially mercury-free gaseous component of said sample to the atmosphere.

9. The method of Claim 8 wherein the adsorption powder used in step f) comprises about 40% carbon, about 40% calcium hydroxide, about 10% cupric chloride impregnated carbon and about 10% KI_3 impregnated carbon.

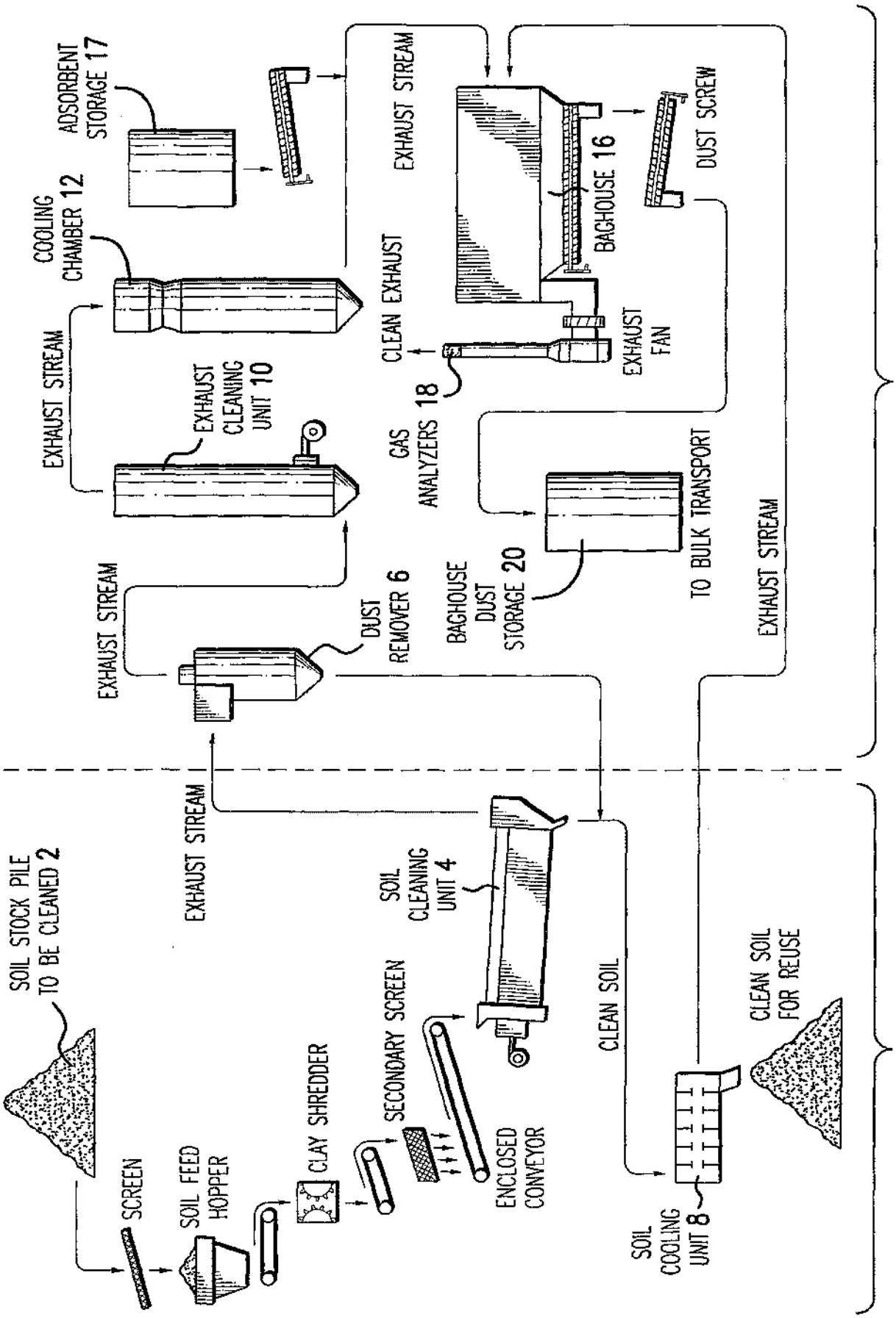

SOIL STOCK PILE TO BE CLEANED 2
SCREEN
SOIL FEED HOPPER
CLAY SHREDDER
SECONDARY SCREEN
ENCLOSED CONVEYOR
SOIL CLEANING UNIT 4
EXHAUST STREAM
DUST REMOVER 6
EXHAUST STREAM
EXHAUST CLEANING UNIT 10
EXHAUST STREAM
COOLING CHAMBER 12
ADSORBENT STORAGE 17
CLEAN EXHAUST
GAS ANALYZERS 18
EXHAUST FAN
BAGHOUSE 16
DUST SCREW
EXHAUST STREAM
BAGHOUSE DUST STORAGE 20
TO BULK TRANSPORT
EXHAUST STREAM
CLEAN SOIL
SOIL COOLING UNIT 8
CLEAN SOIL FOR REUSE
SOIL CLEANING
EXHAUST CLEANING

FIG.1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/05259

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 53/04
US CL :95/133, 134, 141, 900; 96/154; 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)

U.S. : 95/133, 134, 141, 142, 900; 96/108, 132, 135, 154; 423/210

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

NONE

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

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,193,987 A (MANES et al.) 13 July 1965 (13.07.65).	1-9
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A	US 5,409,522 A (DURHAM et al.) 25 April 1995 (25.04.95).	1-9

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier document published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

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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.
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A	US 5,607,496 A (BROOKS) 04 March 1997 (04.03.97).	1-9
A	US 5,659,110 A (HERDEN et al.) 19 August 1997 (19.08.97).	1-9

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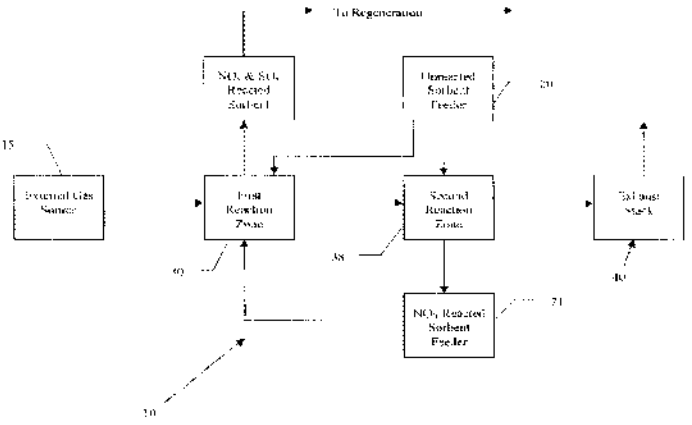
60/238,105	4 October 2000 (04.10.2000)	US
60/239,422	10 October 2000 (10.10.2000)	US
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60/242,830	23 October 2000 (23.10.2000)	US
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60/288,237	2 May 2001 (02.05.2001)	US
60/238,245	2 May 2001 (02.05.2001)	US
60/288,243	2 May 2001 (02.05.2001)	US
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60/288,168	2 May 2001 (02.05.2001)	US
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60/296,005	5 June 2001 (05.06.2001)	US
60/296,004	5 June 2001 (05.06.2001)	US
60/296,007	5 June 2001 (05.06.2001)	US
60/296,003	5 June 2001 (05.06.2001)	US
60/299,363	19 June 2001 (19.06.2001)	US
60/299,362	19 June 2001 (19.06.2001)	US
not yet assigned	31 July 2001 (31.07.2001)	US
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[Continued on next page]

(54) Title: SYSTEMS AND PROCESSES FOR REMOVAL OF POLLUTANTS FROM A GAS STREAM



(57) Abstract: Systems and process for wet and combinations of wet and dry removal of targeted pollutants, such as oxides of sulfur, oxides of nitrogen, and oxides of carbon from combustion and other industrial process gases and processes utilizing the system. Oxides of manganese are utilized as the primary sorbent in the system for removal or capture of pollutants. In wet removal, oxides of manganese are mixed in a slurry which is introduced into reaction zones of the system. In dry removal, the oxides of manganese are introduced from feeders into reaction zones of the system where they are contacted with a gas from which pollutants are to be removed. Removal may occur in single-stage, dual-stage, or multi-stage systems with at least one of the reaction zones being a wet scrubber. A variety dry scrubber may be utilized in combination wet and dry removal systems. Process parameters, particularly system differential pressure, are controlled by electronic controls to maintain minimal system differential pressure, and to monitor and adjust pollutant removal efficiencies. Reacted sorbent may be removed from the reaction action zones for recycling or recycled or regenerated with useful and marketable by-products beins recovered during regeneration.

WO 02/28513 A2

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SYSTEMS AND PROCESSES FOR REMOVAL OF POLLUTANTS FROM A GAS STREAM

Field of the Invention

The invention relates to the systems and processes for removal of pollutants, such as oxides of sulfur, oxides of nitrogen, oxides of carbon, totally reduced sulfides, fly ash, mercury compounds, and elemental mercury from gases generated from the burning of fossil fuels and other process gases with electronic control of operational parameters such as, differential pressure across the system, gas temperature, and removal efficiency. The systems and processes of the invention employ oxides of manganese as the primary sorbent to effect removal of pollutants, such as oxides of sulfur and/or oxides of nitrogen, and may further employ other sorbent materials and chemical additives separately and in conjunction with oxides of manganese to effect the removal of other target pollutants, e.g., using alumina to remove mercury.

Background of the Invention

During combustion of fuels that contain sulfur compounds, oxides of sulfur (SO_X), such as sulfur dioxide (SO_2), and sulfur trioxide (SO_3) are produced as a result of oxidation of the sulfur. Some fuels may contain nitrogen compounds that contribute to the formation of oxides of nitrogen (NO_X), which are primarily formed at high temperatures by the reaction of nitrogen and oxygen from the air used for the reaction with the fuel. These reaction compounds, SO_X and NO_X, are reported to form acids that may contribute to "acid rain." Federal and state regulations dictate the amount of these and other pollutants, which may be emitted. The regulations are becoming more stringent and plant operators are facing greater difficulties in meeting the regulatory requirements. Many technologies have been developed for reduction of SO_X and NO_X, but few can remove both types of pollutants simultaneously in a dry process or reliably achieve cost effective levels of reduction.

In the past to meet the regulatory requirements, coal-burning power plants have often employed a scrubbing process, which commonly uses calcium compounds to react with SO_X to form gypsum. This waste product is normally discarded as a voluminous liquid slurry in an impoundment and ultimately is capped with a clay barrier, which is then covered with topsoil once the slurry is de-watered over time. Alternatively, some power-plant operators have chosen to burn coal that contains much lower amounts of sulfur to reduce the quantities

of SO_X emitted to the atmosphere. In the case of NO_X, operators often choose to decrease the temperature at which the coal is burned. This in turn decreases the amount of NO_X produced and therefore emitted; however, low temperature combustion does not utilize the full heating value of the coal, resulting in loss of efficiency.

Turbine plants normally use natural gas, which contains little or no sulfur compounds, to power the turbines, and therefore virtually no SO_X is emitted. On the other hand at the temperature that the turbines are commonly operated, substantial NO_X is produced. In addition to Selective Catalytic Reduction (SCR) processes for conversion of NO_X to nitrogen, water vapor, and oxygen, which can be safely discharged, some operators choose to reduce the temperature at which the turbines are operated and thereby reduce the amount of NO_X emitted. With lower temperatures the full combustion/heating value of natural gas is not realized, resulting in loss of efficiency. Unfortunately for these operators, newer environmental regulation will require even greater reduction of SO_X and NO_X emissions necessitating newer or more effective removal technologies and/or further reductions in efficiency.

Operators of older coal-burning power plants are often running out of space to dispose of solid wastes associated with use of scrubbers that use calcium compounds to form gypsum. Operators of newer plants would choose to eliminate the problem from the outset if the technology were available. Additionally, all power plants, new and old, are faced with upcoming technology requirements of further reducing emissions of NO_X and will have to address this issue in the near future. Thus, plants that currently meet the requirements for SO_X emissions are facing stricter requirements for reduction of NO_X for which there has been little or no economically feasible technology available.

The nitrogen oxides, which are pollutants, are nitric oxide (NO) and nitrogen dioxide (NO_2) or its dimer (N_2O_4). The relatively inert nitric oxide is often only removed with great difficulty relative to NO_2. The lower oxide of nitrogen, nitrous oxide (N_2O), is not considered a pollutant at the levels usually found in ambient air, or as usually discharged from air emission sources. Nitric oxide (NO) does however; oxidize in the atmosphere to produce nitrogen dioxide (NO_2). The sulfur oxides considered being pollutants are sulfur dioxide (SO_2) and sulfur trioxide (SO_3).

Typical sources of nitrogen and sulfur oxide pollutants are power plant stack gases, automobile exhaust gases, heating-plant stack gases, and emissions from various industrial process, such as smelting operations and nitric and sulfuric acid plants. Power plant

emissions represent an especially formidable source of nitrogen oxides and sulfur oxides, by virtue of the very large tonnage of these pollutants and such emissions discharged into the atmosphere annually. Moreover, because of the low concentration of the pollutants in such emissions, typically 500 ppm or less for nitrogen oxides and 3,000 ppm or less for sulfur dioxide, their removal is difficult because very large volumes of gas must be treated.

Of the few practical systems, which have hitherto been proposed for the removal of nitrogen oxides from power plant flue gases, all have certain disadvantages. Various methods have been proposed for the removal of sulfur dioxide from power plant flue gases, but they too have disadvantages. For example, wet scrubbing systems based on aqueous alkaline materials, such as solutions of sodium carbonate or sodium sulfite, or slurries of magnesia, lime or limestone, usually necessitate cooling the flue gas to about 55° C in order to establish a water phase. At these temperatures, the treated gas requires reheating in order to develop enough buoyancy to obtain an adequate plume rise from the stack. U.S. Pat. No. 4,369,167 teaches removing pollutant gases and trace metals with a lime slurry. A wet scrubbing method using a limestone solution is described in U.S. Pat. No. 5,199,263.

Considerable work has also been done in an attempt to reduce NO_X pollutants by the addition of combustion catalysts, usually organo-metallic compounds, to the fuel during combustion. However, the results of such attempts have been less successful than staged combustion. NO_X oxidation to N_2 is facilitated by ammonia, methane, et al. which is not effected by SO_X is described in U.S. Pat. No. 4,112,053. U.S. Pat. No. 4,500,281 teaches the limitations of organo-metallic catalysts for NO_X removal versus staged combustion. Heavy metal sulfide with ammonia is described for reducing NO_X in stack gases in U.S. Pat. No. 3,981,971.

Many fuels, and particularly those normally solid fuels such as coal, lignite, etc., also contain substantial amounts of bound or fuel sulfur with the result that conventional combustion produces substantial amounts of SO_X pollutants which are also subject to pollution control. It has generally been the opinion of workers in the art that those conditions employed in staged combustion, particularly two-stage rich-lean combustion for NO_X reduction, will likewise lower the level of SO_X emissions. However, it has been found that little or no reduction in SO_X emissions can be obtained in a two-stage, rich-lean combustion process. Indeed, it has been found that the presence of substantial amounts of sulfur in a fuel also has a detrimental effect on NO_X reduction in a two-stage, rich-lean process.

Considerable effort has been expended to remove sulfur from normally solid fuels, such as coal, lignite, etc. Such processes include wet scrubbing of stack gases from coal-fired burners. However, such systems are capital intensive and the disposal of wet sulfite sludge, which is produced as a result of such scrubbing techniques, is also a problem. Cost inefficiencies result from the often-large differential pressures across a wet scrubber removal system; differential pressures in excess of 30 inches of water column (WC) are not unusual. Also, the flue gases must be reheated after scrubbing in order to send them up the stack, thus reducing the efficiency of the system. Both U.S. Pat. Nos. 4,102,982 and 5,366,710 describe the wet scrubbing of SO_X and NO_X.

In accordance with other techniques, sulfur scavengers are utilized, usually in fluidized bed burners, to act as scavengers for the sulfur and convert the same to solid compounds which are removed with the ash. The usual scavengers in this type of operation include limestone (calcium carbonate) and dolomite (magnesium-calcium carbonate) because of availability and cost. However, the burning techniques are complex and expensive to operate and control; and the burner equipment is comparatively expensive. Dissolving coal or like material in a molten salt compound is described in U.S. Pat. No. 4,033,113. U.S. Pat. No. 4,843,980 teaches using alkali metal salt during the combustion of coal or other carbonaceous material with further efficiency by adding a metal oxide. A sulfur scavenger added upstream to a combustion zone is described in U.S. Pat. No. 4,500,281.

The combustion gas stream from a coal-burning power plant is also a major source of airborne acid gases, fly ash, mercury compounds, and elemental mercury in vapor form. Coal contains various sulfides, including mercury sulfide. Mercury sulfide reacts to form elemental mercury and SO_X in the combustion boiler. At the same time other sulfides are oxidized to SO_X and the nitrogen in the combustion air is oxidized to NO_X. Downstream of the boiler, in the ducts and stack of the combustion system, and then in the atmosphere, part of the elemental mercury is re-oxidized, primarily to mercuric chloride ($HgCl_2$). This occurs by reactions with chloride ions or the like normally present in combustion reaction gases flowing through the combustion system of a coal-burning power plant.

Many power plants emit daily amounts of up to a pound of mercury, as elemental mercury and mercury compounds. The concentration of mercury in the stream of combustion gas is about 4.7 parts per billion (ppb) or 0.0047 parts per million (ppm). Past efforts to remove mercury from the stream of combustion gas, before it leaves the stack of a power plant, include: (a) injection, into the combustion gas stream, of activated carbon particles or

particulate sodium sulfide or activated alumina without sulfur; and (b) flowing the combustion gas stream through a bed of activated particles. When activated carbon particle injection is employed, the mercuric chloride in the gas stream is removed from the gas stream in a bag house and collected as part of a powder containing other pollutants in particulate form. Mercuric chloride and other particulate mercury compounds that may be in the gas stream can be more readily removed from the gas stream at a bag house than can elemental mercury. Activated carbon injection for mercury removal along with an activated particle bed is described in U.S. Pat. No. 5,672,323.

When the gas stream flows through a bed of activated carbon particles, mercury compounds are adsorbed on the surface of the activated carbon particles and remain there. Elemental mercury, usually present in vapor form in combustion gases, is not adsorbed on the activated carbon to any substantial extent without first being oxidized into a compound of mercury. U.S. Pat. No. 5,607, 496 teaches the oxidation of mercury and subsequent absorption to particles and utilization of alumina are described therein.

Sodium sulfide particle injection can be utilized to form mercuric sulfide (HgS), which is more readily removable from the gas stream at a bag house than is elemental mercury. The conversion of mercury to a sulfide compound with subsequent capture in a dust separator is detailed in U.S. Pat. No. 6,214,304.

Essentially, all of the above techniques create solid waste disposal problems. The solids or particulates, including fly ash, collected at the bag house and the spent activated carbon removed from the bed of activated carbon, all contain mercury compounds and thus pose special problems with respect to burial at landfills where strictly localized containment of the mercury compounds is imperative. The concentration of mercury compounds in particulates or solids collected from a bag house is relatively minute; therefore, a very small quantity of mercury would be dispersed throughout relatively massive volumes of a landfill, wherever the bag house solids or particulates are dumped. Moreover, with respect to activated carbon, that material is relatively expensive, and once spent activated carbon particles are removed from an adsorbent bed, they cannot be easily regenerated and used again.

In the activated alumina process, mercury compounds in the gas stream can be adsorbed and retained on the surface of activated particles, but much of the elemental mercury will not be so affected. Thus elemental mercury in the combustion gas stream is

oxidized to form mercury compounds (e.g. mercuric chloride), and catalysts are employed to promote the oxidation process. However, such processes do not capture SO_X and NO_X.

The use of oxides of manganese to remove sulfur compounds from gas streams is known in the art. Oxides of manganese are known to form sulfates of manganese from SO_X and nitrates of manganese from NO_X when contacted with a gas containing these pollutants. U.S. Pat. No. 1,851,312 describes an early use of oxides of manganese to remove sulfur compounds from a combustible gas stream. U.S. Pat. No. 3,150,923 describes a dry bed of oxides of manganese to remove SO_X. A wet method to remove SO_X with oxides of manganese is described in U.S. Pat. No. 2,984,545. A special filter impregnated with manganese oxide to remove totally reduced sulfur compounds is described in U.S. Pat. No. 5,112,796. Another method in U.S. Pat. No. 4,164,545 describes using an ion exchange resin to trap the products of manganese oxide and SO_X and NO_X. The use of certain types of oxides of manganese to remove SO_X is disclosed U.S. Pat. Nos. 3,723,598 and 3,898,320. Some of the known methods of bringing oxides of manganese in contact with a gas stream, i.e., sprayed slurries, beds of manganese ore or special filters, have been cumbersome. Although the prior art teaches the use of oxides of manganese to remove SO_X and/or NO_X, they do not teach an adaptable system or process that can capture SO_X and/or NO_X and other pollutants with oxides of manganese and monitor and adjust system operational parameters, such as differential pressure, to provide real-time system control.

Bag houses have traditionally been used as filters to remove particulates from high volume gas streams. U.S. Pat. No. 4,954,324 describes a bag house used as a collector of products generated through the use of ammonia and sodium bicarbonate to remove SO_X and NO_X from a gas stream. U.S. Pat. No. 4,925,633 describes a bag house as a site of reaction for SO_X and NO_X with the reagents, ammonia and alkali. U.S. Pat. No. 4,581,219 describes a bag house as a reactor for highly efficient removal of SO_X only with a calcium-based reagent and alkaline metal salt. Although these prior art discloses and teach the use of bag houses for removal of particulates and as a reaction chamber, they do not teach the use of bag houses in an adaptable system capable of monitoring and adjusting system operational parameters, such as differential pressure, to capture SO_X and/or NO_X and other pollutants with oxides of manganese.

In view of the aforementioned problems of known processes for removal of SO_X, NO_X, mercury compounds, and elemental mercury as well as other pollutants from combustion gases, process gases, and other industrial waste gases, it would be desirable to

provide a dry process for removal of SO_X and NO_X as well as other pollutants from a gas stream. It is further desirable to have a dry removal process that eliminates the environmental impacts of the disposal of large volumes of mercury containing solids and particulates and significant amounts of gypsum generated during SO_X wet removal processes.

Wet removal processes can result in significant differential pressures across a removal system. Differential pressures above 30 inches of water column have been observed in wet removal processes. Such large differential pressures are costly because significant energy must be expended to counter the differential pressure and provide a waste gas stream with sufficient energy to flow up and out of a stack. A system and process that can accomplish pollutant removal with minimal or controlled differential pressure across the system therefore would be desirable and cost effective for most industry sectors processing or emitting significant amounts of combustion gases, process gases, and other industrial gases.

The calcium compounds utilized in SO_X wet scrubbing methods form gypsum in the process. They are purchased and consumed in significant quantities and once gypsum is formed the calcium compounds cannot be recovered, at least not cost-effectively. Thus, it would be desirable to have a removal method employing a sorbent that not only can remove pollutants from a gas stream but that can be regenerated, recovered, and then recycled or reused for removal of additional pollutants from a gas stream.

To realize such a system and process, it would need to incorporate process controls and software that can monitor and adjust operational parameters from computer stations onsite or at remote locations through interface with a sophisticated electronics network incorporating an industrial processor. This would allow a technician to monitor and adjust operational parameters in real-time providing controls of such operational parameters as system differential pressure and pollutant capture rates or removal efficiencies. Such a network would be desirable for its real-time control and off-site accessibility.

In light of increased energy demand and recent energy shortages, it would be desirable to be able to return to operational utility idled power plants that have been decommissioned because their gypsum impoundments have reached capacity. This could be accomplished with retrofits of a system employing a regenerable sorbent in a dry removal process that does not require the use of calcium compounds. Such a system would also be readily adapted and incorporated into new power plants that may be coming on line. Utility plants and independent power plants currently in operation could readily be retrofitted with such a system. Further, such a system could be of significant value in enabling emissions

sources to comply with emission standards or air quality permit conditions. With the reductions in emissions of pollutants such as NO_X and SO_X, marketable emissions trading credits could be made available or non-attainment areas for state or national ambient air quality standards may be able to achieve attainment status. Such scenarios would allow for development in areas where regulatory requirements previously prohibited industrial development or expansion.

The systems and processes of the present invention in their various embodiments can achieve and realize the aforementioned advantages, objectives, and desirable benefits.

Summary of the Invention

The invention is directed to an adaptable system for wet removal and combination wet and dry removal of SO_X and/or NO_X and/or other pollutants from gases and to processes employing the system.

In an embodiment of the invention the adaptable system for wet removal of target pollutants from gases with minimal differential pressure across the system is comprised of at least one reaction zone which is a wet scrubber. The wet scrubber is supplied with an acidic aqueous slurry of a sorbent of regenerable oxides of manganese and is configured for introduction of a gas containing at least one target pollutant at a temperature below the boiling point of the slurry. The gas is contacted with the sorbent for a time sufficient to effect capture of the target pollutant at a targeted capture rate set point for the target pollutant. The gas is substantially stripped of the target pollutant through the formation of a reaction product of the target pollutant and the oxides of manganese. The reaction zone is further configured to allow the gas to be vented from the reaction zone. Differential pressure across the system is regulated so that any differential pressure across the system is no greater than a predetermined level.

The system may have a single wet scrubber, or multiple wet scrubber in series for removal of target pollutants. In a dual stage removal system, the two reaction zones of the system may be both wet scrubbers, a wet scrubber followed by a dry scrubber, or a dry scrubber followed by a wet scrubber.

In another embodiment of the invention, the system is utilized in processes the removal of target pollutants from a gas stream. Gas containing a target pollutant is introduced into the reaction zone of the system. The gas is contacted with the sorbent in the sorbent slurry of the system for a time sufficient to effect the capture of the target pollutant at

a targeted capture rate set point for the target pollutant through the formation of a reaction product of the target pollutant and oxides of manganese to substantially strip the gas of the target pollutant;. The gas is vented gas from the reaction zone. These processes can be carried in single reaction zone or in multiple reaction zones of the system.

In another embodiment of the invention a process for the regeneration of oxides of manganese from a solution containing sulfate and nitrate anions and manganese cations formed when the reaction product of the removal of SO_X and NO_X from a gas stream with a sorbent of oxides of manganese, comprising the steps of:

A. providing first and second anion exchangers having an anion exchange resin loaded therein, the anion exchange resin having chloride in the exchange position on the resin;

B. passing a solution containing sulfate and nitrate anions through the first anion exchanger to elute the chloride to form manganese chloride while capturing the sulfate anion on the resin;

C. passing the solution containing nitrate anions through the second anion exchanger to elute the chloride to form manganese chloride while capturing the nitrate anion on the resin;

D. adding a soluble carbonate or hydroxide compound to the solution to precipitate manganese carbonate or manganese hydroxide;

D. separating the manganese carbonate or manganese hydroxide from the solution; and

E. heating the manganese carbonate or manganese hydroxide to form regenerated oxides of manganese.

Brief Description of the Drawings

Figure 1 is a schematic block diagram showing a system according to the invention.

Figure 2 is a schematic block diagram showing a system according to the invention.

Figure 3 is a schematic block diagram showing a system according to the invention.

Figure 4 is a block diagram showing a system according to the invention.

Figure 5 is a block diagram showing a system according to the invention.

Figure 6 is a perspective view of a commercially available bag house.

Figure 7 is an end elevation view of a commercially available bag house.

Figure 8 is a top plan view of a commercially available bag house.

Figure 9 is a side elevation view of a commercially available bag house.

Figure 10 is a sectional view of an inverted bag house according to the invention.

Figure 11 is a top plan view of an inverted bag house according to the invention.

Figure 12 is a flow diagram of a bag house reactor according to the invention.

Figure 13 is a block diagram of a system according to the invention.

Figure 14 is a block diagram of a system according to the invention.

Figure 15 is a block diagram of a system according to the invention.

Figure 16 is a flow diagram an electronic control system useful in the invention.

Figure 17 is electronic control panel display.

Figure 18 is electronic control panel display.

Figure 19 is electronic control panel display.

Figure 20 is a block diagram of a control sub-element according to the invention for regulating differential pressure.

Figure 21 is a control sub-element according to the invention for control of SO_X or NO_X capture rate or sorbent feed rate.

Figure 22 is a control sub-element according to the invention for control of bag house gas inlet temperature.

Figure 23 is a control sub-element according to the invention for control of variable venturi position(s).

Figure 24 is a control sub-element according to the invention for control of SO_X or NO_X capture rate, differential pressure, and sorbent feed rate.

Figure 25 is a control sub-element according to the invention for control of SO_X or NO_X capture rate, differential pressure, sorbent feed rate, and variable venturi position.

Figure 26 is a block diagram of a system and process according to the invention.

Figure 27 is a block diagram of a system and process according to the invention.

Figure 28 is a block diagram of system according to the invention.

Figure 29 is a graph plotting NO_X values over time.

Figure 30 is a graph plotting SO_X values over time.

Detailed Description of the Invention

The invention relates to systems and processes for removal of SO_X and/or NO_X as well as other pollutants, from a gas stream. In the invention, gas containing SO_X and/or NO_X is introduced into a first reaction zone where the gas is contacted with a sorbent of

regenerable oxides of manganese and/or regenerated oxides of manganese. The sorbent may interact with the pollutants in a gas stream as a catalyst, a reactant, an absorbent or an adsorbent. The oxides of manganese react with the SO_X and the NO_X to form, respectively, sulfates of manganese and nitrates of manganese.

"Nitrates of manganese" is used herein to refer to and include the various forms of manganese nitrate, regardless of chemical formula, that may be formed through the chemical reaction between NO_X and the sorbent and includes hydrated forms as well.

Similarly, "sulfates of manganese" is used herein to refer to and include the various forms of manganese sulfate, regardless of chemical formula that may be formed through the chemical reaction between SO_X and the sorbent and includes hydrated forms as well.

"Target pollutant(s)" means the pollutant or pollutants that are targeted for removal in the system.

"Substantially stripped" means that a pollutant has been removed from a gas at about a targeted capture rate whether by interaction with a sorbent or physical removal in a solid-gas separator. With respect to pollutants removed by interaction with a sorbent, it further contemplates that removal up to a targeted capture rate for that pollutant may be commenced in a first reaction zone and completed in a subsequent reaction.

"Reacted sorbent" means sorbent that has interacted with one or more pollutants in a gas whether by chemical reaction, adsorption or absorption. The term does not mean that all reactive or active sites on the sorbent have been utilized since all such sites may not actually be utilized.

"Unreacted sorbent" means virgin sorbent that has not intereacted with pollutants in a gas.

Some of the reaction zones may also serve as solid-gas separators rendering the gas free of solids and particulates, such as sorbent, whether reacted or unreacted, fly ash, and mercury compounds, so as to allow the gas that is substantially stripped of SO_X and/or NO_X or other pollutants to be vented from the reaction zone and passed to another reaction zone or routed up a stack to be vented into the atmosphere. The solids and particulates which include the reacted and unreacted sorbent, fly ash, and the like, are retained within reaction zones that are solid-gas separators and may be subsequently removed for further processing.

Reaction zones may be multi-stage removal systems which would incorporate additional reaction zones. The reaction zones utilized in single stage, dual stage, or multi-stage removal may be a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed,

a pipe/duct reactor, a moving bed, a bag house, an inverted bag house, bag house reactor, serpentine reactor, and a cyclone/multiclone.

The gases that may be processed in the invention are most gases containing SO_X and/or NO_X. Such gases may be generated by the combustion of fossil fuels in power plants, heating plants and various industrial processes, such as the production of taconite pellets by taconite plants, refineries and oil production facilities, gas turbines, and paper mills. Combustion for heating and other process steps at such facilities generate waste or flue gases that contain SO_X and NO_X in various concentrations, typically but not limited to 500 ppm or less for NO_X and 3000 ppm or less for SO_X. Further, the gases may contain other removable pollutants, such as fly ash, and mercury (Hg), as elemental Hg in vapor form or mercury compounds in particulate form, in small concentration, e.g., 0.0047 ppm (4.7 ppb). The gases may further contain hydrogen sulfide and other totally reduced sulfides (TRS) and other pollutants. These gases may typically have temperatures typically ranging from ambient temperature to below the thermal decomposition temperature(s) of nitrates of manganese and to below the thermal decomposition temperature(s) of sulfates of manganese. Gases generally within this temperature range can be processed in the system of the invention.

The primary sorbent useful in the invention are oxides of manganese, which may be found in manganese ore deposits or derived synthetically. Manganese compounds of interest occur in three different oxidation states of +2, +3, and +4; this gives rise to a range of multivalent phases, which provide oxides of manganese with a great diversity of atomic structures and thus mineral forms. Examples of these mineral forms include, but are not limited to, pyrolusite (MnO_2), ramsdellite (MnO_2), manganite (MnOOH or $Mn_2O_3 \cdot H_2O$), groutite (MnOOH), and vernadite ($MnO_2 \cdot nH_2O$) to name a few. This is reported by Jerry E. Post in his article "Manganese Oxide Minerals: Crystal structures and economic and environmental significance," Proc. Nat'l. Acad. Sci, U.S.A., Vol. 96, pp. 3447-3454, March 1999, the disclosure of which is incorporated herein by this reference.

One of the most common of the various forms of oxides of manganese is manganese dioxide, MnO_2. The pyrolusite form of this mineral is often the primary mineral form in manganese deposits. Pyrolusite is composed predominantly of the compound MnO_2. This oxide of manganese exhibits at least two crystalline forms. One is the gamma form, which is nearly amorphous. The other is a beta form that exhibits pronounced crystalline structure. The term "oxides of manganese" as used herein is intended to refer and include the various

forms of manganese oxide, their hydrated forms, and crystalline forms, as well as manganese hydroxide (e.g. $Mn(OH)_2$), etc.

With reference to the removal of SO_X and/or NO_X, the relative capture or removal efficiencies of oxides of manganese may be understood by the below calculation(s) of loading rates. In order to assess the economics of the system and processes of the invention, it is necessary to determine the gas removal efficiencies of the sorbent. Gas capture efficiency based upon test results may be calculated by dividing weight of gas removed by weight of sorbent. This provides an approximate picture of system operations, but does not account for stoichiometry of the reactions or interference between reactive gases in a multiple-gas system. The stoichiometric gas capture ratio is described below.

For the purpose of this assessment the overall reactions believed to occur between the sorbent, oxides of manganese, and sulfur dioxide (SO_2) and nitric oxide (NO) are shown below, with molecular weights shown above each species.

87 64 151

$MnO_{2\,(solid)} + SO_{2\,(gas)} \Rightarrow MnSO_{4\,(solid)}$ (1 mole MnO_2 captures 1 mole SO_2)

87 60 32 179

$MnO_{2\,(solid)} + 2NO_{(gas)} + O_{2\,(gas)} \Rightarrow Mn(NO_3)_{2\,(solid)}$ (1 mole MnO_2 captures 2 moles NO)

These reactions may occur in multiple steps. Molecular weights are shown above each species. Based on these reactions, the theoretical maximum stoichiometric gas capture by weight of MnO_2 sorbent is the ratio of the molecular weights of the products versus the reactants which is 73% for SO_2 or 69% for NO, for systems containing only one reactive gas. For a system containing two reactive gases, depending on reaction characteristics, the maximum stoichiometric gas capture will be lower for both gases. If reaction speeds are assumed to be equal for both reactive gases, maximum stoichiometric gas capture for each gas should be proportional to the percentage of each gas present.

For example, during a 48-hour test, two reactive gases, SO_2 and NO were present at approximately 430 ppm and 300 ppm, respectively. Total weights of reactive inlet gases treated were:

$SO_2 = 98.45$ lb. NO = 47.02 lb. total = 145.47 lb.

Therefore, SO_2 and NO represented 67.7% and 32.3% respectively, of reactive gases present. If the theoretical maximum stoichiometric gas capture for a single-gas system is corrected to

these reactive gas weight proportions, the theoretical maximum percentage capture for each gas by MnO_2 weight is:

SO_2: (0.73 single-gas) x (0.67 for the 48-hr. test) = 0.489 = 48.9%

NO: (0.69 single-gas) x (0.323 for the 48-hr. test) = 0.223 = 22.3%

Therefore, the theoretical maximum weights of gases captured by 289 lb., for example, of sorbent for the 48-hour test would be:

SO_2: (289 lb. Sorbent) x (0.489) = 141.4 lb. SO_2

NO: (289 lb. Sorbent) x (0.323) = 98.35 lb. NO

Actual gas capture experienced in the 48-hour test was 23.94 lb. of SO_2 and 4.31 lb. of NO. For the 2-gas system, stoichiometric gas capture was:

SO_2: (23.94 lb. captured) / (141.4 lb. SO_2 possible) = 16.9% (of theoretical maximum)

NO: (4.31 lb. captured) / (64.41 lb. possible) = 6.69% (of theoretical maximum)

Oxides of manganese, once reacted with SO_X and NO_X to form sulfates of manganese and nitrates of manganese respectively, can be regenerated. There are essentially two general methods of regeneration, thermal decomposition and chemical decomposition.

In thermal decomposition, the sulfates of manganese and/or nitrates of manganese are heated in an oxidizing atmosphere whereupon manganese oxide is formed and nitrogen dioxide and/or sulfur dioxide are desorbed and captured. The captured nitrogen dioxide or sulfur dioxide can be reacted with other chemicals to produce marketable products.

In the chemical decomposition or regeneration of manganese oxide, the sulfates of manganese and/or nitrates of manganese are dissolved from the used sorbent in a dilute acidic aqueous slurry to which, after separation and recovery of the washed sorbent, other compounds such as alkali or hydroxides or carbonates may be added and manganese oxide is precipitated out of solution and removed. The solution, now free of oxides of manganese, can be routed on for further processing or production of marketable products such as alkali or ammonium sulfates and nitrates. The regeneration of manganese oxide and production of useful or marketable products through thermal or chemical decomposition is further discussed below.

In the process of regeneration, the regenerated oxides of manganese are in particle form and are defined by the chemical formula MnO_X, where X is about 1.5 to 2.0. The regeneration process may be engineered to yield oxides of manganese having a particle size ranging from 0.1 to 500 microns. Oxides of manganese in this range are useful in the

invention. Preferably, the oxides of manganese will have a particle size of less than 300 microns, and more preferably of less than 100 microns. The regenerable oxides of manganese and/or regenerated oxides of manganese are typically fine, powdery, particulate compounds.

Reactivity of dry sorbents may generally be related to its particle surface area. Particles or particulates all have weight, size, and shape, and in most cases they are of inconsistent and irregular shape. In the case of fine powders it is often desirable to know how much surface area a given quantity of powder exhibits, especially for particles that are chemically reactive on particle surfaces, or are used as sorbents, thickeners or fillers. (Usually measurements of surface area properties are done to compare several powders for performance reasons.) Particles may also have microscopic pores, cracks and other features that contribute to surface area.

The BET (Brunauer-Emmett-Teller) method is a widely accepted means for measuring the surface area of powders. A powder sample is exposed to an inert test gas, such as nitrogen, at given temperature and pressures, and because the size of the gas molecules are known at those conditions, the BET method determines how much test gas covers all of the exterior surfaces, exposed pores and cracks with essentially one layer of gas molecules over all of the particles in the powder sample. Optionally, the analyst can use other test gases such as helium, argon or krypton; and can vary from 1 to 3 relative test pressures, or more, for better accuracy. From this, a measure of total surface area is calculated and usually reported in units of square meters of particle surface area per gram of powder sample (m^2/g). Generally, coarse and smooth powders often range in magnitude from 0.001 to 0.1 m^2/g of surface area, and fine and irregular powders range from 1 to 1000 m^2/g. Since the interactions between a sorbent and the pollutant occurs primarily at the surface of sorbent particle, surface area correlates with removal efficiency. The oxides of manganese useful in the invention are fine and irregular powders and thus may have a surface area ranging from 1 to 1000 m^2/g. Preferably the sorbent will have a surface area of greater than 15 m^2/g, and more preferably of greater than 20 m^2/g.

With reference to Figure 1, a system according to the invention is illustrated in block diagram form. The system 10 may be seen as comprised of a feeder 20 and a first reaction zone 30 and a second reaction zone 38. The feeder 20 would contain a supply of sorbent of regenerable oxides of manganese and/or regenerated oxides of manganese. The feeder 20 is configured to handle and feed oxides of manganese, which, upon regeneration, are in particle

form and defined by the chemical formula MnO_X where X is about 1.5 to 2.0. The first reaction zone 30 is configured for introduction of the sorbent in a gas containing SO_X and NO_X. In one embodiment, the first reaction zone 30 may be a section of pipe/duct, possibly configured as a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed, a pipe/duct reactor, a moving bed, a bag house, an inverted bag house, bag house reactor, serpentine reactor, and a cyclone/multiclone. The second reaction zone 38 a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed, a pipe/duct reactor, a moving bed, a bag house, an inverted bag house, bag house reactor, serpentine reactor, and a cyclone/multiclone. Preferably, the second reaction zone is a bag house, such as commercially available bag house, an inverted bag house according to the invention, or a bag house reactor according to the invention.

The gas containing SO_X and NO_X, or other pollutants, comes from a gas source 15 external to the system. The gas is introduced into the first reaction zone 30 and is contacted with sorbent introduced into the first reaction zone 30 from the feeder 20 and is contacted with the sorbent for a time sufficient to primarily effect SO_X capture at a targeted SO_X capture rate. For purpose of discussion, and not wishing to be held to a strict interpretation, with respect to effecting a certain capture, it has been observed that oxides of manganese can more readily capture SO_2 in a gas stream absent of NO, and also can more readily capture NO in a gas stream absent of SO_2, than when the gas stream contains both SO_2 and NO. SO_X capture tends to proceed at a much faster rate than NO_X capture when the two pollutants are present in a gas stream.

The gas and sorbent may be introduced separately or commingled before introduction into a reaction zone. Once the gas and sorbent have been contacted for sufficient time, the SO_X is captured by reacting with the sorbent to form sulfates of manganese to substantially strip the gas of SO_X. The gas substantially stripped of SO_X passes from the first reaction zone 30 into the second reaction zone 38. The second reaction zone 38 is configured for introduction of sorbent and the gas substantially stripped of SO_X. In the second reaction zone 38, the gas is further contacted with sorbent for a time sufficient to primarily effect NO_X capture at a targeted NO_X capture rate. The NO_X is captured by reacting with the sorbent to form nitrates of manganese to substantially strip the gas of NO_X. The second reaction zone 38 is further configured so that the gas which has been substantially stripped of both SO_X and NO_X is rendered free of reacted and unreacted sorbent. The gas may then be vented from the second reaction zone 38 to a stack 40 where the gas is released to the atmosphere.

Differential pressure across the reactor system is regulated by a control sub-element (not shown in Figure 1) so that any differential pressure across the system is no greater than a pre-determined level. As is later described, the control sub-element may control other system parameters such as feeder rate, SO_X and/or NO_X capture rate, and the inlet gas temperature into the reaction zones. Thus, the system of the invention is highly adaptable and, in another embodiment, is generally comprised of a feeder 20, a first reaction zone 30, a second reaction zone 38, and at least one control sub-element for regulating process parameters.

In another embodiment of the invention, the system is comprised of a feeder 20 as previously described and a modular reaction unit 60 comprised of at least three interconnected reaction zones. With reference to Figure 2, where the reaction zones are three interconnected bag houses 62, 64, 66, the modular reaction unit may be understood. The bag houses 62, 64, 66 are connected so that a gas containing SO_X and/or NO_X can be routed through any one of the bag houses, any of the two bag houses in series, or all of the at least three bag houses in series or in parallel or any combination of series or parallel. Each bag house is separately connected to the feeder 20 and to the external gas source 15. Through these connections, sorbent and gas can be introduced into each bag house where SO_X and NO_X capture can occur when the gas is contacted with sorbent for a time sufficient to allow formation of sulfates of manganese, nitrates of manganese, or both. The system in this embodiment may also include control sub-elements 50 (not shown) for regulating various process parameters. The reaction zones of the modular unit 60 are not limited to bag houses and may be any combination of reaction zones useful in the inventory. If the bag houses are operated independently of each other, then the section of pipe or duct (pipe/duct) preceding the bag house and that which is connected to an inlet of each bag house conveys gas into each bag house and is also configured as a first reaction zone 30, a pipe/duct reactor, into which gas containing SO_X and NO_X flows along with the sorbent. The gas is mixed with the sorbent in the pipe/duct reactor for a sufficient time to achieve SO_X capture at a targeted capture rate. In this mode, the system operates as illustrated in Figure 1 with each bag house 62, 64, 66 being a second reaction zone 38 into which the gas that has been substantially stripped of SO_X passes from the first reaction zone 30, pipe/duct reactor.

With reference to Figure 3, another embodiment of the invention is shown. In this embodiment, the system 10 is comprised of a feeder 20, and three bag houses 70, 76, and 78, a common conduit 73 and a diverter valve 74. Gas and sorbent are introduced into the first bag house 70 which serves as a first reaction zone of a two-staged SO_X/NO_X removal system

where primarily SO_X capture occurs. The gas substantially stripped of SO_X then passes from the first bag house 70 into the common conduit 73. As shown in Figure 3, the common conduit 73 is Y-shaped, but may be of any shape that allows gas to flow from the first bag house 72 and to be directed to the second and third bag houses 76, 78 which each function as the second reaction zone of a two-staged SO_X/NO_X removal system.

In the Y-shaped common conduit 73 can be seen a diverter valve 74 illustrated as a dotted line at the fork of the "Y". The diverter valve 74 is positioned in the common conduit 73 so as to direct the flow of gas from the first bag house 70 to the second bag house 76 and/or the third bag house 78. The diverter valve 74 has variable positions, in the first position gas from the first bag house 70 is directed to the second bag house 76, in the second (variable) position gas from the first bag house 70 is directed to both the second and third bag houses 76,78, and in the third position, as illustrated in Figure 3, the gas from the first bag house 70 is directed to the third bag house 78. Gas exiting the second and third bag houses 76 and 78 may be vented and directed for further processing or handling (e.g. directed to stack 40 or directed to a subsequent reactor for Hg removal). The system of this embodiment may incorporate any combination of the reaction zones useful in the invention and is not intended to be limited to bag houses.

However, when the reaction zones are bag houses, the system illustrated in Figure 3 may further comprise an off-line loading circuit 42. The off-line loading circuit 42 is brought into use after the filter bags have been pulsed to clean them of filter cake so reacted sorbent can be removed for recycling or regeneration. There may be more than one off-line loading circuit 42, as shown in Figure 3, each separately connected to a bag house 76 and 78. The off-line loading circuit is connected to a sorbent feeder and a bag house via an off-line loading circuit conduit and incorporates a fan for blowing air commingled with sorbent into the bag houses 76 and 78 in order to pre-load the fabric filter bags in the bag houses by building a filter cake thereon. The air passing through the bags and cake thereon is vented from the bag house. When the bag house is ready to come back on line, the off-line loading circuit can be closed or switched off and the diverter valve 74 moved to a position to permit the flow of process gas through the bag house that is being brought back on line.

When NO_X is captured by the sorbent, the sorbent may not be completely loaded or spent thus having remaining reactive sites. Even though it may no longer be effective as an efficient sorbent for NO_X at this point, the sorbent may have reactive sites that could be utilized efficiently for SO_X capture. Thus, the partially loaded reacted sorbent or NO_X-

reacted sorbent in a second reaction zone of a two-stage SO_X/NO_X removal system could be removed from the second reaction zone and fed into the first reaction zone to allow additional SO_X capture with, or loading onto, the sorbent. This would decrease the frequency at which sorbent regeneration is needed and reduce the amount of virgin or unreacted sorbent that would need to be introduced into the first reaction zone.

With reference to Figure 4 a system according to the invention utilizing counter-flow feed of NO_X-reacted sorbent is illustrated in a block flow diagram. The system 10 is comprised of a first reaction zone 30, a second reaction zone 38, a feeder 20 containing virgin or unreacted sorbent, and a NO_X-reacted sorbent feeder 21. The first reaction zone 30 of system 10 is connected to external gas source 15 and gas flows from the external gas source 15 to the first reaction zone 30, from the first reaction zone 30 to the second reaction zone 38, and from the second reaction zone 38 is either vented to stack 40 or directed on to another system unit such as a mercury-sorbent reactor (not shown). The feeder 20 can feed virgin or unreacted sorbent into the first reaction zone 30 and the second reaction zone 38. NO_X-reacted sorbent is removed from the second reaction zone and is conveyed from the second reaction zone to the first reaction zone via NO_X-reacted sorbent feeder 21 where the NO_X-reacted sorbent with available reaction sites is further contacted with a gas containing both SO_X and NO_X to remove and capture SO_X.

Using reacted sorbent feeders allows sorbent to be recycled to a reaction zone where unreacted sites on the surface of the sorbent can be utilized. Through the mechanical operations of removing reacted sorbent from a reaction zone and returning it to the same or another reaction zone, the amount of virgin or unreacted sorbent that has to be introduced into the system is reduced. A sorbent may be recycled this way several times before regeneration is necessary due to the reduction in available reaction sites on the surface of sorbent particles. This represents significant cost savings and more economical and complete use of the sorbent.

During operation, the surfaces of sorbent particles may become obstructed, for example, by compaction or agglomeration. The physical manipulation and handling of the reacted sorbent re-orients the particles making unexposed surfaces available to capture targeted pollutants.

The recycling of reacted sorbent in this way may proceed as shown in Figure 4 in a counter-flow manner as discussed above. Recycling may also proceed by removing reacted sorbent from a reaction zone conveying it to a reacted sorbent feeder and introducing or re-

introducing the reacted sorbent into the same reaction zone. This is shown in Figure 28, where reacted sorbent feeder 21A receives reacted sorbent conveyed from the first reaction zone 30 and reacted sorbent from reacted sorbent feeder 21A is re-introduced into the first reaction zone 30. Further, reacted sorbent from second reaction zone 38 is conveyed to reacted sorbent feeder 21B and re-introduced into the second reaction zone 38. This may be desirable where a first targeted pollutant is being captured in the first reaction zone and a second targeted pollutant is being captured in the second reaction zone. If, for example, SO_X is being captured in the first reaction zone 30, the SO_X reacted sorbent when it is spent or ceases to be effective for SO_X removal, can then be routed for regeneration and recovery of sulfates as alkali or ammonium sulfate, useful commercial product. Similarly, if NO_X is the pollutant being captured in the second reaction zone 38, the NO_X reacted sorbent can be removed when it ceases to be effective for NO_X removal and directed for regeneration and recovery to produce alkali or ammonium nitrates, again, useful commercial by-products.

Capture rates may be affected by the gas inlet temperature as it enters a reaction zone and may need to be adjusted, cooled or heated to achieve a desired capture rate for SO_X and/or NO_X. This can be accomplished with a heat exchanger. As is illustrated in Figure 5, the system may further include a heat exchanger preceding each reaction zone of a system of the invention. In Figure 5, the system of the invention as illustrated is substantially the same as the illustration of Figure 1, depicting first and second reaction zones 30 and 38, feeder 20, external gas source 15, and stack 40. In Figure 5, heat exchangers 72A, 72B have been introduced into the system before each reaction zone. The heat exchangers 72A, 72B may be utilized to heat or cool the gas stream prior to entry into each reaction zone. As the gas enters into the system, if the gas temperature is above the thermal decomposition temperature(s) of either sulfates of manganese or nitrates of manganese, the heat exchangers 72A, 72B will operate to cool the gas to a desired temperature based upon whether SO_X capture or NO_X capture is the primary pollutant captured in the reaction zone. Similarly, if the gas were below a desired temperature set point, the heat exchangers 72A, 72B will operate to heat the gas to the desired temperature. The heat exchangers 72A, 72B may be a gas-to-gas cooler or a heater unit, or other suitable means for accomplishing heating and cooling of gases to assure that the gas inlet temperature at a targeted temperature or within an acceptable range.

As previously mentioned above, the gases entering the system from external gas source 15 may be any of a variety of process or industrial gases. These gases when generated encompass a range of temperatures. Due to simple economics and the design of various

plants and facilities for efficient use of waste heat which is captured or transferred to provide heat for various processes at a facility, these process gases will typically have a temperature ranging from 250° F. to 350° F or 120° C to 180° C. In less typical situations, these gases may have temperatures upwards of 1000° F, or 540° C. Gases at these temperatures are readily processed in the systems of the invention and the heat exchangers 72A, 72B can be utilized to maintain the gas within these temperature ranges if desired. The system can also process gases at much higher temperatures such as 1000° F. For purposes of SO_X and NO_X capture, the gas temperature should not exceed, respectively, the thermal decomposition temperature(s) of sulfates of manganese and nitrates of manganese. Given that different forms or species of these sulfates and nitrates, the thermal decomposition temperature would depend upon the species formed during capture. It has been reported that that sulfates of manganese may thermally decompose at temperatures approximating 950°C. Similarly, nitrates of manganese are believed to thermally decompose at temperatures ranging up to 260 °C. The system of the invention can process gases approaching these thermal decomposition temperatures. But, more typically, the system in practice will be operated in temperature ranges approximating those of process gases from industrial sources.

Heat or waste heat from the process gases of a facility may be utilized in the regeneration and recovery processes discussed herein below. Further, the waste heat may be utilized for purposes of sorbent preheating which serves to "activate" sorbent prior to introduction into a reaction zone. Although the exact mechanism of activation is not known, it is generally known that oxides of manganese can be "activated" with heat. Thus, as can be seen in Figure 28, a system according to the invention may further include a sorbent preheater 22 which may actually be part of or separate from sorbent feeder 20. The source of heat for the sorbent preheater may be any heat source, but waste heat from facility processes can be economically efficiently utilized for this purpose.

The SO_X and/or NO_X capture rate may be regulated by the amount of sorbent fed into the reaction zones. In order to regulate capture rate, gas measuring devices, such as continuous emission monitors (CEMS), are utilized to measure the composition of the gas at the inlet to the reaction zone and at the outlet of the reaction zone. With reference to Figure 14, the gas flows from the external gas source 15 and past CEMS 80A where the gas composition is measured prior to entry into first reaction zone 30. Another CEMS 80B is provided after the first reaction zone 30 to measure the concentration of the gas substantially stripped of SO_X and/or NO_X as it passes from the first reaction zone 30. As in Figure 1, the

gas may be vented to a stack 40, passed to a second reaction zone 38, or another system unit for further processing.

In the system of the invention, a bag house may serve as a reaction zone and/or as a solid gas separator, since bag houses are solid-gas separators. A conventional, commercially available bag house 82 is depicted in Figures 6 through 9. Figure 6 is a perspective view of a bag house 82. Figure 7 is an end elevation view showing a bag house 82. Figure 8 is a top plan view of a bag house 82. Figure 9 is a side elevation view of a bag house 82. Within the bag house 82 are a plurality of bags 88 also referred to as filter fabric bags shown in Figures 7 through 9. As can be seen in figure 7 through 9, the bag house 82 has a plurality of filter fabric bags 88 suspended therein. Typically, they are suspended from a frame or support structure at the top of the bag house 82. The filter bags 88 may be of various shapes, e.g., conical or pyramidal, and include an internal frame and suitable fabric filter. Those skilled in the art would be able to select suitable filter fabric materials from those commercially available. Gas and entrained sorbent enters the bag house 82 through the bag house inlet 92, shown in Figures 7 through 9, and by virtue of an applied differential pressure, gases are forced through the fabric of the bags 88 and the entrained sorbents are separated from the gas by forming a filter cake on the surface of the bags 88. The filter cake thus formed is a reaction medium where pollutants are contacted with and removed by the sorbent. The commingled gases and sorbents move vertically upward and contact the fabric and/or the filter cake formed thereon. The bags 88 are configured to permit the gases to be directed from the outside to the inside of the bags to a conduit at the top of the bag house 82 and then to the bag house outlet 98, shown in Figures 6 through 9.

While the bag house 82 is in operation, the filter bags 88 may be periodically pulsed or otherwise agitated in order to adjust differential pressure across the bag house 82, which frees some or all of the filter cake and allows gas to flow more freely through the filter cake and the fabric filter bags. If the filter cake is allowed to get too thick, excess differential differential pressure across the bag house or the system of the invention may result. Thus, the pulse intensity or frequency can be utilized to regulate or adjust differential pressure. When the bag house 82 is taken off line, the bags 88 may be pulsed to free the bags 88 of virtually all reacted and unreacted sorbent not otherwise removed during normal operations. The reacted and unreacted sorbent or filter cake fall from the bags 88 by gravity into a hopper 112 (seen in Figures 7 and 9) at the bottom of the bag house 82 for subsequent removal from the

bag house hopper 112. Removal from the hopper 112 may be accomplished with a screw conveyor or by other appropriate means, even manually.

A thicker filter cake will lead to increased removal efficiency, but at the price of extra power required to force the external gas source through the reaction zone. In one example, more power is required for an induction fan to pull exhaust gases through the bag house when the filter cake thickness is greater. The differential pressure may thus be maintained at an optimal level, trading off increased power requirements against the increased pollutant removal. In addition, the thicker the filter cake the longer the residence time of the sorbent material in the system. Longer residence time of the gas in the filter cake results in better removal efficiencies. Higher sorbent loading rates results in less material that will have to be regenerated. This may also be taken into consideration in setting the differential pressure set point.

In Figures 7 and 9, the plurality of filter bags is shown in position within the bag house. Also shown near the top of the bag house 82 is a pulse valve 124 utilized to pulse the fabric bags 88 in order to reduce filter cake thickness or to free the filter cake from the bags 88. The bag house may be provided with a number of pulse valves 124. During operation, these pulse valves 124 may be activated sequentially or randomly in order to pulse the bags 88 in order to regulate and control differential pressure across the bag house 82 or the system as a whole. When the bag house is taken off-line, the bags may be pulsed to free the bags of virtually all filter cake so that reacted and unreacted sorbent may be removed.

The bag house illustrated in Figure 6 through 9 is of a conventional design. In Figures 10 and 11, a novel bag house according to the invention is illustrated. This bag house, which can be utilized in the system of the invention, is referred to as an inverted bag house 140. The inverted bag house 140 eliminates the need for high can velocities, and permits downward, vertical flow of gases and reacted and unreacted sorbent. The inverted bag house 140 is comprised of a bag house housing 142, at least one inlet 145, a plurality of fabric filter bags 88, a support structure 149 for the filter bags, a hopper 152 to receive and collect reacted and unreacted sorbent, an outlet 154, and a conduit 158. The bag house housing permits the introduction of gases and reacted and unreacted sorbent entrained in the gases, has a top and a bottom and is configured for gases to flow vertically downward from the top to the bottom of the bag house. The inlet 145 is located near the top of the bag house housing and is configured for the introduction of gases and reacted and unreacted sorbent entrained in the gases into the bag house. The plurality of fabric filter bags 88 are configured

to allow gas to flow from the outside of the bags 88 to the inside of the bags 88 under an applied differential pressure and to prevent the passage of reacted and unreacted sorbent from the outside to the inside of the bags 88, thereby separating reacted and unreacted sorbent from the gas and forming a filter cake on the bags 88. The support structure 149 is configured to receive and support the fabric filter bags 88 and to provide openings through which reacted and unreacted sorbent may be freely passed downward into the hopper 152 by gravity. The hopper 152 is configured to receive the reacted and unreacted sorbent and to permit the removal of the reacted and unreacted sorbent. The inverted bag house 140 also has an outlet 154 located near the bottom of the housing 142 below the bags 88 and above the hopper 152. The outlet 154 is connected to a conduit 158 located below the fabric filter bags 88 and positioned to receive gas passing through the fabric filter bags. Conduit 158 conveys gas to the outlet so that the gas may be vented or passed from the inverted bag house 140.

In Figure 12, a bag house reactor 150 of the invention is illustrated. This bag house reactor 150 can also be utilized in the system in place of a conventional bag house. The bag house reactor 150 has interior surface 154 and exterior surface 152. It may be viewed as having an upper section 156, central section 157 and lower section 158. Generally located in the central and/or lower sections 157, 158 is a variable venturi 160. The purpose of the variable venturi 160 is to adjust the velocity of gas flowing through the venturi opening within the bag house reactor 150. The variable venturi 160 is configured to adjust the position of the variable venturi by varying the space or distance between the variable venturi 160 and the interior surface 152 of the bag house reactor 150. In order to vary position a variable venturi position detector 367 shown in Figure 23) for determining the position of the variable venturi 160 and a variable venturi positioner 368 (shown in Figure 23) for adjusting the position of the variable venturi 160 are provided.

With the variable venturi 160 contacting the interior surface 154 of the bag house reactor 150, gas cannot flow from the lower section 158 to the central and upper sections 156, 157 of the bag house. By opening the space between the variable venturi 160 and the interior surface 154, gas is allowed to flow through the reactor 150. Gas introduced through gas distribution conduit 164 and the gas distribution port 162 flows from the lower section 158 to above the variable venturi 160 and into the central and upper sections 156, 157, and to the filter bags 88. When the space between the variable venturi 160 and the interior surface 154 is wide, the gas flows at lower velocities which allows some of the sorbent suspended above the variable venturi 160 to fall into the hopper 112.

There is also a sorbent distribution port 166 connected to a sorbent feed conduit 168. The sorbent distribution port 166 is positioned above the variable venturi 160 to allow the introduction of sorbent into the upper section 156 of the bag house reactor 150. The sorbent distribution port 166 is configured to allow introduction of sorbent into the bag house. Port 162 is configured to allow introduction of gas into the bag house reactor.

The bag house reactor 150 has a plurality of fabric filter bags 88 secured therein. The fabric filter bags are mounted in the upper section 156 of the bag house reactor 150 and extend downward into the central section 157. At the bottom of the bag house reactor in the lower section 158, is a sorbent hopper 112 where reacted and unreacted sorbent is collected. The sorbent hopper is connected to outlet 172. Outlet 172 has an outlet valve 176 which in the open position allows for the removal of sorbent from the hopper 112. A vent 180 is located in the top section 156 of the bag house reactor 150. Gases flowing through the bag house reactor 150 pass from the bag house reactor 150 through the vent 180 and may be directed on for further processing or venting to the atmosphere.

Sorbent entrained in gases containing pollutants such as SO_X and NO_X can begin reacting with the sorbent during transport in the sorbent feeder conduit 168. Since SO_X is more reactive than NO_X, the more reactive SO_X is primarily captured while it is being transported to the bag house reactor 150 in the first sorbent feeder conduit 164. At lower gas velocities the larger solids will abrade into finer solids and re-fluidize. The finer solids will travel upward through the opening between the variable venturi 160 and the interior surface 154 where the sorbent is suspended to create a pseudo fluidized-bed above the variable venturi 160 and the finest particules will travel upwards to form a filter cake on the surface of the fabric filter bags 88. By adjusting the position of the variable venturi 160 increasing or decreasing the space between the variable venturi 160 and the interior surface 154 of the bag house reactor 150 gas velocity is correspondingly decreased or increased. In operation, the variable venturi may be positioned to achieve a gas velocity sufficient to suspend a selected coarse fraction sorbent just above the orifice to create a pseudo-fluidized bed which may primarily or preferentially capture SO_X, since SO_X is more reactive than NO_X. Partially stripped gas flows upward from the pseudo-fluidized bed carrying the finer fraction sorbent onto the filter bags. The resulting filter cake provides a reaction medium where "slower" reactions, such as NO_X removal may occur. The variable venturi 160 position may be adjusted to achieve the desired thickness of filter cake on the fabric bags 88 thereby increasing or decreasing the differential pressure across the system also to balance overall

differential pressure by changing the venturi restriction. The fabric filter bags 88 may also be pulsed to partially remove filter cake and thus regulate differential pressure. The gas flow rate entering port 162 can be adjusted to regulate upward gas velocity so that the bags 88 may be pulsed to allow some of the loaded sorbent to fall into the hopper 112 without being reentrained in the gas or redeposited on the bags 88.

Using the variable venturi 160, one can operate the system so that sorbent suspended above the venturi, loaded with the faster reacting gases, can primarily be captured by falling to the hopper before being carried up to the filter bags 88. The fraction of sorbent loaded with faster reacting gases can then be removed from the hopper 112 by opening the outlet valve 176 so that that fraction may be removed from the hopper 112 through the outlet 172. Later the fabric filter bags 88 can be pulsed to release the sorbent loaded with slower reacting gases which would then fall through the variable venturi 160 into the hopper 112. The sorbent loaded with slower reacting gases could then be removed from the hopper through loaded sorbent outlet 172 after the outlet valve 176 has been opened. This could allow for the separate processing of the different loaded sorbent fractions to regenerate the sorbent and produce useful by-products.

Differential pressure, which represents sorbent filter cake thickness, is only one of several process parameters that can be controlled in the system in order to achieve desired levels of SO_X and NO_X removal efficiencies and cost advantages of the system. NO_X and SO_X removal efficiency may be regulated by various processes, including sorbent feeder rate and temperature control at the inlet to the reaction zones of the system. These controls are achieved by the control sub-elements or electronics, which include hardware and software and also are referred to herein below as control loops.

Referring now to Figure 13, a differential pressure control loop 300 is illustrated. External gas source 15 is illustrated feeding first reaction zone 30, which in turn feeds generally an output gas stream 316, which can feed either stack 40 or second reaction zone 38. The differential pressure across first reaction zone 30 may be measured as illustrated as difference in pressure between the inlet pressure 306 and the outlet pressure 304. In the example illustrated, inlet pressure 306 and outlet pressure 304 feed a differential pressure cell 308, which sends a differential pressure signal 310 to a differential pressure controller 302.

Differential pressure controller 302 can be any appropriate controller, including a proportional integral derivative (PID) controller. As used herein, PID controllers may be understood to operate using any combination of the proportional, integral, and derivative

components. Differential pressure controller 302 can accept a set point 312, indicating the desired differential pressure across first reaction zone 30. Set point 312 can be human or computer generated. As discussed below, differential pressure controller 302, and other controllers, may be implemented as a stand-alone controller, distributed control system, as a PID block in a programmable logic controller (PLC), or as a set of discrete calculations within a PLC. Differential pressure controller 302 generates an output signal 314 to control the differential pressure across first reaction zone 30. In embodiments where first reaction zone 30 includes a bag house or uses solids-filtering media, differential pressure controller 302 output signal 314 may control the shaking, pulsing, or other removal of sorbent which has formed a filter cake on the filter medium.

In one embodiment, first reaction zone 30 includes numerous filter bags which can have an exterior containing sorbent material and an interior having a lower pressure, acting to pull the sorbent material against the bag filter media. In one example of the invention, a compressed air jet, pulse valve 124, is periodically discharged within the interior of the filter. In one embodiment, the compressed air pulse is sufficiently strong to dislodge a portion of caked sorbent material from the filter material even during normal operation of the bag house, not requiring the shut down of the bag house. In one embodiment, the individual bags are sequentially pulsed to dislodge a portion of caked sorbent material. The frequency of the pulsing may be increased in order to maintain a thinner filter cake thickness. Thus, increasing the frequency of the periodic pulsing of each filter bag will maintain a smaller filter cake thickness, and thus result in a smaller differential pressure across the bag house as a whole. In one embodiment, filter bags are grouped by row, with each row periodically pulsed at the same instant. In some embodiments, output 314 from differential pressure controller 302 includes a frequency for pulsing filters within a bag house reaction zone. Differential pressure controller 302, in response to a higher differential pressure than set point, may increase the frequency of filter pulsing through output 314. Conversely, in response to a lower differential pressure than set point, differential pressure controller 302 may decrease the frequency of filter pulsing through output 314.

In one embodiment, the individual filter bags are formed of cylindrical filter media disposed about a rigid cylindrical cage, with the compressed air jet, pulse valve 124, disposed within the cylindrical rigid cage. After a period of time, the sorbent material filter cake builds up on the outside of the filter media, forming a thick filter cake. The pulsed air jet can force the filter media momentarily away from the cylindrical rigid cage, thereby cracking the

caked sorbent material and dislodging it, thereby allowing the sorbent material to fall under gravity to be collected and removed from the reaction zone.

A thicker filter cake can lead to increased pollutant removal efficiency, but at the price of extra power required to force the external gas source through the reaction zone. In one example, more power is required for an induction fan to pull exhaust gases through the bag house when the filter cake thickness is greater. The differential pressure may thus be maintained at an optimal level, trading off increased power requirements against the increased pollutant removal. In addition, as the filter cake thickness increases the contact or residence time of the gas with sorbent material in the system increases, resulting in more complete reaction. Therefore less material will have to be regenerated. This may also be taken into consideration in defining the differential pressure set point.

Referring now to Figure 14, an emissions control loop 320 is illustrated. A gas stream may be seen to flow from gas source 15, through a first continuous emission monitor system (CEM) 80A, then to first reaction zone 30, then to a second CEM 80B. A sorbent feeder 20 may be seen to feed material to first reaction zone 30. Feeder 20 may be a screw feeder having a variable speed screw, auger, pneumatic conveyor, or other method to move sorbent, within.

CEM 80A and CEM 80B can represent a NO_X analyzer and or a SO_X analyzer. In one embodiment, CEM 80A is a chemiluminescent monitor, for example, Thermo Electron model 42H. In one embodiment, CEM 80A includes a SO_X monitor such as Bovar Western Research model 921NMP, utilizing a spectrophotometric method. In some embodiments, CEM 80A and CEM 80B include both NO_X and SO_X analyzers. A feed controller 322 may be seen to accept a first input 328 from an outlet CEM signal 325. Controller input 328 may be used as a feedback signal to control the feeder rate. In some embodiments, a feeder controller 322 also has a second input 330 accepting an inlet measurement signal 324, also including pollutant concentration data. Second input 330 may be used to display the incoming gas concentrations and/or to calculate percentage removal set points in the system. Feeder controller 322 also accepts a set point signal 326, indicating the desired feed rate and/or the desired NO_X or SO_X concentration exiting first reaction zone 30. Feeder controller output 332 can be a variable frequency drive signal, among other available signals, to control the speed of feeder 20.

Feeder controller 322 may be any suitable controller, including a PID controller utilizing any combination of its individual modes. In one embodiment, set point 326 is set at

a desired concentration for either NO_X or SO_X, depending on the embodiment. The gas concentration signal 325 from CEM 80B can be used by feeder controller 322 to calculate output signal 332. When the gas concentration is higher than indicated as desirable by set point 326, output 332 can be increased to increase the speed of feeder 20, which will put more sorbent into first reaction zone 30, thereby dropping the pollutant concentration. Conversely, when pollutant gas concentration 325 is lower than required, feeder controller output 332 can be decreased to decrease the rate of sorbent addition from feeder 20 into first reaction zone 30.

Referring now to Figure 15, the gas to be cleaned may be seen to flow from external gas source 15, through a first heat exchanger 72A, through first reaction zone 30, through second heat exchanger 72B, through a second reaction zone 38, and to stack 40. Figure 15 illustrates a system having two reaction zones and two heat exchangers. The temperature to the first reaction zone 30 may be seen to be controlled by a first temperature controller 340, which accepts a set point 344 and a temperature input 342, and generates an output 346 to first heat exchanger 72A. As previously discussed, the maximum desired temperature in the reaction zone may depend on the thermal decomposition temperature(s) of the sulfates of manganese or nitrates of manganese, depending on whether NO_X and/or SO_X are being removed. Lower temperature set points will be above the dew point of the system and adjusted automatically or manually as needed. In one embodiment, the temperature to be controlled is measured at the reaction zone itself, rather than at the outlet from the heat exchanger, in order to more directly measure the temperature in the reaction zone. In one embodiment, temperature controller 340 output 346 may be a variable analog signal or other variable signals used to control a variable speed blower to control the outlet temperature from heat exchanger 72A. Temperature controller 340 may increase/decrease the cooling air passing through heat exchanger 72A when the temperature in first reaction zone 30 is greater/less than set point 344.

A second temperature controller 350 may be seen to accept a temperature input 352 from second reaction zone 38 and a set point 354, and to generate an output 356 for heat exchanger 72B. Second temperature controller 350 may be similar to first temperature controller 340. In one embodiment, heat exchanger 72B is used to cool the incoming gas, using ambient air as the cooling medium. As discussed previously with respect to temperature controller 340, second temperature controller 350 may increase/decrease the

output to a variable speed drive coupled to a blower when the temperature of second reaction zone 38 is greater/less than set point 354.

Figure 15 also illustrates how a first feeder 20A may feed material to first reaction zone 30. A second feeder 20B may be used to feed sorbent material to second reaction zone 38. First feeder 20A and second feeder 20B may be controlled as previously described with respect to feeder 20 in Figure 14.

Referring now to Figure 16, a control and data acquisition system 400 for controlling and monitoring the previously described processes is illustrated. System 400 may be seen to include generally a programmable logic controller (PLC) 402 and a local on-site computer 440. Both PLC 402 and local computer 440 may be coupled to the World Wide Web 424. PLC 402 and local computer 440 may be accessed over World Wide Web 424 by a user PC 428, a hand-held computer such as a Palm Pilot 430, and other devices 426 which can access World Wide Web 424.

PLC 402 may be seen to include a PLC rack 403. In one example, PLC 402 is an Allen Bradley PLC. In one example, the Allen Bradley PLC is a PLC 5. PLC rack 403 may be seen to include a PLC processor module 408, and Ethernet module 410, and a DC power supply 412. PLC 402 may be seen to include an output bus 406, for example a Control net bus 406. Bus 406, in the present example, may be seen to be coupled to numerous input/output cards 404. Input/output cards 404 may be seen to include a discrete I/O cards 404A, mixed discrete and analog I/O cards 404B, discrete I/O cards 404C, discrete and analog I/O cards 404D, more discrete and analog cards I/O 404E, a variable frequency drive card 404F, and a second variable frequency drive card 404G. The discrete I/O may be commonly used to accept inputs from discrete switches such as limit switches, and the output used to open and shut valves and to start and stop motors. The analog I/O may be used to accept input analog measurements from sensors and to control variable position output devices. The variable frequency drive outputs may be used to control variable speed motors, for example, variable speed motors used to control airflow pass the heat exchangers.

PLC 402 may be seen to be coupled to an Ethernet hub 420 via an Ethernet cable 418. In one embodiment, a DSL modem 422 enables Ethernet hub 420 to be accessed from World Wide Web 424. Local computer 440 may also be seen to be coupled to Ethernet hub 420 via an Ethernet cable 444. Ethernet cable 444 can be coupled to an Ethernet card 446. Similarly, local computer phone line 442 may be coupled to a PC modem card 450. The PC modem card can provide access to World Wide Web 424 when a DSL modem line is not available or

is not functioning. Local computer 440 may be seen to include software 448 which can include, for example, Microsoft Windows 2000 as an operating system that is providing both server and terminal functionality. Software component 448 can include an Allen Bradley OLE Process Control (OPC) module 452, as well as an Intellution ® OPC server component 454. The IFIX process monitoring and control package by Intellution is used in one embodiment. An Intellution process database component 456 may also be included. Allen Bradley OPC server 452 can provide communication between local on-site computer and Allen Bradley PLC 402.

Intellution OPC server 454 can provide communication between the Allen Bradley inputs and outputs and the Intellution process monitoring and control system residing within local computer 440. Intellution process database 456 may be used to monitor and control the entire process. Intellution Work Space 458 may be used to allow access to monitor, display, and change current data, and a historical data area 460 may be used to trend historical process data. An Access/Oracle RDB component 462 may also be included to provide database reporting. In one embodiment, a report module, for example, a Microsoft Excel or Crystal report component 464 may also be provided. In some embodiments, an Intellution web server component 466 is provided, as is a Microsoft Internet Information Server (IIS) module 468. In some embodiments, local on-site computer 440 has a local terminal or CRT as well to display, monitor, and change data residing in the Intellution Work Space 458.

In some embodiments, most or all of the controls discussed below in the present application are implemented within control system 400. In one embodiment, most or all controls are implemented within Allen Bradley PLC 402. For example, PID control blocks can be implemented using provided Allen Bradley PID blocks, or the blocks can be created from primitive mathematical operations using ladder logic. Control blocks such as the table blocks and selector blocks of Figures 24 and 25 may be implemented within Allen Bradley PLC 402 using standard blocks. Local on-site computer 440 may be used to store and output values such as PID set points and selector switch values from local computer 440 to registers or control blocks within PLC 402. For example, the set points to heat exchanger, differential pressure, and feed rate control blocks may reside within local computer 440 and be downloaded to PLC 402. The set points may be obtained by local computer 440 from a local terminal and/or from World Wide Web 424 from devices 426, 428, and/or 430, protected by appropriate security. Local computer 440 can be used to provide historical trending, operator interface, alarming, and reporting.

Referring now to Figure 17, a process graphic 450, as displayed on a human-machine interface is displayed. Process graphic 450 may be displayed, for example, on an Intellution IFIX system. Process graphic 450 can be updated in real time and can reside on a personal computer, for example. Process graphic 450 includes a manual switch 458 and an automatic switch 459 for controlling the control mode of the differential pressure across the bag house. Process graphic 450 also includes a table of values 460 including the differential pressure set point, the actual differential pressure and the inlet temperature to the bag house. An output table 462 is also illustrated, including the bag house outlet temperature, the flue gas flow rate, the inlet pressure to the bag house and the outlet pressure from the bag house. A bag house 452 is shown diagrammatically including an inlet 454 and an outlet 456. An outlet emission table 464 is also illustrated, including the SO_2, the NO_X level, and the O_2 level. Process graphic 450 may be used to monitor and control the bag house differential pressure, as previously discussed.

Referring now to Figure 18, a process graphic 470 is illustrated as may be displayed on an Intellution IFIX process graphic. Process graphic 470 can monitor and control the absorbent feeder speed, including an increase button 471 and a decrease button 472. The actual feeder speed in pounds of sorbent per hour is illustrated at feeder speed 483. A scrubber inlet table 473 is illustrated, including a SO_2 level, a NO level, a NO_2 level, a NO_X level, a CO level, and an O_2 level. A scrubber outlet table 474 includes the same levels as the inlet, but at the scrubber outlet. A NO_X control section 475 on the process graphic includes a manual button 476 and an auto button 477, as well as a set point 478. In automatic mode, set point 478 may be used to control the feeder speed using the NO_X set point. Similarly, an SO_2 control section 479 includes a manual control button 480 and an auto control button 481, as well as a set point 482. In automatic mode, set point 479 may be used to control the feeder speed using the SO_2 set point.

Referring now to Figure 19, a process graphic 490 is illustrated, as may be found on a process control and monitoring station. A cooler 491 is illustrated, having an inlet 492 and an outlet 493, with the inlet and outlet temperatures being displayed in real time. Cooler 491 may be a heat exchanger as previously discussed. Process graphic 490 includes a manual button 494 and an auto button 495. The bag house inlet temperature is displayed at 498 as is the cooler set point 497. When in the automatic mode, the fan speed may be controlled by a PID controller using set point 497. Process graphic 490 also includes an outlet emission table 496, including the SO_2 level, the NO_X level, and the O_2 level.

Referring now to Figure 20, differential pressure control loop 300 is illustrated in block diagram form. Differential pressure controller 302 may be seen to accept set point 312 and actual differential pressure 310, and to generate output signal 314 to control the differential pressure across bag house 30. As previously discussed, differential pressure set point 312 may be set taking into account the desired pollutant removal target of the system, the power required to force gas through the filters, and the desired rate of sorbent replenishment.

Referring now to Figure 21, sorbent feeder control loop 320 is illustrated in block diagram form. As previously discussed, feeder control loop 320 can include a reaction zone CEM unit 80B that generates an output signal from the NO_X and/or SO_X emission analyzers. Emissions/Feeder controller 322 can accept the NO_X or SO_X measured emission level through controller input 328, and accepts a set point 326 indicating the desired NO_X and/or SO_X concentration. Controller 322 may also send a controller output 332 to sorbent feeder 20. As previously discussed, sorbent feeder 20 may be a variable speed screw feeder, accepting a variable analog drive signal among others as its input from feeder controller 322. The process trade-offs in setting set point 326 are as previously described.

Figure 22 illustrates a control loop 341 for controlling the temperature of bag house 82. Temperature controller 340 is as previously described with respect to Figure 15. Temperature controller 340 accepts a bag house temperature input 342 and desired bag house input temperature set point 344, generating controller output 346 which can be fed as a fan speed control to heat exchanger 72A. The control scheme rationale is as previously described with respect to Figure 15.

Referring now to Figure 23, a variable venturi control loop 361 is illustrated. Figure 23 illustrates a venturi position controller 360, which accepts a venturi position set point 362 and an actual venturi position input 364, generating a controller output 366 which can be accepted by a variable venturi positioner at 368. The actual position of the variable venturi position may be measured by a position detector 367. In one embodiment, the variable venturi position may be measured in units of 0 to 100%. Venturi set point 362 may be set as a function of one of several desired process parameters.

The variable venturi position may be set to control the space between the variable venturi 160 and interior surface 154, the cross-sectional flow area, available for the bag house inlet gas to flow around the flow occluding devise, variable venturi 160, thereby controlling the fluidization velocity of the gas. When the flow cross-sectional area is decreased, the gas

flow velocity increases, which can be used to support a deeper fluidized bed depth of sorbent material. If the gas flow velocity is made very high, only the densest sorbent particles will be able to descend against the swiftly rising gas and be collected from the system. If the fluid velocity is set very low, even the lightest particles will be able to settle out of the system quickly, thereby increasing the need for regeneration or recycling of material back to the reaction zone for more loading. A higher gas flow velocity will, in effect, create a fluidized bed reactor, having a fluidized bed of sorbent material held in place by the upwardly rising gas stream. A rapidly moving gas stream will also carry more sorbent particles to the fabric bags 88 filter to form a filter cake. Conversely, a slowly moving gas flow around the variable venturi 160 will allow many sorbent particles to fall and be collected prior to becoming caked upon the bags 88. A deeper fluidized bed will create higher differential pressures and a shallow fluidized bed will create lower differential pressures. Removal efficiencies may be taken into consideration when setting SO_X and/or NO_X fluidized bed depth. Variable venturi controller 360 may be any suitable controller, including a PID controller, utilizing any combination of its modes.

Referring now to Figure 24, a control scheme 370 is illustrated for controlling sorbent feeder 20 using one set of inputs selected from the group including NO_X concentration, SO_X concentration, and reactor zone differential pressure. The control of sorbent feeder 20 may be accomplished by selecting one of the aforementioned control inputs, where the selection may be based on the greatest deviation from set point or error.

An error generator 373 may be seen to accept several actual measurement signals 384, as well as several set points 385. The actual signals and set points may be used to generate corresponding errors, for example, using subtraction. Error generator 373 may be seen in this example to output a NO_X error 373A, a SO_X error 373B, and a differential pressure error 373C. The outputs from error generator 373 may be accepted by an error selector gate 374, with one of the input errors selected and output as the error to a controller error input 382. Error selector gate 374 may be operated manually to accept one of the several input errors in some embodiments. In other embodiments, error selector gate 374 may automatically select the largest error or deviation, to control based on the process variable or parameter most requiring attention. For example, sorbent feeder 20 may be controlled based upon the NO_X concentration, the SO_X concentration, or the differential pressure across the reaction zone.

Error selector gate 374 may select the highest deviation, or the highest percent of deviation, of these three error inputs. Error selector gate 374 can generate a selector output

386 which can be used to select which of the inputs a gain selector 372 is to select. Similarly, error selector gate 374 may output a selector output 383 which can be accepted by a set point selector gate 376 to select from various set points provided to the selector gate.

A gain table 371 may be implemented as a table in a fixed database, for example, a series of registers in a PLC. Gain table 371 may be seen to include a NO_X gain 371A, a SO_X gain 371B, and a differential pressure gain 371C. The gains from gain table 371 may be seen to feed gain selector block 372. A gain selector output 377 may be sent to a controller gain input 379.

A set point table 375 may be seen to include a NO_X set point 375A, a SO_X set point 375B, and a differential pressure set point 375C. The set points may be used as inputs to selector gate 376, with selector output 383 being used to select one of the input set points. Selector gate 376 may be seen to output one of the selected set points to controller set point input 380.

Control scheme 370 thus provides a system and method for controlling the sorbent feeder rate based upon any one of the NO_X concentrations, the SO_X concentration or the differential pressure across the reaction zone. This can be accomplished using the selector blocks previously discussed while only requiring a single controller. Controller 378 can be, for example, a PID controller, using any combination of its individual modes.

Referring now to Figure 25, a control scheme 390 is illustrated, similar in some respects to control scheme 370 of Figure 24. Control scheme 390 includes similar control blocks, tables, and outputs as previously described in Figure 24. Control scheme 390 further includes the variable venturi control as one of the possible sets of inputs, gains, and set points to be used to control sorbent feeder 20. Gain table 371 may be seen to include a variable venturi gain 371D. Error generator 373 may be seen to generate a variable venturi error 373D. Set point table 375 may be seen to include a variable venturi set point 375D. Control scheme 390 may thus operate in a manner similar to control scheme 370 of Figure 24, but allowing for control based on the venturi position.

Various components of the system of the invention have been discussed above. Many of the components of the system are commercially available from various original equipment manufacturers and are known to those of ordinary skill in the art. Further, one skilled in the art will recognize and understand that the reaction zones and other units of the system of the invention may be connected by pipes, ducts, and lines , etc. which allow gas and/or sorbent to flow through and within the system and that reaction zones are in flow through

communication in dual and multi stage embodiments of the invention. In addition to the aforementioned system components, the system may further include various hoppers, conveyors, separators, recirculation equipment, horizontal and vertical conveyors, eductors. Further, there may be modulating diverter valves, vibrators associated with feeders, compressors to provide instrument air to pulse filter fabric bags, as well as various meters and sampling ports.

In addition to removing SO_X and NO_X, the system and processes of the invention can be utilized to remove mercury (Hg) and fly ash. Gases emanating from combustion of fuels, which contain mercury and sulfides, include mercury compounds, mercury vapor, ash, SO_X and NO_X. These gases and solids are commingled with oxides of manganese and are transported at a sufficient velocity as a gas-solids mixture to a reactor, which may be a bag house or other reactor/separating device. During transport and during residence in the reactor, oxidation-reduction reactions occur. These reactions cause the conversion of mercury vapor to mercury compound(s), and sorbent and/or alumina adsorb the mercury compound(s). As disclosed above, SO_X and NO_X are removed through reaction with oxides of manganese to form sulfate and nitrate compounds of manganese. These reaction products, unreacted sorbent (if any) alumina, adsorbed mercury, and ash are trapped and collected in the bag house and clean, substantially stripped gases are vented to the stack. Thus, during the processing of gases with the system of the invention, mercury and mercury compounds may also be removed. The reacted and unreacted sorbent when removed from the reaction zones of the system may be further processed to generate useful products and to regenerate the sorbent as described herein below.

The system of the invention in its various embodiments may be utilized in a process for removal of oxides of sulfur and/or oxides of nitrogen, mercury (compounds and vapor), and other pollutants from a gas stream. The processes generally involve providing a system according to the invention, whether single stage, dual-stage, or multi-stage. Gas and sorbent are introduced into a reaction zone and contacted for a time sufficient to effect capture of the targeted pollutant(s) thereby substantially stripping the gas of the targeted pollutant(s). In a single-stage removal process, the reaction zone would need to be a solid-gas separator operating as a reaction zone or else followed by a solid-gas separator in order to render the gas that has been substantially stripped of a target pollutant free of solids so that the gas may either be vented or directed for further processing. In a dual-stage removal process, the second reaction would preferably be a solid-gas separator operating as a reaction zone. And,

in a multi-stage removal process the last reaction zone in the series of reaction zones through which the process gas is directed would need to be a solid-gas separator operating as a reaction zone or else followed by a solid-gas separator in order to render the gas that has been substantially stripped of a target pollutant free of solids so that the gas may either be vented or directed for further processing. Generally, configuring the systems and processes of the invention to incorporate a solid-gas separator as the last reaction zone in a sequence of removal steps would be most economical and efficient.

A process according to the invention is described below using single-stage and dual-stage systems of the invention for purposes of illustration. It should be readily understood by those skilled in the art that the processes as described can be adapted to multi-stage removals and to removal of various targeted pollutants with or without the addition of other sorbent materials or chemical additives, as appropriate.

Removal of SO_X and/or NO_X can be accomplished in a single single-stage removal system. Sorbent and gas containing SO_X and/or NO_X are introduced into a reaction zone 30 where the gas and sorbent are contacted for a time sufficient to substantially strip the gas of SO_X and/or NO_X. If SO_X is the primary target pollutant, the gas may be introduced at temperatures typically ranging from about ambient temperature to below the thermal decomposition temperature(s) of sulfates of manganese. If NO_X is the primary target pollutant, the gas would be introduced at temperatures typically ranging from about ambient temperature to below the thermal decomposition temperature(s) of nitrates of manganese. If both pollutants are present, NO_X will not be captured if the temperature of the gas is above the thermal decomposition temperature of nitrates of manganese. In the reaction zone, the gas would be contacted with the sorbent for a time sufficient to effect capture of the pollutant at a targeted capture rate. If both pollutants are to be captured, the capture rate for the primary targeted pollutant would control or utilize a control sub-element, such as control loop 320 of Figure 14 or control loop 390 of Figure 25. The capture rate for the targeted pollutants can be monitored and adjusted. The reaction zone would preferably be a solid-gas separator that renders the gas free of solids, such as reacted and unreacted sorbent and any other particulate matter in the gas so that the gas may be vented from the reaction zone or directed for further processing, after contacting the gas with sorbent for a sufficient time.

In a dual-stage removal process, a system of the invention having at least two reaction zones, first and second reaction zone 30, 38 as in Figure 1, is provided. It should be understood that the system could be a system of the invention such as the modular reaction

units illustrated in Figures 2 and 3. With reference to Figure 2, any of the bag houses 62, 64, 66 could serve as first and second reaction zones 30, 38 depending upon how the gas is directed through the system. Further, with reference to Figure 3, the first bag house 70 would correspond to first reaction zone 30 and either or both of the second and third bag houses 76, 78 would correspond to second reaction zone 38. Additionally, it is understood that other reaction zones may be substituted for the bag houses of Figures 2 and 3 and the process as described could be carried out.

However, for purposes of illustration, the dual-stage removal process is discussed with reference to Figure 1. In this process of the invention, gas and sorbent are introduced into first reaction zone 30 . The gas is contacted with the sorbent for sufficient time to primarily effect SO_X capture at a targeted capture rate. The gas is rendered free of solids and then vented from the first reaction zone 30. Sorbent and the gas that has been substantially stripped of SO_X are then introduced into second reaction zone 38. In the second reaction zone, the gas is contacted with the sorbent for a sufficient time to primarily effect NO_X capture at a targeted capture rate. The gas is rendered free of solids and then vented from the second reaction zone 38. The vented gas may be directed to stack 40 to be vented or emitted into the atmosphere or directed on for further processing.

With the processes of the invention, other pollutants that can be captured with oxides of manganese can be removed. For example, without being limited or bound by theory, Applicants believe that mercury compounds adsorb onto oxides of manganese. Applicants further believe that, in the system and processes of the invention, elemental mercury is oxidized to form oxides of mercury which also adsorb onto oxides of manganese. Additionally, hydrogen sulfide (H_2S) and other totally reduced sulfides (TRS) can be removed utilizing oxides of manganese. More specifically, Applicants postulate that the sulfur in TRS may be oxidized to form SO_2 which is known to react with oxides of manganese to form sulfates of manganese. Further still, Applicants believe that CO is oxidized to CO_2 which in turn reacts with the sorbent to form carbonated of manganese ($MnCO_3$) from which useful products can be recovered and oxides of manganese regenerated.

It is known that mercury compounds may be removed from gases by adsorption on fly ash and/or alumina. Thus, alumina may be introduced with the sorbent in a reaction zone for purposes of removing mercury compounds and elemental mercury that has be oxidized to form oxides of mercury. Thus, elemental mercury that is not oxidized and therefore not captured by the sorbent in a first or second reaction zone may be captured in a third reaction

zone, which may be referred to as a mercury-alumina reactor or an alumina reactor. With respect to single-stage removal, the mercury compounds may be removed in a reaction zone by contacting the gas with sorbent for a time sufficient for the mercury compounds to adsorb on to the sorbent, and alumina if mixed with the sorbent to thereby substantially strip the gas of mercury. Further, if the reaction zone is a solid-gas separator, mercury compounds adsorbed to fly ash would also be removed, thereby substantially stripping the gas of mercury compounds. In a dual-stage, the mercury compounds would similarly be removed, but depending upon which reaction zone is also a solid gas separator.

Thus, the system and process of the invention are readily understood to include and contemplate the removal of not only SO_X and/or NO_X but other pollutants, such as mercury compounds, elemental mercury, CO, CO_2, TRS, and H_2S.

The system and process of the invention has been tested at several power plants utilizing a SO_X and/or NO_X removal demonstration unit embodying a system according to the invention. The demonstration unit utilized a bag house as the second reaction zone and a pipe/duct as a first reaction zone in a dual stage removal system. The test runs and results are summarized in the following examples.

Example 1

NO_X concentrations were determined using EPA method 7E, chemiluminesent analysis method, and analyzed with a model 42H chemiluminescent instrument manufactured by Thermo Electron Inc. Sulfur dioxide (SO_2) concentrations were measured utilizing, a spectrophotometric analysis method employing a Bovar Western Research Spectrophotometric model 921NMP instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C. Gas flow rates in standard cubic feet per minute (scfm) were measured using AGA method #3, utilizing a standard orifice plate meter run. The demonstration was conducted utilizing a series of test runs on live gas streams from a power plant. Said power plant operates steam boilers which are fired on high sulfur coal. During test runs, NO_X and SO_2 concentration readings were taken continuously alternating from the inlet and the outlet of the demonstration unit. Gas flow rates were measured continuously. The demonstration tests were performed utilizing two different forms of sorbent. The tests conducted utilized various forms of oxides of manganese as sorbent. The tests were performed with and without bag house filter pulsing. The following table summarizes the results and operational parameters:

Range of Operation Parameters	
Range of NO_X Concentrations Processed by the Demonstration Unit	14.14 to 320 ppm
Range of SO_2 Concentrations Processed by the Demonstration Unit	300 to 1800 ppm
Range of Gas Flow through the Demonstration Unit	250 to 2000 scfm
Range of Pressure Across the Bag House	0.5" to 10.0" of H_20
Range of Bag House Temperatures	60° F to 246° F
Maximum NO_X steady state Removal Rate	96.0%
Maximum SO_2 steady state Removal Rate	99.8%

Example 2

A test using the demonstration unit according to the invention, utilizing oxides of manganese as the sorbent was conducted on a simulated gas stream containing varying levels of NO_X. Oxides of manganese powders that were used during this test described generally by 60% of particles less than 45 microns in size and having a BET surface area of approximately 30 m^2/g. Knowing that there is a competition for reaction sites between SO_2 and NO_X, a series of tests was conducted to gather data on the efficiency of NO_X capture in the absence of SO_2. Synthetic NO_X gas was made on site by use of high-concentration bottle gas which was diluted into the inlet gas stream and processed by the demonstration unit. The bag house was pre-loaded with oxides of manganese prior to introduction of test gas by operating the demonstration unit's blower at high speed (typically about 1200 scfm), and feeding the oxides of manganese into the gas stream at a high rate (between 40% and 90% of feeder capacity) in order to form a suitable filter cake on the fabric bags in the bag house. Gas from cylinders containing NO_X, 20% NO, and 20% NO_2, (20,000 ppm) was metered into the bag house inlet through a rotameter-type flow gage. NO_X concentrations were measured at the bag house inlet and outlet on an alternating basis throughout the testing with the demonstration unit's continuous emissions monitoring system (CEMS), utilizing a Thermo Electron model 42H Chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C.

Tests were performed at varying levels of bag house differential pressure (measured in inches of water column) and flow rates (measured in scfm). The NO_X inlet concentrations ranged from 18.3–376.5 ppm with flow rates ranging from 260-1000. It has been determined that varying levels of filter cake thickness affect the NO_X and SO_2 removal. A thicker filter cake increases the quantity of sorbent exposed to the gas, thus increasing the micro-reaction zone within the filter cake. As a representation of the sorbent filter cake depth, the differential pressure across the bag house (referred to as ΔP) was measured between 2.00"-9.67" of WC (expressed in inches of water column). NO_X concentrations were recorded once the system was in steady state and the readings were stable for up to 20 minutes. The following table illustrates the level of NO_X removal achieved as a function of inlet concentration, gas flow rate, and bag house differential pressure:

Summary of Bottle Gas NO_X Reduction Test

Run No.	Inlet NO_X (ppm)	Outlet NO_X (ppm)	% Reduction	ΔP (in. H_2O)	Flow Rate (scfm)
1	25.5	3.3	87.1	2.00	260
2	140.1	8.5	94.0	3.86	500
3	102.0	10.5	89.7	7.71	1000
4	324.9	17.4	94.7	7.78	1000
5	195.0	15.1	92.3	7.85	1000
6	46.7	8.4	81.9	7.85	1000
7	200.3	32.5	83.8	3.0 to 4.0	1000
8	28.2	6.2	78.0	7.80	500
9	57.8	11.4	80.3	2.10	500
10	84.9	8.9	89.5	3.80	500
11	86.0	8.9	89.7	3.80	500
12	194.5	11.5	94.1	3.80	500
13	317.5	12.7	96.0	3.80	500
14	376.5	26.7	92.9	2.10	500
15	376.5	26.7	92.9	2.10	500
16	18.3	4.0	78.1	4.45	509
17	83.5	8.7	89.6	4.45	509
18	40.1	5.9	85.3	4.45	509
19	83.5	8.7	89.6	4.45	509
20	21.5	4.5	79.2	4.74	500
21	45.7	6.5	85.8	4.75	500
22	92.1	8.6	90.7	4.75	500
23	201.1	11.5	94.3	4.76	500
24	317.5	14.0	95.6	4.79	500
25	52.1	10.0	80.9	9.67	1000
26	82.4	12.0	85.5	9.67	1000
27	105.4	13.2	87.5	9.65	1000
28	224.0	18.5	91.8	9.67	1000
29	328.4	23.1	93.0	9.67	1000
30	100.2	15.0	85.0	9.67	1000

Example 3

A further test of the demonstration unit according to the invention utilizing oxides of manganese as the sorbent, was conducted on a live exhaust gas slipstream from a 170 MW coal fired boiler. The boiler was operating on high sulfur coal of approximately 4-6% sulfur, resulting in emission concentrations of SO_2 in the range of 1200-2000 ppm and NO_X

concentrations in the range of 280-320 ppm. A slipstream averaging 1000 scfm was diverted from the main stack exhaust and routed to the demonstration unit for reaction and sorption by the sorbent oxides of manganese. SO_2 and NO_X concentrations were measured at the scrubber inlet and outlet of the bag house on an alternating basis throughout the testing with the demonstration unit's continuous emissions monitoring system (CEMS). SO_2 concentrations were measured utilizing a Bovar Western Research model 921NMP spectrophotometric analyzer and NO_X concentrations were measured utilizing a Thermo Electron model 42H chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C.

SO_2 removal efficiencies of 99.8% and NO_X removal efficiencies of 75.3% were achieved while processing on average 1000 scfm of exhaust gas at temperatures typically ranging from 150° F to 250° F. Test runs were conducted with varying levels of bag house differential pressures ranging from 0.5" to 8.6" of WC, which represents various levels of filter cake thickness. Tests were also conducted with different rates of bag house filter bag pulsing and varying levels of oxides of manganese feed rates. Oxides of manganese powders that were used during this test described generally by 60% of particles less than 45 microns in size and having a BET surface area of approximately 30 m^2/g. The following table gives an example of SO_2 and NO_X data collected during a test in which 1000 scfm was processed by the dry scrubber at an inlet temperature of 250 °F, and a differential pressure of 5.75" of WC. Data was collected once the demonstration unit was in a steady state of NO_X and SO_2 removal for a period of 30 minutes. The results are summarized in the below table:

Pollutant	Inlet ppm	Outlet ppm	ppm % Removal
Oxides of Nitrogen (NO_X)	285.9	70.5	75.3%
Sulfur Dioxide (SO_2)	1703	3.9	99.8%

Example 4

An additional series of demonstration tests of the demonstration unit, utilizing oxides of manganese as the sorbent, was conducted on a live exhaust gas slipstream from a 75 MW coal fired boiler. This boiler was operating on Powder River Basin (PRB) coal, resulting in emission concentrations of SO_2 in the range of 340-500 ppm with NO_X concentrations in the range of 250-330 ppm. A slipstream ranging from 500-1000 scfm was diverted from the main stack exhaust and routed to the demonstration unit for reaction and sorption by the

oxides of manganese. Oxides of manganese powder that were used during this test described generally by 60% of particles less than 45 microns in size and having a BET surface area of approximately 30 m^2/g. SO_2 and NO_X concentrations were measured at the bag house inlet and outlet on an alternating basis throughout the test with the demonstration unit's continuous emissions monitoring system (CEMS). SO_2 concentrations were measured utilizing a Bovar Western Research model 921NMP spectrophotometric instrument and NO_X concentrations were measured utilizing a Thermo Electron model 42H chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C.

SO_2 and NO_X reduction efficiencies were measured at 99.9% and 91.6% respectively. Testing was conducted with varying degrees of differential pressure (ΔP) across the bag house to affect the residence time of the targeted pollutants. Reaction chamber temperatures ranged from 150° F to 280° F. It was determined that longer residence times resulted in improved capture rates for NO_X. However, the fact that the SO_2 reaction occurs so rapidly and completely, the SO_2 reduction efficiency remains nearly complete (99.9%) at even the lowest of residence times. While operating the scrubber at 0.5"-1.0" of WC across the bag house, a pollutant concentration reduction efficiency of 99.8% for SO_2 and 40.0% for NO_X was achieved. It is from these results that the concept for a two stage reaction chamber system develops, whereby the first reaction chamber captures the majority of SO_2 and a small fraction of NO_X, while the second "polishing" stage completes the NO_X removal to desired levels of efficiency, predetermined and controlled by the system operator. Data was collected once the dry scrubber was in a steady state of NO_X and SO_2 removal for a period of 30 minutes. The following table gives an example of SO_2 and NO_X data collected during a testing in which 500 scfm was processed by the demonstration unit at an inlet temperature of 250 °F, and a differential pressure of 8.7" of WC:

Pollutant	Inlet ppm	Outlet ppm	ppm % Removal
Oxides of Nitrogen (NO_X)	268.1	22.4	91.6%
Sulfur Dioxide (SO_2)	434.3	0.5	99.9%

Example 5

In an attempt to determine the effectiveness of SO_2 and NO_X removal, a series of lab-scale tests were conducted utilizing a glass reactor. The reactor was designed to mimic the gas-solid interactions known to be present in the aforementioned demonstration unit. The

glass reactor had a diameter of 2 inches with a length of approximately 24 inches. 50.0 grams of oxides of manganese were suspended in the reactor using a fritted glass filter allowing for flow of the gas stream, while keeping the oxides of manganese suspended. Approximately 3 inches above the fluidized bed of oxides of manganese, a sintered stainless steel filter was arranged to simulate a bag house filter bag. The reactor was heated during the testing to 250°F.and the gas flow rate was metered at a constant 6 liters per minute (lpm). Simulated exhaust gas was produced by use of a calibration gas standard having the following composition: CO_2= 17.35%, NO_X=391 ppm, SO_2=407 ppm, CO=395 ppm, and balance N_2 . The simulated flue gas stream passed through the fluidized bed of oxides of manganese, where the flow carried a portion of the sorbent up onto the filter, thus creating a filter cake, which mimics a bag house reactor chamber.

SO_2 and NO_X concentrations were measured continuously from the reactor outlet utilizing a continuous emissions monitoring system (CEMS). SO_2 concentrations were measured utilizing a Bovar Western Research model 921NMP spectrophotometric instrument and NO_X concentrations were measured utilizing a Thermo Electron model 42H chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C. Removal efficiencies of 99.9% for SO_2 as well as 99.9% for NO_X were measured and duplicated for several test runs. Inlet temperature was 250° F, with a differential pressure of 2.00" of WC. The following table gives an example of SO_2 and NO_X data collected during testing in which 6 lpm of gas was processed by a glass reactor:

Pollutant	Inlet (ppm)	Outlet (ppm)	Sorbent Weight (g)	% Removal	Flow rate (lpm)	ΔP (in H_2O)	Temp. (° F)	Time with >94% Removal
Oxides of Manganese Type A								
NO_X	391	17.21	50	95.6%	6	2.00	250	29 min
SO_2	407	0.1	50	99.9%	6	2.00	250	>54 min
Oxides of Manganese Type B								
NO_X	391	0.1	50	99.9%	6	2.00	250	60 min
SO_2	407	0.1	50	99.9%	6	2.00	250	>90
Oxides on Manganese Type C								
NO_X	391	0.2	50	99.9%	6	2.00	250	34 min
SO_2	407	0.1	50	99.9%	6	2.00	250	>68 min

The tests of this Example 5 were conducted with three different lots of manganese oxide sorbent. Figures 29 and 30 are, respectively, graphs plotting NO_X and SO_X concentrations at the outlet of the glass reactor versus time. The three different oxides of manganese are represented by the symbols "◇" for type A sorbent, "△" for type B sorbent, and "□" for type C sorbent in Figure 29 and 30. Type A sorbent is an oxide of manganese powder generally at 60% of particles less than 45 microns in size and having a BET surface area of approximately 30 m^2/g. Type B sorbent is an oxide of manganese powder generally at 100% of particles less than 45 microns in size and having a BET surface area of approximately 200 m^2/g. Type C sorbent is an oxide of manganese powder generally at 80% of particles less than 45 microns in size and having a BET surface area of approximately 90 m^2/g. The graph of Figure 30, confirms the above statements regarding near immediate and complete SO_X capture upon contact with the sorbent. The graph of Figure 29 shows a range of capture efficiency over time for NO_X and that different forms of oxide manganese may be able to provide more efficient capture of NO_X. The type B sorbent performed the best before break-through, followed by type C. Useful captures were observed for all three types. With the process controls of the invention a wide variety of oxides of manganese can be utilized to effect removal at targeted capture rates. Further, the graphs of Figures 29 and 30 show that high removal or capture rates can be achieved and sustained over time. The operational parameters of the systems of the invention can be monitored and adjusted to attain and maintain removal or capture rates at these high levels.

As mentioned above, the reacted or loaded sorbent can be recycled and/or regenerated after being removed from a reaction zone. For recycling purposes the reacted sorbent may simply be reintroduced into another reaction zone. For example with reference to Figure 4, the system has first and second reaction zones 30, 38 which are connected to feeder 20 which contains unreacted or virgin sorbent. Gas from external gas source 15 is introduced into first reaction zone 30 along with sorbent fed from feeder 20. The gas is contacted with sorbent for a time sufficient to remove a target pollutant, such as SO_X, and after being rendered free of solids is vented from the first reaction zone 30. The gas is then introduced in the second reaction zone 38 along with sorbent from feeder 20. In the second reaction zone 38, the gas is contacted with gas for a time sufficient to remove another target pollutant, here NO_X. During operation, the level of NO_X loading on the reacted sorbent in second reaction zone 38 reaches the point where the sorbent no longer efficiently removes NO_X. When the point is reached, the NO_X. reacted sorbent is removed from the second reaction zone 38 and conveyed

or transported to NO_X reacted sorbent feeder 21. The NO_X reacted sorbent, which has unused reactive sites available for further SO_X capture, is fed or introduced into the first reaction zone 30 for additional loading or reaction with SO_X in the gas introduced from external gas source 15. When the recycled NO_X reacted sorbent reaches the point where SO_X capture can no longer be achieved at a targeted rate of removal, the now NO_X and SO_X reacted (or loaded) sorbent is removed from the first reaction zone and routed for regeneration. In this way, the amount of virgin or unreacted sorbent that is utilized in the first reaction zone can be reduced and the additional load or reactive sites available on the NO_X reacted sorbent can be utilized.

During a wet regeneration process the reacted surfaces of the sorbent may be removed and the remaining sorbent may be refreshed. This will be understood with reference to Figure 26. In a wet regeneration, reacted sorbent is removed from a reaction zone, a reaction chamber in Figure 26, and washed in an aqueous dilute acid rinse. Since the interaction between pollutants and the sorbent is believed to be a surface-controlled phenomenon, only a small fraction of the oxides of manganese is reacted with the pollutant. It is this small fraction of the sorbent that can be removed by washing or rinsing which thereby "activates" the sorbent by making unreacted surface area available. The solubility in water of nitrates of manganese is greater than the solubility of sulfates of manganese by at least an order of magnitude in cold water and by at least several orders of magnitude in warm to hot water. This differential in solubility can be advantageously utilized in the regeneration process.

The sulfates and nitrates of manganese on the surface of the sorbent particles dissolve off into solution in the dilute acid bath, leaving clean sorbent that can be readily separated from the rinse or bath by known means, such as settling and decanting, filtering, centrifuging or other suitable techniques. As is further discussed below, the clear filtrate or solution containing dissolved sulfates and/or nitrates of manganese are directed to a regeneration vessel for regeneration of sorbent and production of useful by-products. The clean sorbent is then dried in, for example, a kiln to remove excess moisture. The heat for this drying step may be waste heat generated by combustion which is transferred or exchanged from combustion or process gases at an industrial or utility plant. After drying, the clean sorbent may be pulverized as necessary to reduce the clean sorbent to particle sizes useful in the system of the invention. The cleaned or "activated" sorbent is then conveyed or otherwise transported to the unreacted sorbent feeder(s) and thus, recycled.

Again with reference to Figure 26, the regeneration of sorbent and production of useful by-products can be understood. The solution or filtrate containing the dissolved sulfates and nitrates of manganese is passed from the acidic bath to a regeneration vessel to which alkali hydroxides such as potassium hydroxide (KOH) or sodium hydroxide (NaOH), or ammonium hydroxide (NH_4OH) is added. The addition of these hydroxides, yield respectively, a solution containing nitrates and/or sulfates of potassium, sodium, or ammonium and a precipitate of manganese hydroxide ($Mn(OH)_2$). These solutions can be made into fertilizer products or other products such as explosives. Air or oxygen may be bubbled into or otherwise introduced into the reaction vessel to further the regeneration of the sorbent. The precipitate may be removed with or without the prior introduction of air or oxygen and then dried and heated to form oxides of manganese, MnO_X where X is between about 1.5 to 2.0.

Instead of hydroxide compounds, soluble carbonate compounds, e.g., alkali carbonates, such as potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), or ammonium carbonate ($(NH_4)_2CO_3$) may be added to the solution or filtrate in an regeneration vessel. The addition of carbonates will yield a manganese carbonate precipitate and a solution containing nitrates and/or sulfates of potassium, sodium, or ammonium. The precipitate is separated from the solution, dried and heated to thermally decompose the manganese carbonate to form oxides of manganese and CO_2 gas which may be vented or captured and containerized as a marketable product. The oxides of manganese may be further heated in an oxidizing atmosphere to complete the sorbent regeneration, to form oxides of manganese, MnO_X where X is between about 1.5 to 2.0.The oxides of manganese are separated from the solution, much as the cleaned or reactivated sorbent after the acid wash step, and are then dried and pulverized before being conveyed to a virgin or unreacted sorbent feeder. The filtrate from the separation containing useful sulfates and nitrates that can then be further processed into marketable products.

Oxides of manganese may also be regenerated in a dry or thermal regeneration process, taking advantage of the thermal decomposition temperature(s) of nitrates of manganese. This regeneration process may be understood with reference to Figure 27. The process illustrated and discussed herein is based upon a removal process where NO_X is the target pollutant with nitrates of manganese being formed in the removal step in the reaction zone, a reaction chamber in Figure 27. The NO_X reacted sorbent is removed from the reaction chamber and conveyed to a first kiln. In the first kiln, the reacted sorbent is heated

to a temperature at or above the thermal decomposition temperature(s) of nitrates of manganese and NO_2 desorbs or is otherwise driven off. Oxides of manganese, MnO_X where X ranges from about 1.5 to 2.0 are formed in the first kiln which may be heated with waste process heat from the local plant. The regenerated oxides of manganese from the first kiln may be conveyed to a second kiln heated with waste process heat. Air or oxygen are introduced into the second kiln to more completely oxidize the regenerated sorbent so that the X of MnO_X ranges from about 1.5 to 2.0.

If the sorbent was SO_X-reacted the thermal regeneration would proceed much as described for NO_X, except the first kiln would be heated to a temperature at or above the thermal decomposition temperature of sulfates of manganese and SO_2 would desorb or otherwise driven off. With out being bound by theory, Applicants believe that nitrates of manganese thermally decompose at temperatures between about 130° C to about 260° C, while sulfates of manganese tend to liquefy at the temperatures over which nitrates of manganese thermally decompose. Applicants further believe that sulfates of manganese heated to these temperatures in the presence of a reducing agent, e.g., CO, H_2, etc., will decompose to SO_2 and MnO. Thus, if the sorbent were reacted with both SO_X and NO_X, NO_2 could be driven off first by heating reacted sorbent in a kiln to a first temperature at which nitrates of manganese thermally decompose so that NO_2 can be generated and directed for further processing. A reducing agent could then be introduced and the reacted sorbent further heated to desorb SO_2. Alternatively, the reacted sorbent could be heated to a second temperature, the thermal decomposition temperature of sulfates of manganese with SO_2 being desorbed and directed for further processing. The desorbed SO_2 can be directed to a wet scrubber containing water and an optional oxidant to form sulfuric acid. This acid liquor can then be marketed as is or further processed. This further processing would involve the addition of an ammonium or alkali hydroxide solution to form useful sulfates. In either case, the regenerated sorbent is further heated in an oxidizing atmosphere to more completely oxidize the regenerated sorbent so that the X of MnO_X ranges from about 1.5 to 2.0.Referring back to Figure 27, the desorbed NO_2 can be directed to a wet scrubber containing water and an oxidant to form nitric acid. This acid liquor can then be marketed as is or further processed. This further processing would involve the addition of an ammonium or alkali hydroxide solution to form useful nitrates, such as KOH as illustrated in figure 27.

In addition to regeneration of sorbent and production of useful by-products from the sulfates and nitrates of manganese, elemental mercury can be recovered from NO_X, SO_X

reacted sorbent that further has mercury compounds adsorbed thereon can be processed to generate and recover elemental mercury. The reacted sorbent is removed from a reaction zone of a system according to the invention and conveyed to a first kiln, the reacted sorbent is heated to a first temperature to desorb NO_2 which is routed for further processing into marketable products. The reacted sorbent is then heated a second temperature to desorb elemental mercury which is routed to a condenser for recovery as a marketable product. The sorbent is then rinsed to wash away any ash and to dissolve sulfates of manganese into solution to form a liquor. Any ash in the liquor is separated out and the ash routed for further handling. Alkali or ammonium hydroxide is added to the liquor to form an unreacted sorbent precipitate of oxides of manganese and a liquor containing alkali or ammonium sulfates. The liquor contains rinsed sorbent. The rinsed sorbent and unreacted sorbent precipitate and are separated from the liquor and the liquor is routed for further processing into marketable products or for distribution and/or sale as a useful by-product. The rinsed sorbent and sorbent precipitate are dried to form unreacted sorbent which can then be pulverized to de-agglomerate the unreacted sorbent.

Ion exchange can also be utilized as a mechanism for the separation and recovery of useful sulfate and nitrates. The dissolved sulfates and nitrates of manganese in the filtrate or solution left after washing SO_X and/or NO_X reacted sorbent can be processed in anion exchangers, permitting the recovery manganese cations and separation of the sulfate and nitrate anions. To accomplish this separation, the aqueous solution containing dissolved sulfates and nitrates is passed across or through a bed or column of an anion exchange resin that has an affinity for one of the two anions to remove one of the two anions. The resin with absorb the anion, for instance the sulfate, while permitting the nitrate to pass through the bed or column. Additionally, the solution stripped of sulfate can then be passed across or through a second bed or column of yet a second anion exchange resin to remove the nitrate. After the resin is loaded, the vessel containing the resin can be taken off-line and the resin therein stripped of the captured anion and recovered for reuse.

Suitable anion exchange resins and vessels are known to and readily identified by those skilled in the art. For purposes of illustration, the anion exchange resin has a chloride in the exchange position on the resin. The chloride is eluted while capturing the sulfate and/or nitrate anions. The solution, after passing through the anion exchanger or exchangers in series, will contain manganese chloride from which manganese carbonate or manganese hydroxide is precipitated with the addition of a soluble carbonate or hydroxide compound;

and oxides of manganese can be regenerated from the precipitate as discussed above. The sulfates and/or nitrates loaded on the resin can in turn be eluted with a solution containing chlorides of potassium, sodium or ammonium in order to generate useful sulfates and nitrate by-products for marketing or further processing. The filtrate or solution left over after precipitate formation can be utilized for this purpose.

Liquid mercury can also be recovered from mercury adsorbed to alumina in an alumina reactor. The mercury-reacted alumina from the reactor is heated to drive off or desorb mercury. The mercury vapor is then directed to a condenser where it is condensed to form liquid mercury which is a marketable product.

With the system and processes of the invention, CO and CO_2 in a gas stream can also be captured. Applicants believe that CO in a gas stream is oxidized to form CO_2 when contacted with the sorbent. The CO_2 in turn reacts with oxides of manganese to form $MnCO_3$. Thus, in the processes of the invention, manganese carbonate may be formed either during the capture of CO and CO_2 with the sorbent or during a regeneration step in which soluble carbonate compounds are utilized. Manganese carbonate is insoluble in water. Thus, sorbent that has been utilized to capture CO and CO_2 must be thermally regenerated. Sorbent loaded with manganese carbonate must be removed from the system of the invention and heated to thermally regenerate oxides of manganese, releasing CO_2 which may be compressed and containerized for sale or other marketable purposes. The heating of the loaded sorbent may be carried out in either two stages or in two separate heating units or kilns. In the first stage, the sorbent would be heated to thermally decompose the manganese carbonate, driving off CO_2 after which the sorbent would be further heated to complete the sorbent regeneration. In the second stage, the heating would continue either in the same or a second hearting unit or kiln. The second heating stage preferably would be in an oxidizing atmosphere being carried out with the introduction of air or oxygen in order to complete the regeneration of the sorbent to form oxides of manganese, MnO_X where X is between about 1.5 to 2.0.

The above examples of regeneration processes are provided by way of example and are not intended to limit the processes, both known and unknown, for regeneration of oxides of manganese and for recovery of useful and marketable by-products that may be incorporated into the processes of the invention.

The combustion of fossil fuels (e.g., coal, oil, and natural gas) liberates three major air pollutants: (1) particulates (2) sulfur dioxide (SO_2) and (3) oxides of nitrogen (NO_X). Wet scrubbing, electrostatic precipitators and bag houses can remove particulates such as fly ash. Using mechanical filters or electrostatic precipitators does not remove SO_2, SO_3, NO_2, N_2O_4, NO, or N_2O_3. Prior technologies have used wet scrubbing for the process as a means of sorbing SO_X and NO_X. Water is effective as a scrubbing medium for the removal of SO_2; removal efficiencies can be improved by the addition of chemical absorbents such as calcium, magnesium and sodium. However, nitrogen oxide (NO) is essentially insoluble in water, even with the use of sorbtion chemicals. Residence times required and liquid-to-gas surface areas have proven to be impractical where high gas flow rates are encountered such as boiler flue gas.

Some of the economics involved in the wet scrubbing process involve high-energy consumption; on the average 4-5% of a plant gross power generation is consumed in the process. For example: (1) high differential pressure of a venturi / absorber tower requires 30" of WC or a bag house and scrubber combination requires even higher static pressures. (2) Large volumes of high pressure scrubbing liquor injected through nozzles into the scrubbing apparatus. (3) Slurry tanks requiring continual vigorous agitation. (4) High horsepower required to force water-saturated non-buoyant flue gas up the stack.

Environmental drawbacks of existing systems include large quantities of minerals used as sorbents and the insoluble sulfites or sulfate formed from the scrubbing reaction. The precipitate is then taken to landfills or holding ponds. Some other disadvantages of existing systems are fouling of the internal scrubber components with hard scale, increasing operational labor and maintenance costs. Some complex regenerative systems use large quantities of chemicals required to react with the millions of gallons of slurry used every day.

The dry scrubbing process described in this patent is effective in removing nearly all NO_X and SO_X. Differential pressure requirements through the scrubber should typically not exceed 10 inches of water column and residence times within the sorbent cake are typically less than 1 second. Volumes of sorbent used in this invention in comparison to the wet slurry volumes are miniscule and recharging of reaction zones are done periodically. While stack gases remain dry and hot, some waste heat will be used in the drying of washed and re-generated sorbent. Operational costs of the reaction zone(s) are similar to operating an ash bag house; also capital expenditures are estimated to be reasonable requiring standard off-the-shelf equipment and instrumentation.

As a summary, the equipment is used in the dry scrubbing process is much less complex than the wet scrubber process thus requiring lower operational maintenance costs and a reduced operating staff. Chemical and raw material costs are expected to be similar with less waste effluent produced. The major cost savings will be in the reduced power consumption expected to be significantly less than that of a wet scrubbing system, with fan horsepower reduction making up the majority of the savings.

Although economics favor the use of dry scrubbing processes, removal of target pollutants with the sorbent can be accomplished with wet methods or combinations of wet and dry methods. In the system of the invention, wet scrubbers can serve as reaction zones in the place of or in combination with the reaction zones previously described for dry removal. Wet scrubbers useful in the systems and processes of the invention may be of several types, including but not limited to slurry, sprayer, cascading, and others known to those skilled in the art. Whether the wet scrubber is a slurry, sprayer, cascading or other know type of scrubber, an acidic slurry of oxides of manganese is utilized. The acidity serves to enhance the effective removal of the target pollutants. For SO_X and/or NO_X removal, the pH of the slurry is preferably 2.0 or less and more preferably between about 1.5 and about 1.75

The gas should be introduced into the wet scrubber at a temperature below the boiling point of the solution or slurry to prevent excess evaporation of the sorbent slurry. Since gases processed in the system of the invention typically are at elevated temperatures, the gas may be cooled to below the boiling point utilizing a heat exchangers 72A, 72B preceding the reaction zone as is shown in Figure 5. The gas containing target pollutants is introduced into the wet scrubber and contacted with the slurry for a time sufficient to effect capture of a target pollutant at a target capture rate set point for pollutants such as SO_X and/or NO_X, CO and/or CO_2 or TRS, forming respectively, sulfates and/or nitrates of manganese, manganese carbonate, or sulfates of manganese. While the sorbent itself is not soluble in the slurry, reactions products such as sulfates and nitrates of manganese are and dissolve immediately into solution. Manganese carbonate, being insoluble in aqueous solution, does not dissolve.

With respect to the removal of CO and/or CO_2 to manganese carbonate, when the sorbent is no longer effective for pollutant removal at a target capture rate set point, the reacted sorbent must be separated from the slurry for regeneration of the sorbent and recovery of useful by-products. This is accomplished through the thermal decomposition of the manganese carbonate as previously described.

With respect to the sulfates and/or nitrates of manganese formed in wet removal, the sorbent must be periodically separated from the solution. The sorbent, which is by virtue of being in solution, is essentially clean or "activated" and can be returned to the scrubber in a slurry or added to a slurry requiring additional sorbent. The point at which periodic separation would need to be carried out generally depends upon the capacity of the slurry to retain additional solute in solution, the saturation point of the solution. The frequency at which separation must be carried may be affected through temperature adjustment, since generally a saturated solution can dissolve additional solute at increased temperatures. However, as previously noted, the temperature should not be increased to the boiling point of the solution. Further, simply increasing the volume of the slurry with the addition of acidic aqueous solution can decrease the separation frequency, as long as the wet scrubber has sufficient capacity for the increased volume of the slurry. Further still, the periodic separation can be minimized by bleeding of the aqueous solution containing solute from the scrubber and with simultaneous feeding of additional, fresh aqueous solution into the scrubber to maintain the slurry in an unsaturated state. The solution that has been bled from the wet scrubber can be retained in a holding tank, vessel or other suitable container until a sufficient volume has be accumulated and then processed to regenerate oxides of manganese and to recover useful and marketable by-products.

In a single stage wet removal process a single reaction zone, a wet scrubber, is utilized to remove the target pollutants.. The rate of reaction is related to the solubility of the reaction product of target pollutant and the sorbent. For example the solubility of SO_X is greater than the solubility of NO_X in an aqueous solution; and therefore, a longer residence time is required for NO_X removal than for SO_X removal. The gas once substantially stripped of the target pollutant is vented from the scrubber either to a stack or for further processing. A single wet scrubber can be utilized to remove one or more target pollutants; however, the residence time of the gas in the wet scrubber will be driven by a combination of the solubility of the less soluble of the target pollutants and the target capture rate of that target pollutant. In a single-stage wet removal system the gas is introduced into a reaction zone configured for the introduction of the gas and contacted with the sorbent containing slurry for a time sufficient to effect capture of the target pollutant(s) at the target capture rate set point of the target pollutant(s). The target pollutant is captured by reaction with the sorbent to form reaction products. The reaction products may be soluble in the aqueous solution, as with nitrates and sulfates of manganese. Or they may be insoluble as with carbonates of

manganese formed during the removal of CO and/or CO_2. Wet removal methods can be utilized in either case; but are better suited for removal of target pollutants that form soluble reaction products.

Wet removal can also be accomplished in multiple stages with at least two reaction zones in series of which at least one of the reaction zones is a wet scrubbers. This can be illustrated with reference to dual-stage removal of SO_X and NO_X. In dual-stage removal, first and second reaction zones are provided. With both reactions zones being wet scrubber s, gas is introduced into the first reaction zone which is configured for the introduction of a gas containing target pollutants, in this case SO_X and NO_X. In the first reaction zone, the gas is contacted with a sorbent containing slurry for a time sufficient to effect SO_X capture at a target SO_X capture rate set point. The SO_X is captured by reacting with the sorbent to form sulfates of manganese to substantially strip the gas of SO_X. The gas which is substantially stripped of SO_X is vented from the first reaction zone and passed to a second reaction zone, also a wet scrubber, configured for the introduction of the gas substantially stripped of SO_X. In the second wet scrubber the gas is contacted with the sorbent containing slurry for a time sufficient to effect NO_X capture at a target NO_X capture rate set point. The NO_X is captured by reacting with the sorbent to form nitrates of manganese to substantially strip the gas of NO_X. The gas that has been substantially stripped of SO_X and NO_X is vented from the second reaction zone. It is readily understood by those skilled in the art that more than two wet scrubbers could be utilized in series to effect capture of multiple target pollutants and that the sequence of pollutant removal, in a multi-stage removal process, would be determined by the relative solubilities of the reaction products generated from target pollutants with the sorbent.

Dual stage removal may also be carried out with one of the reaction zones being a wet scrubber and the other reaction zone being selected from the group consisting of a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed, a pipe/duct reactor, a moving bed, a bag house, an inverted bag house, bag house reactor, serpentine reactor, and a cyclone/multiclone. Again using SO_X and NO_X for illustrative purposes, the removal can proceed by first wet SO_X removal and dry NOx removal or by first dry SO_X removal and wet NO_X removal. Regardless of the sequence, wet removal and dry removal would proceed as previously described, with the gas substantially stripped of SO_X being directed from the first reaction zone to the second reaction where NO_X removal would occur. In a wet-dry removal system, the first reaction zone would be a wet scrubber; and in dry-wet removal system the second reaction zone would be a wet scrubber. For the dry removal stage, the dry reaction

zone or scrubber , whether the first or second in sequence, is selected from the aforementioned group.

Where the reaction product of the target pollutant is soluble in aqueous solution, the surface area of the oxide of manganese sorbent is not as critical in a wet removal system, i.e., a scrubber, as opposed to a dry removal system. Further, particle size may not be as critical with a liquid medium as opposed to a gas medium; however, particles must be small enough so that the sorbent remains sufficiently mixed in the slurry. Agitators can be used to keep the sorbent sufficiently mixed in the slurry. Generally, oxides of manganese useful as a sorbent for dry removal methods are similarly useful for wet removal methods.

The systems of the invention including those that incorporate wet scrubbers are adaptable; and process parameters, such as differential pressure, inlet gas temperature, and removal efficiency, are monitored and controlled in wet removal systems of the invention with electronic controls just as in dry removal systems according to the invention.

While exemplary embodiments of this invention and methods of practicing the same have been illustrated and described, it should be understood that various changes, adaptations, and modifications might be made therein without departing from the spirit of the invention and the scope of the appended claims.

CLAIMS

1. An adaptable system for wet removal of target pollutants from gases with minimal differential pressure across the system, comprising:

at least one reaction zone, the reaction zone being a wet scrubber supplied with an acidic aqueous slurry of a sorbent of regenerable oxides of manganese, the reaction zone being configured for introduction of a gas containing at least one target pollutant at a temperature below the boiling point of the slurry and contacted with the sorbent therein for a time sufficient to effect capture of the target pollutant at a targeted capture rate set point for the target pollutant, the gas being substantially stripped of the target pollutant through the formation of a reaction product of the target pollutant and the oxides of manganese, the reaction zone being further configured to allow the gas to be vented from the reaction zone; and wherein differential pressure across the system is regulated so that any differential pressure across the system is no greater than a predetermined level

2. Adaptable system as claimed in Claim 1 wherein the system is comprised of two reaction zones, the two reaction zones being a first reaction zone and a second reaction zone.

3. Adaptable system as claimed in Claim 2 wherein the first and second reactions zones are both wet scrubbers.

4. Adaptable system as claimed in Claim 2 wherein the first reaction zone is a dry scrubber selected from the group consisting of a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed, a pipe/duct reactor, a moving bed, a bag house, an inverted bag house, bag house reactor, serpentine reactor, and a cyclone/multiclone and the second reaction zone is a wet scrubber.

5. Adaptable system as claimed in Claim 2 wherein the first reaction zone is a wet scrubber and the second reaction zone is a dry scrubber selected from the group consisting of a fluidized bed, a pseudo-fluidized bed, a reaction column, a fixed bed, a pipe/duct reactor, a moving bed, a bag house, an inverted bag house, bag house reactor, serpentine reactor, and a cyclone/multiclone.

6. Adaptable system as claimed in Claim 1wherein the target pollutant is SO_X and the reaction product formed is sulfates of manganese or the target pollutant is NO_X and the reaction product formed is nitrates of manganese.

7. Adaptable system as claimed in Claim 2 wherein the target pollutants are SO_X and NO_X and SOx is captured in the first reaction zone with sulfates of manganese being

formed as the reaction product and NO_X is captured in the second reaction zone with nitrates of manganese being formed as the reaction product.

8. Adaptable system as claimed in Claim 4 or claim 5 wherein SO_X is captured in the first reaction zone and NO_X is captured in the second reaction zone.

9. Adaptable system of claim 1 wherein the regenerable oxides of manganese, upon regeneration, are in particle form and are defined by the chemical formula MnO_X, where X is about 1.5 to 2.0 and wherein the oxides of manganese have a particle size of less than about 0.1 to about 500 microns and a BET value ranging from about 1 to about 1000m^2/g.

10. An adaptable system for dry removal of carbon monoxide and/or carbon dioxide from gases with minimal differential pressure across the system, comprising:

A. A feeder containing a supply of sorbent of regenerable oxides of manganese and/or regenerated oxides of manganese; wherein the feeder is configured to handle and feed oxides of manganese which, upon regeneration, are in particle form and are defined by the chemical formula MnO_X, where X is about 1.5 to 2.0 and wherein the oxides of manganese have a particle size of less than about 0.1 to about 500 microns and a BET value ranging from about 1 to about 1000m^2/g;

B. At least one reaction zone configured for introduction of the sorbent and a gas containing carbon monoxide and/or carbon dioxide where the gas is introduced at temperatures typically ranging from ambient temperature to below the thermal decomposition temperature(s) of carbonates of manganese carbonate and contacted with the sorbent for a time sufficient to effect the capture of carbon monoxide and/or carbon dioxide at a targeted capture rate set point, the carbon monoxide and/or carbon dioxide being captured by reacting with the sorbent to formcarbonates of manganese to substantially strip the gas of carbon monoxide and/or carbon dioxide the reaction zone being further configured to render the gas that has been substantially stripped of carbon monoxide and/or carbon dioxide free of reacted and unreacted sorbent so that the gas may be vented from the reaction zone; and wherein differential pressure within the system is regulated so that any differential pressure across the system is no greater than a predetermined level.

11. A process for the removal of target pollutants from a gas stream with a system incorporating wet removal comprising the steps of:

A. providing a system according to Claim 1;

B. introducing a gas containing a target pollutant into the reaction of the system;

C. contacting the gas with the sorbent in the sorbent slurry of the system for a time sufficient to effect the capture of the target pollutant at a targeted capture rate set point for the target pollutant through the formation of a reaction product of the target pollutant and oxides of manganese to substantially strip the gas of the target pollutant; and

D. venting the gas from the reaction zone.

12. Process for the removal of target pollutants from a gas stream with a system incorporating wet removal as claimed in Claim 11, wherein the target pollutant is SO_X with sulfates of manganese being the reaction product which is dissolved in solution in the slurry, the process further comprising the steps of:

E. separating the sorbent from the slurry to provide a solution containing dissolved sulfates of manganese; and

F. routing the solution for further processing to regenerate oxides of manganese and recover useful sulfate by-products.

13. Process for the removal of target pollutants from a gas stream with a system incorporating wet removal as claimed in Claim 11, wherein the target pollutant is NO_X with nitrates of manganese being the reaction product which is dissolved in solution in the slurry, the process further comprising the steps of:

E. separating the sorbent from the slurry to provide a solution containing dissolved nitrates of manganese; and

F. routing the solution for further processing to regenerate oxides of manganese and recover useful nitrate by-products.

14. A process for the removal of target pollutants from a gas stream with a system incorporating wet removal comprising the steps of :

A. providing a system as claimed in Claims 2, 3 or 4;

B. introducing a gas containing at least two target pollutants into the first reaction zone of the system;

C. contacting the gas in the first reaction zone with the sorbent for a time sufficient to effect capture of a first target pollutant at a targeted capture rate set point for the first target pollutant through the formation of a reaction product of the first target pollutant and oxides of manganese to substantially strip the gas of the first target pollutant;

D. venting the gas from the first reaction zone;

E. introducing the gas vented from the first reaction zone into the second reaction zone of the system;

F. contacting the gas in the second reaction zone with the sorbent for a time sufficient to effect capture of a second target pollutant at a targeted capture rate set point for the second target pollutant through the formation of a reaction product of the second target pollutant and oxides of manganese to substantially strip the gas of the second target pollutant; and

G. venting the gas from the second reaction zone of the system.

15. Process for the regeneration of oxides of manganese from a solution containing sulfate and nitrate anions and manganese cations formed when the reaction product of the removal of SO_X and NO_X from a gas stream with a sorbent of oxides of manganese, comprising the steps of:

A. providing first and second anion exchangers having an anion exchange resin loaded therein, the anion exchange resin having chloride in the exchange position on the resin;

B. passing a solution containing sulfate and nitrate anions through the first anion exchanger to elute the chloride to form manganese chloride while capturing the sulfate anion on the resin;

C. passing the solution containing nitrate anions through the second anion exchanger to elute the chloride to form manganese chloride while capturing the nitrate anion on the resin;

D. adding a soluble carbonate or hydroxide compound to the solution to precipitate manganese carbonate or manganese hydroxide;

D. separating the manganese carbonate or manganese hydroxide from the solution; and

E. heating the manganese carbonate or manganese hydroxide to form regenerated oxides of manganese.

Figure 1

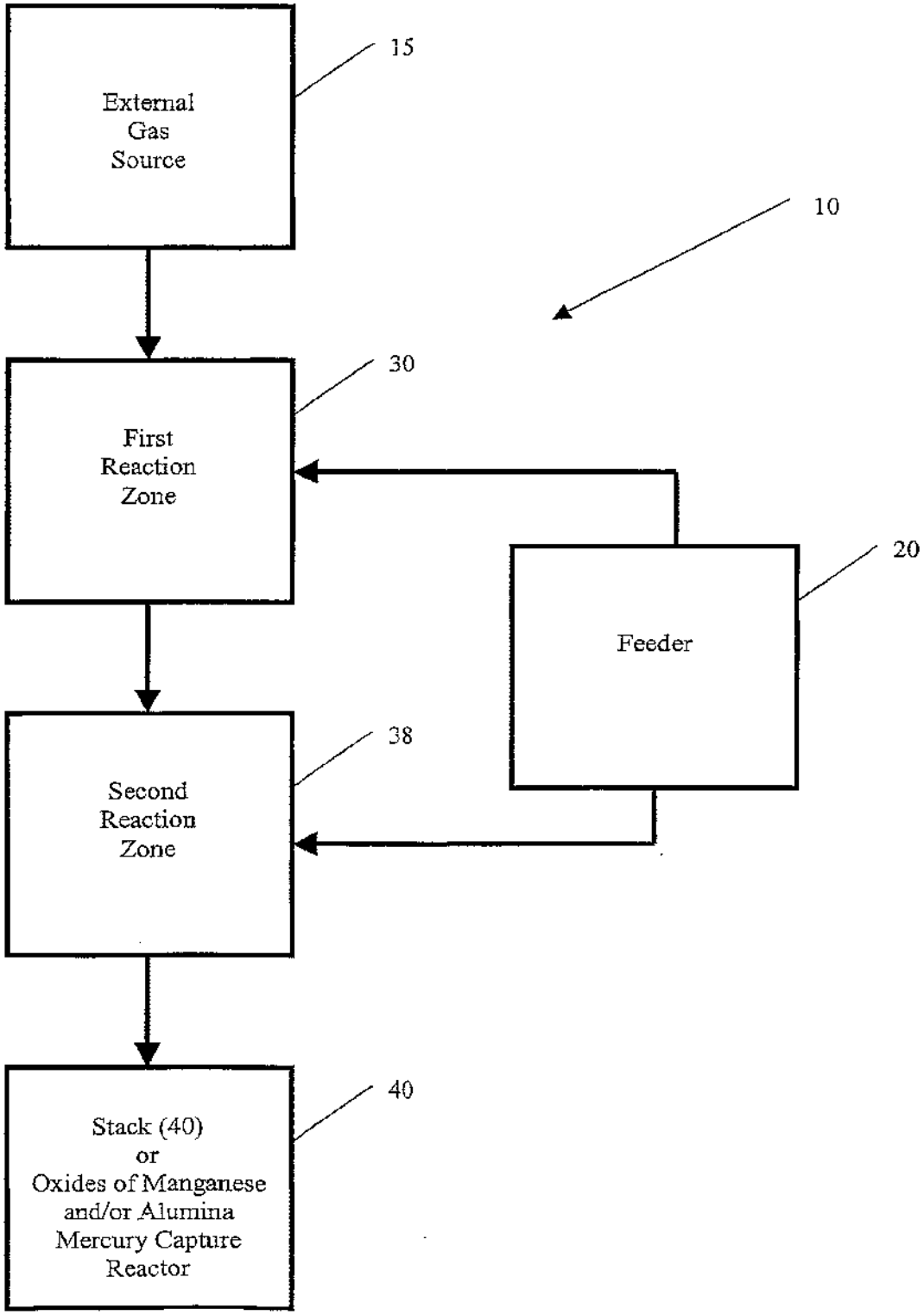

External Gas Source
15
10
30
First Reaction Zone
20
Feeder
38
Second Reaction Zone
40
Stack (40) or Oxides of Manganese and/or Alumina Mercury Capture Reactor

Figure 2

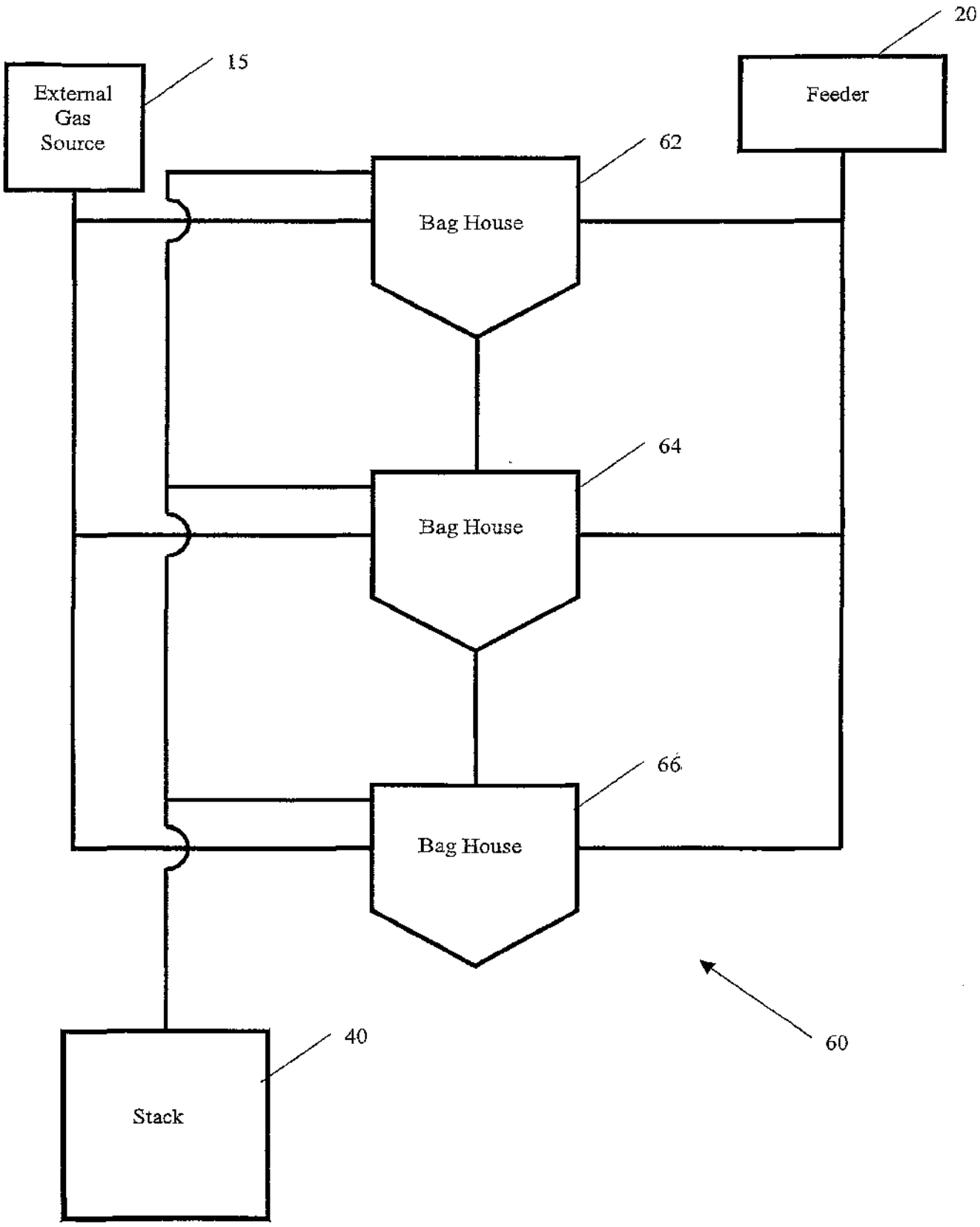
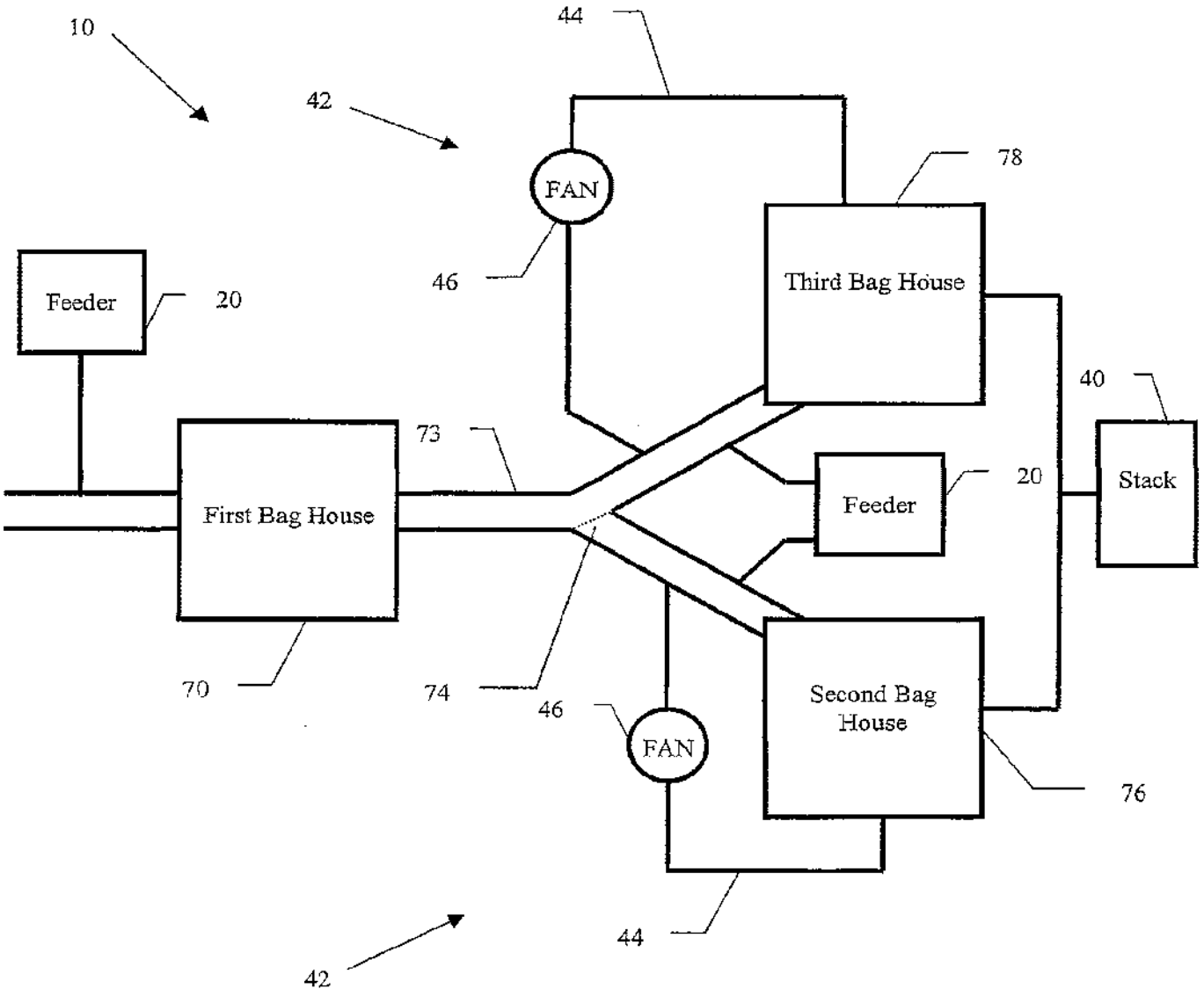

20
15
External Gas Source
Feeder
62
Bag House
64
Bag House
66
Bag House
60
40
Stack

Figure 3


10
42
44
FAN
78
46
Third Bag House
Feeder
20
40
73
First Bag House
Feeder
20
Stack
70
74
46
FAN
Second Bag House
76
44
42

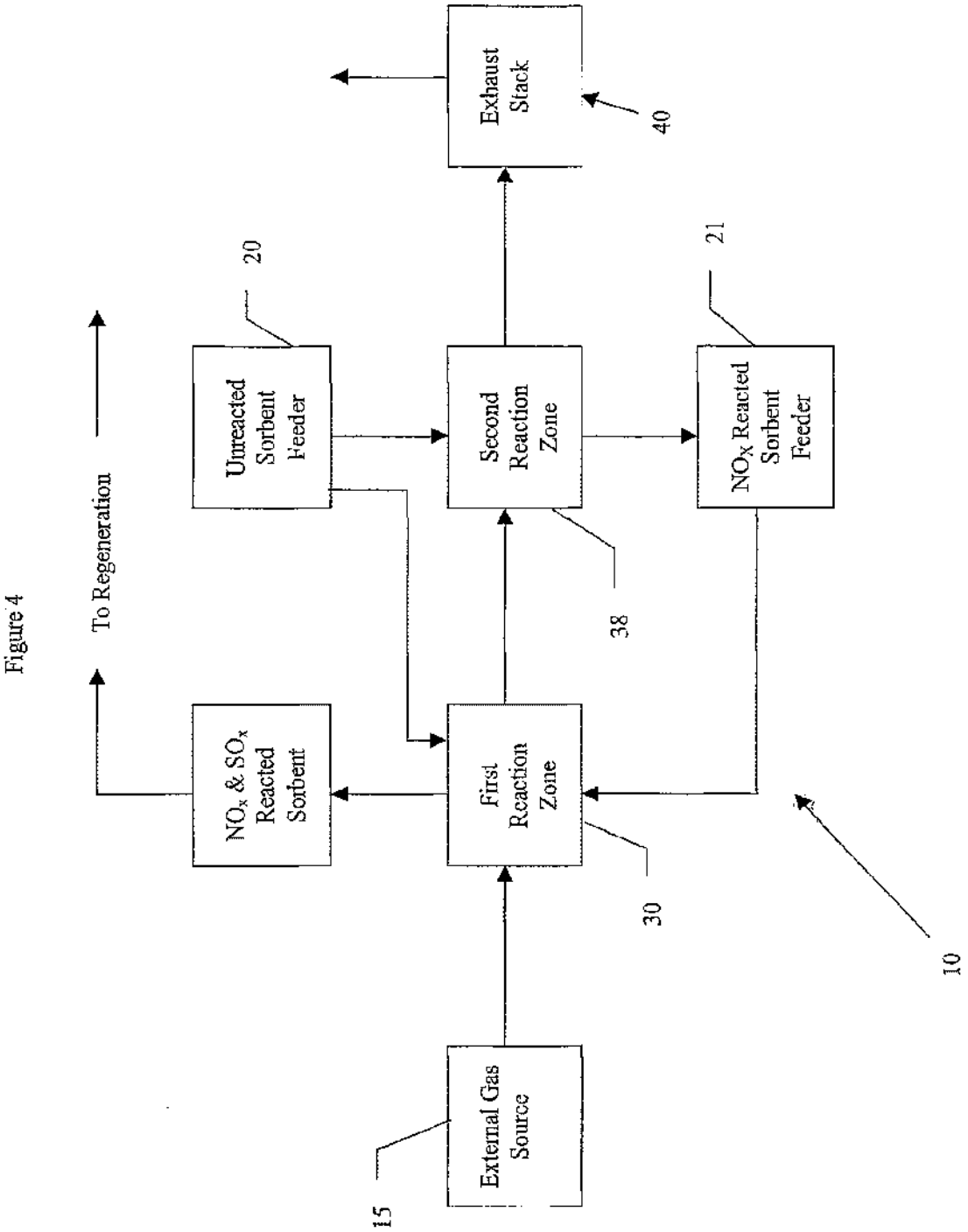
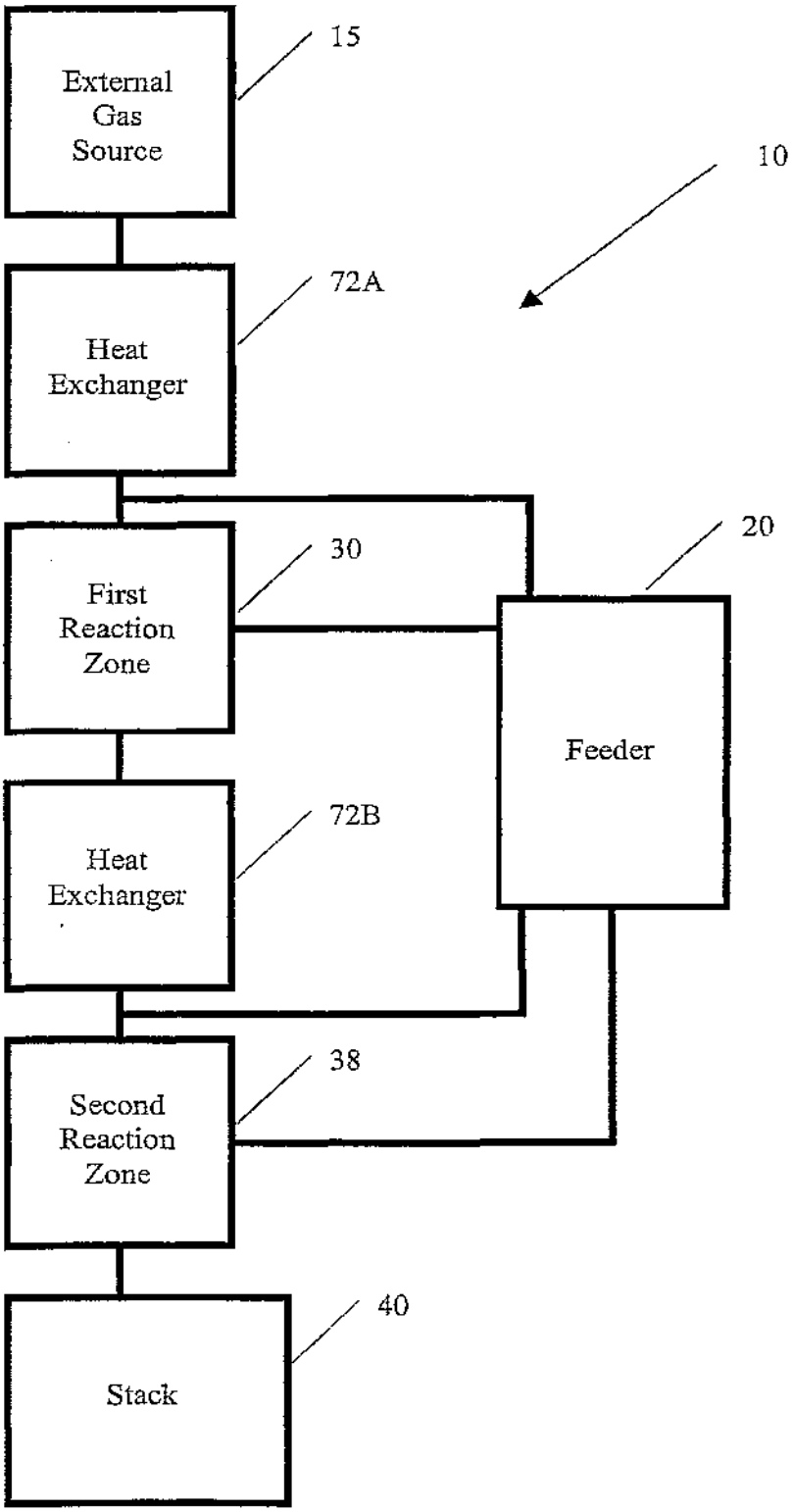

Exhaust Stack
40
20
21
Unreacted Sorbent Feeder
Second Reaction Zone
NO_X Reacted Sorbent Feeder
To Regeneration
38
NO_x & SO_x Reacted Sorbent
First Reaction Zone
30
10
External Gas Source
15

Figure 4

Figure 5


External Gas Source
15
10
72A
Heat Exchanger
First Reaction Zone
30
20
Feeder
Heat Exchanger
72B
Second Reaction Zone
38
Stack
40

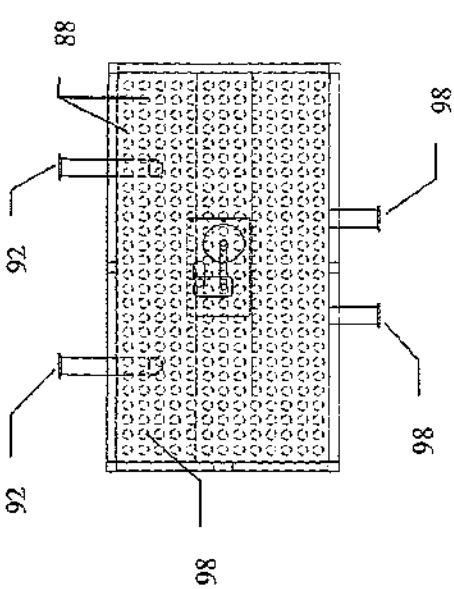


Figure 8

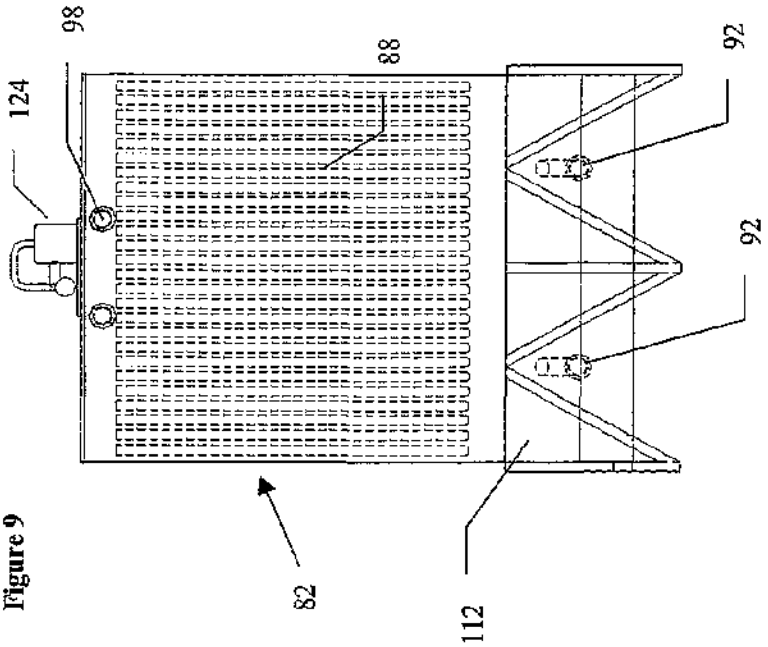


Figure 9

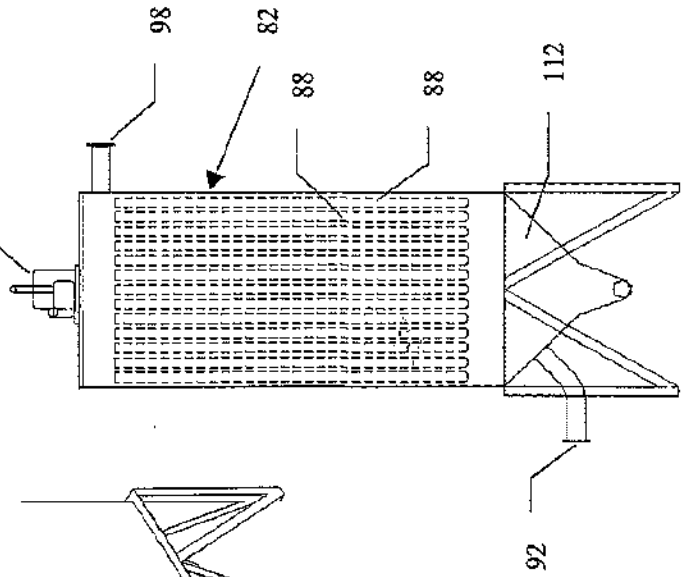


Figure 7

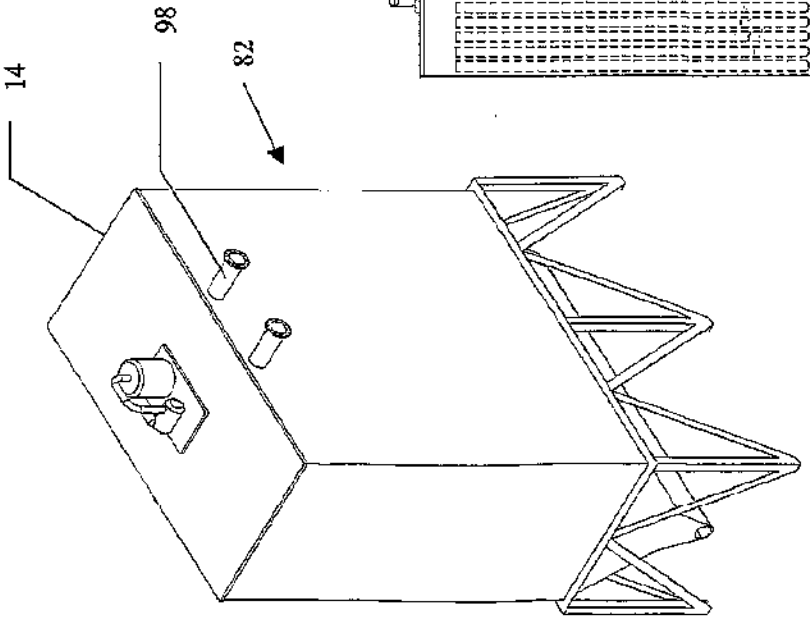


Figure 6

Figure 10

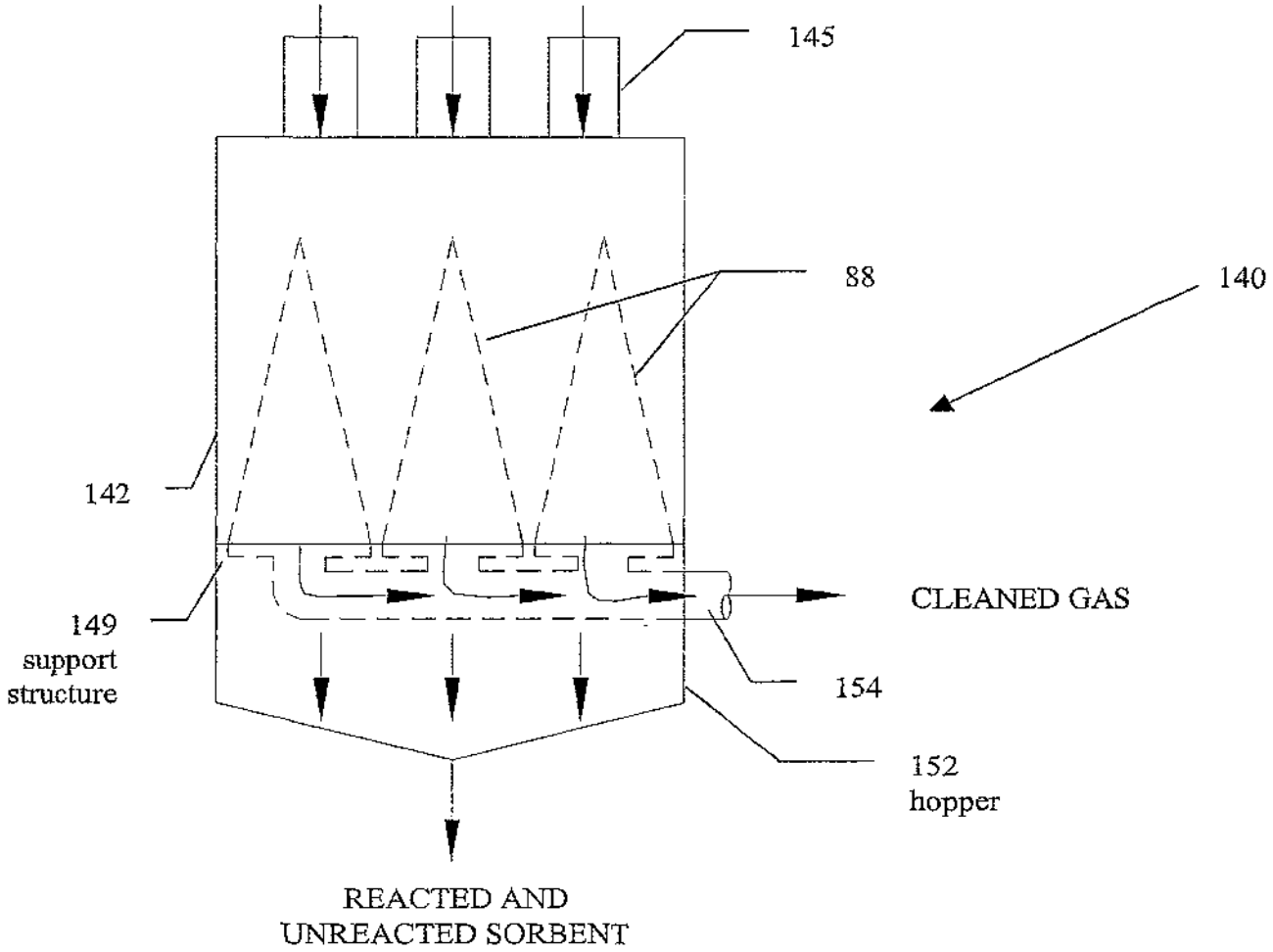


Figure 11

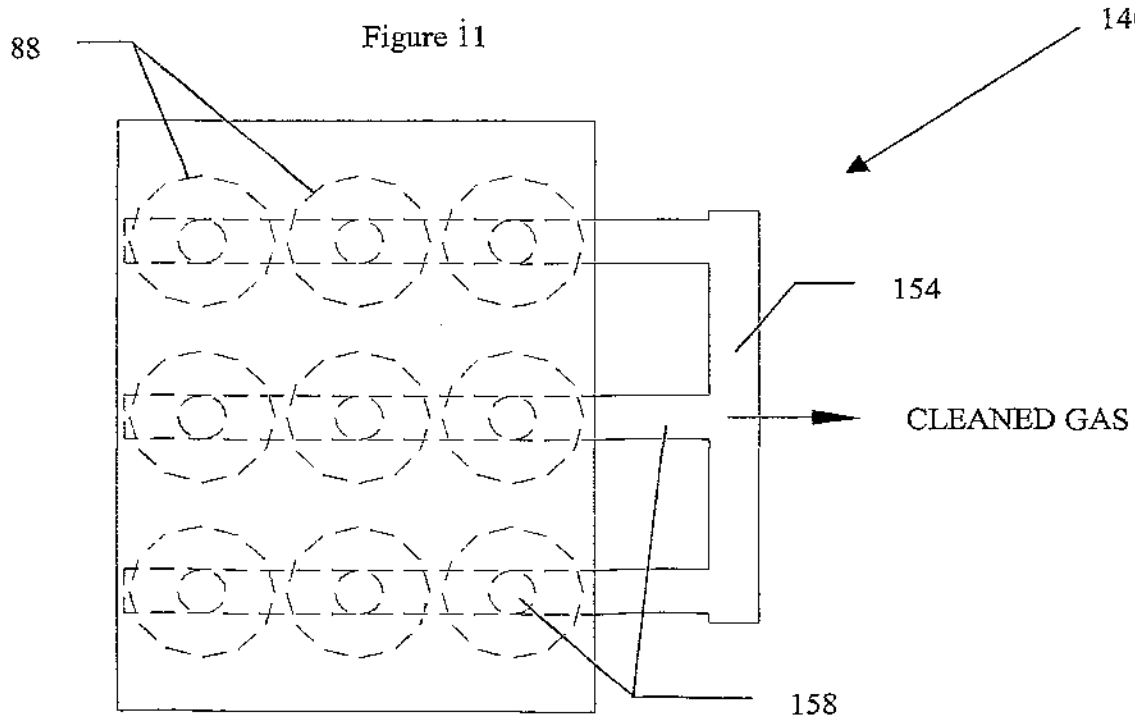


Figure 12

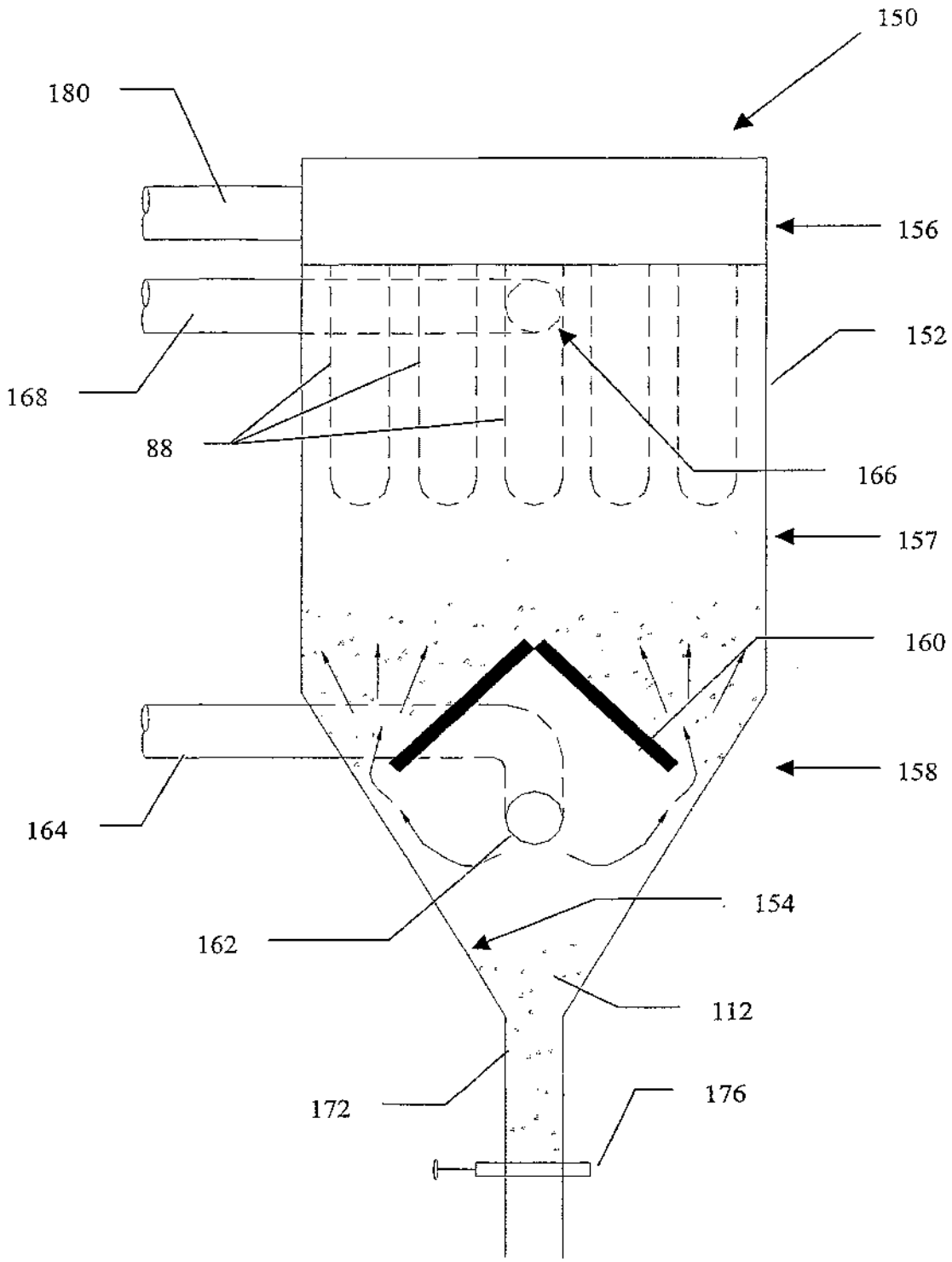


Figure 13

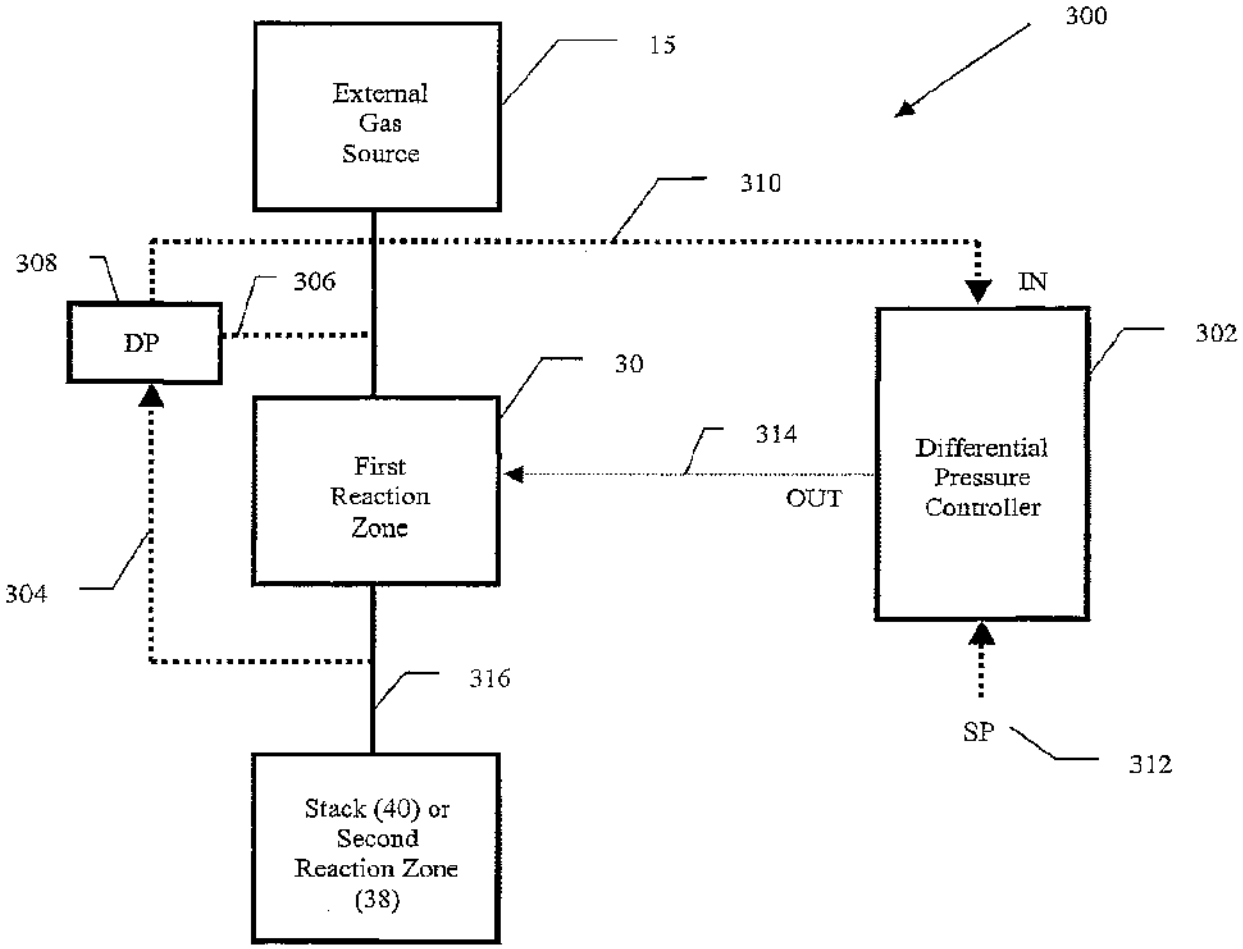

300
15
External Gas Source
310
308
306
IN
DP
302
30
First Reaction Zone
314
OUT
Differential Pressure Controller
304
316
SP
312
Stack (40) or Second Reaction Zone (38)

Figure 14

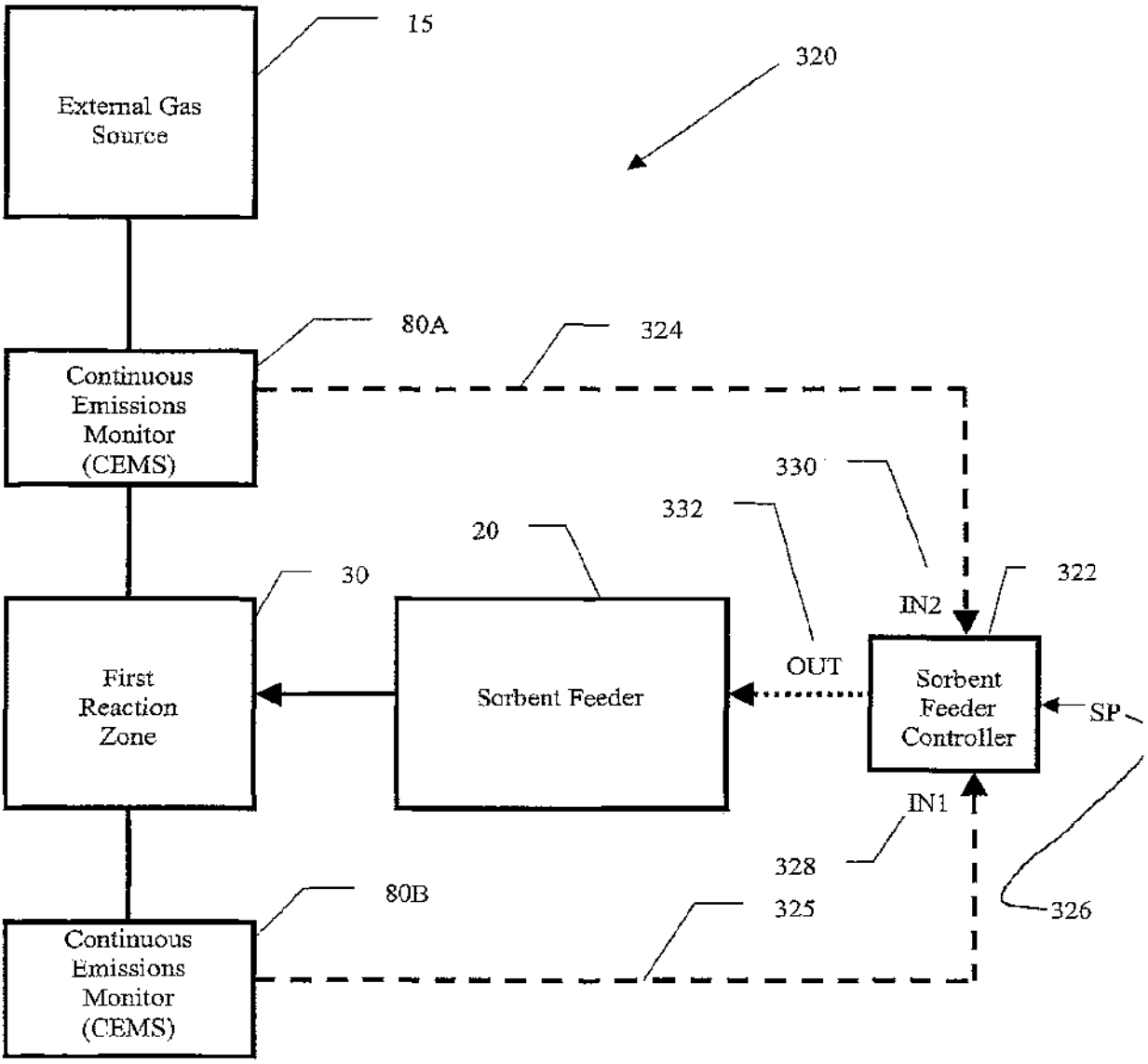

External Gas Source
15
320
Continuous Emissions Monitor (CEMS)
80A
324
330
332
20
30
322
IN2
First Reaction Zone
Sorbent Feeder
OUT
Sorbent Feeder Controller
SP
IN1
328
326
325
80B
Continuous Emissions Monitor (CEMS)

Figure 15

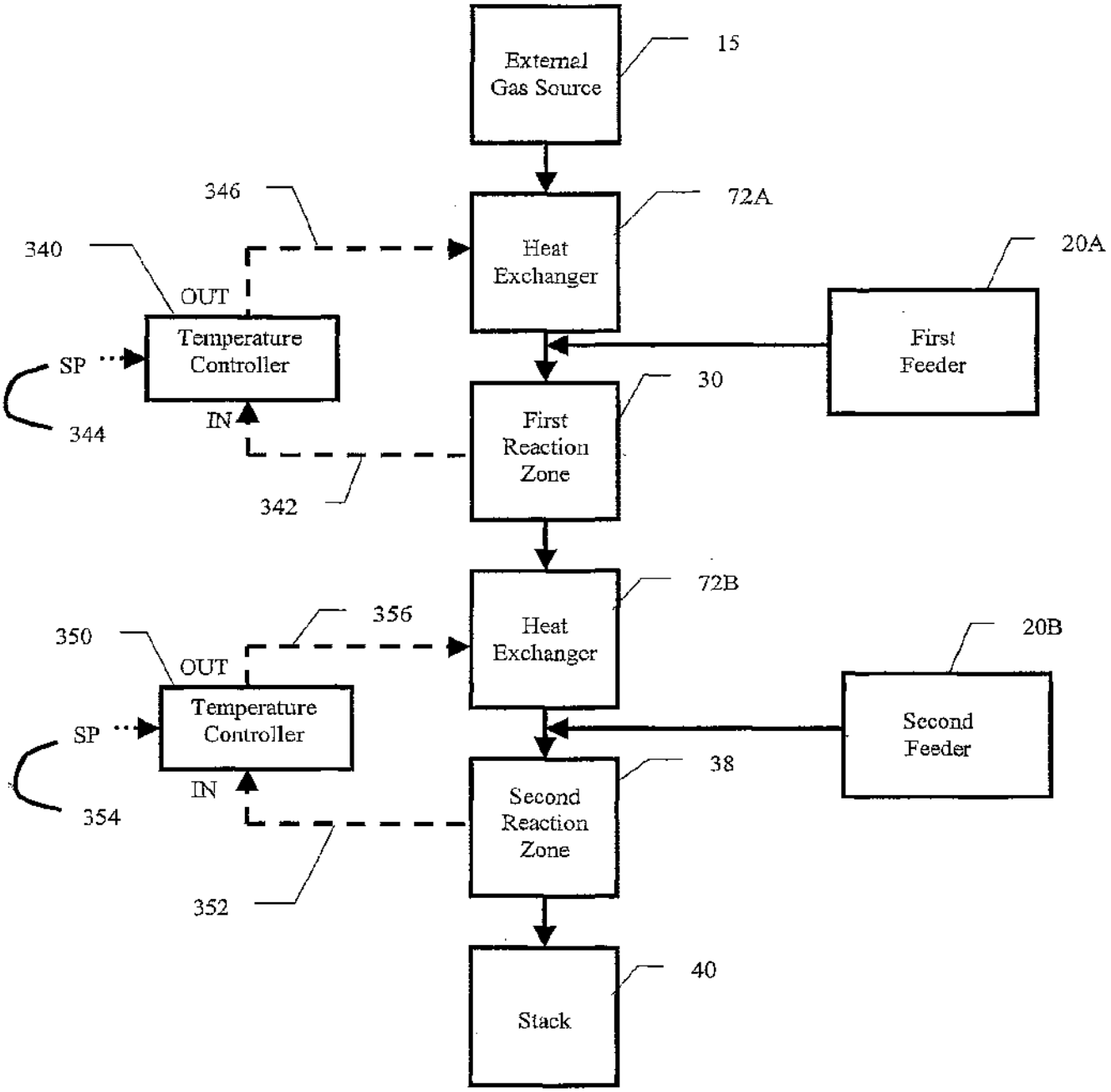

External Gas Source
15
346
72A
340
Heat Exchanger
20A
OUT
Temperature Controller
First Feeder
SP
30
First Reaction Zone
IN
344
342
72B
356
350
Heat Exchanger
20B
OUT
Temperature Controller
Second Feeder
SP
38
Second Reaction Zone
IN
354
352
40
Stack

Figure 16

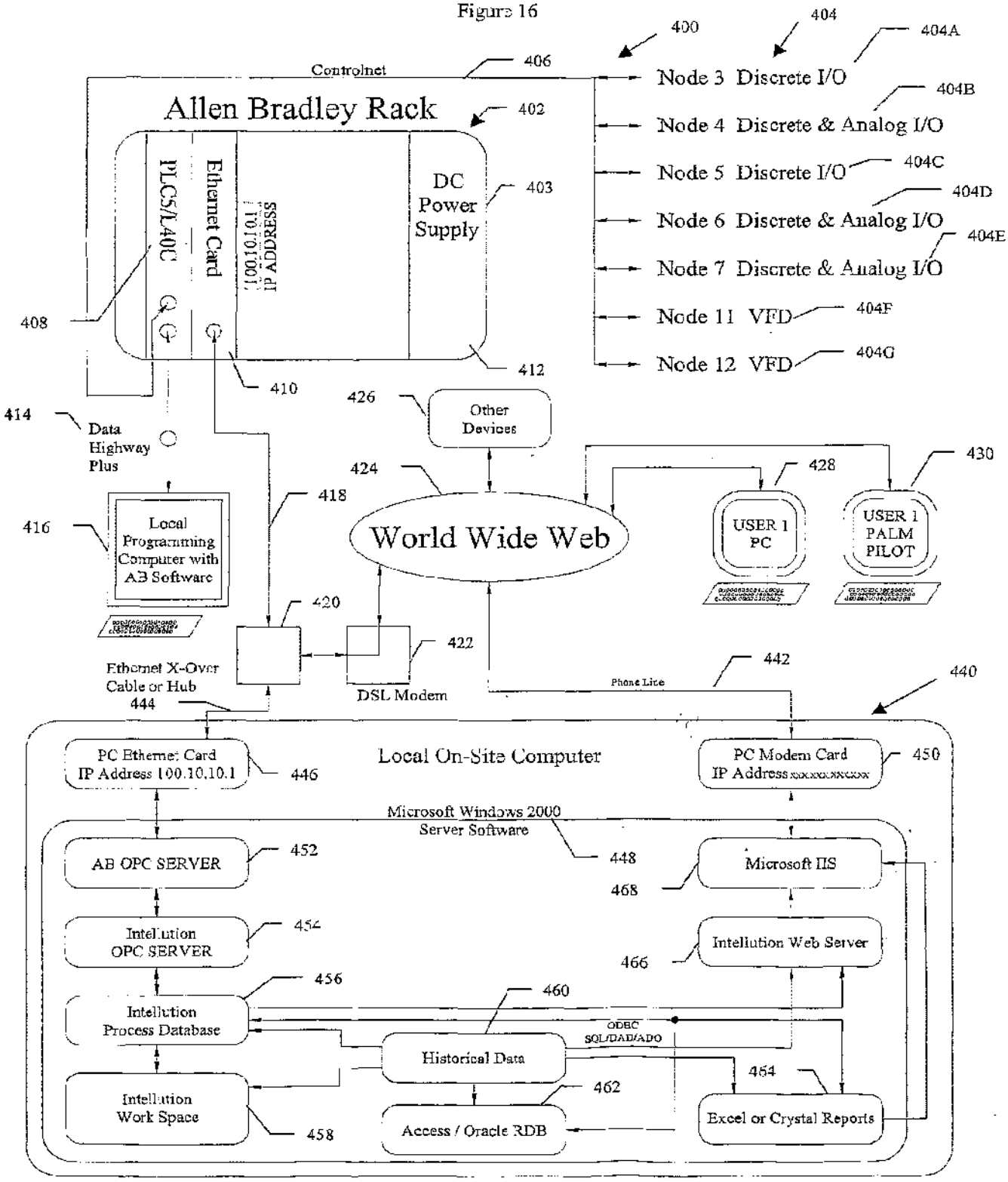

400
404
404A
Controlnet
406
Node 3 Discrete I/O
Allen Bradley Rack
402
404B
Node 4 Discrete & Analog I/O
PLC5/L40C
Ethernet Card
100.10.10.1
IP ADDRESS
DC Power Supply
403
Node 5 Discrete I/O
404C
404D
Node 6 Discrete & Analog I/O
404E
Node 7 Discrete & Analog I/O
408
Node 11 VFD
404F
Node 12 VFD
404G
412
410
426
Other Devices
414
Data Highway Plus
424
428
430
418
Local Programming Computer with AB Software
416
World Wide Web
USER 1 PC
USER 1 PALM PILOT
420
422
Ethernet X-Over Cable or Hub
444
DSL Modem
442
Phone Line
440
PC Ethernet Card IP Address 100.10.10.1
446
Local On-Site Computer
PC Modem Card IP Address xxxxxxxxxxx
450
Microsoft Windows 2000 Server Software
448
AB OPC SERVER
452
Microsoft IIS
468
Intellution OPC SERVER
454
Intellution Web Server
466
456
460
Intellution Process Database
ODBC SQL/DAO/ADO
Historical Data
464
462
Intellution Work Space
458
Access / Oracle RDB
Excel or Crystal Reports

Figure 17

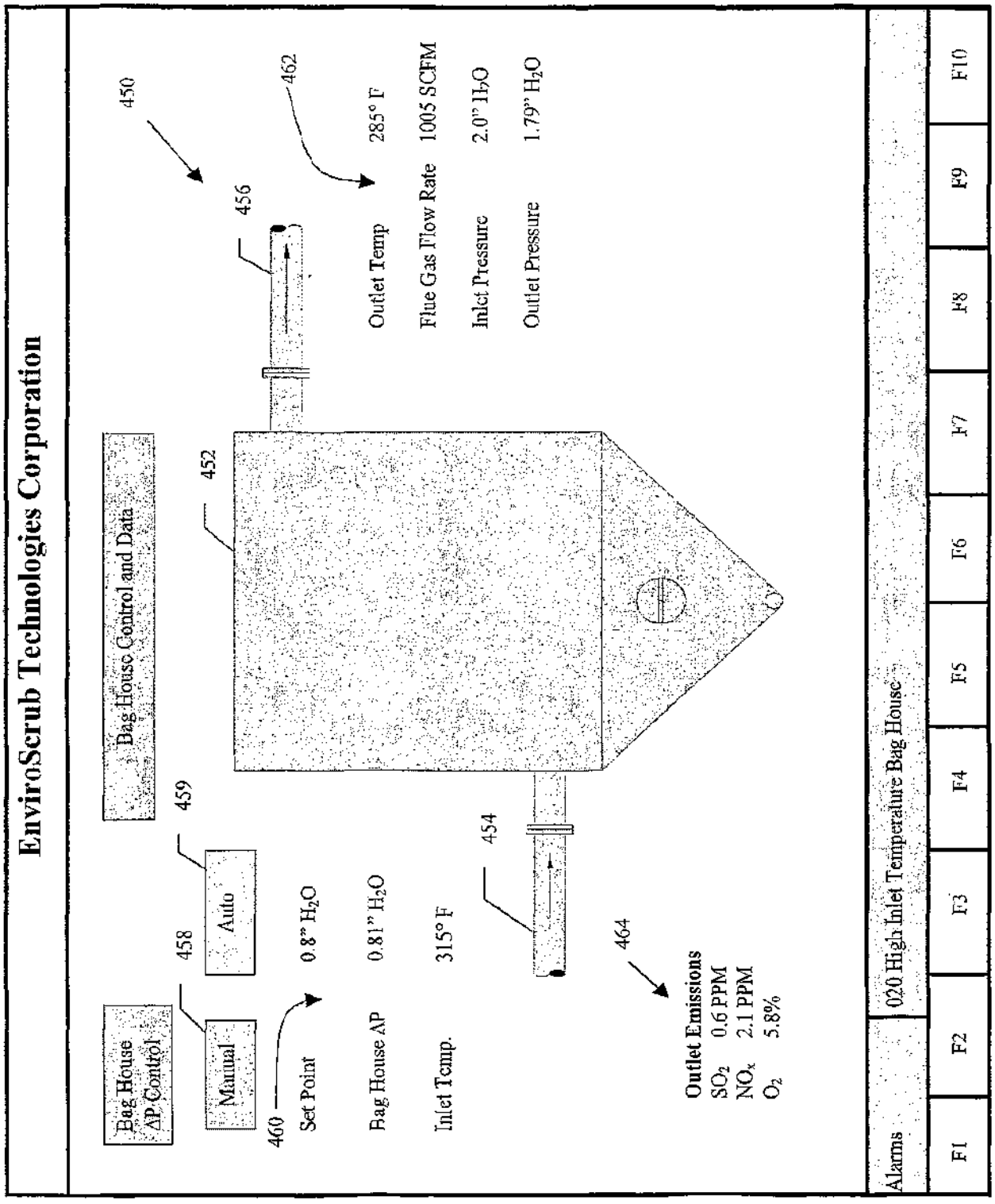

EnviroScrub Technologies Corporation
Bag House Control and Data
Bag House ΔP Control
Manual
Auto
458
459
460
Set Point
0.8" H2O
Bag House ΔP
0.81" H2O
Inlet Temp.
315° F
450
452
454
456
462
464
Outlet Temp
285° F
Flue Gas Flow Rate
1005 SCFM
Inlet Pressure
2.0" H2O
Outlet Pressure
1.79" H2O
Outlet Emissions
SO2 0.6 PPM
NOx 2.1 PPM
O2 5.8%
Alarms
020 High Inlet Temperature Bag House
F1
F2
F3
F4
F5
F6
F7
F8
F9
F10

Figure 18

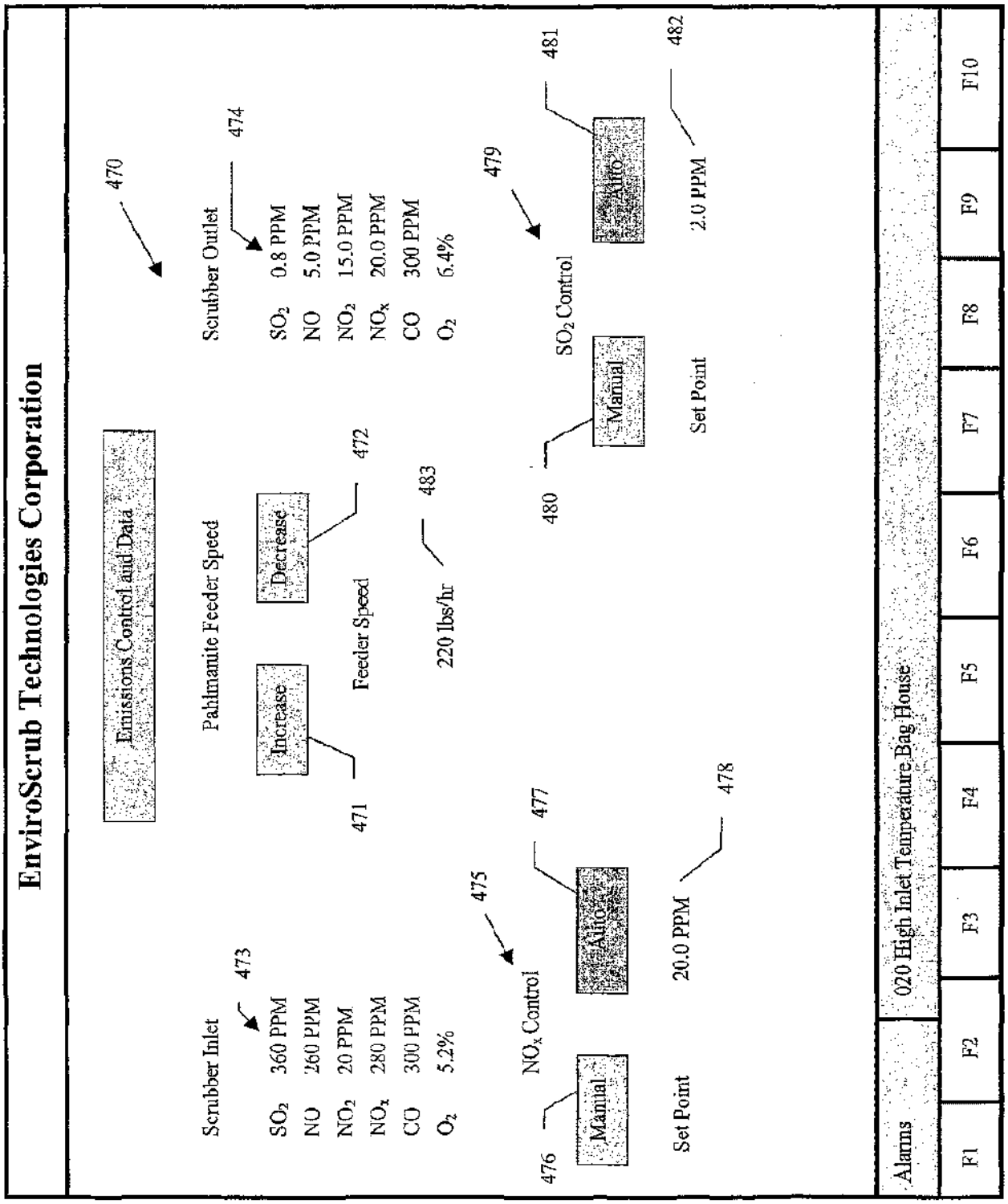

EnviroScrub Technologies Corporation
Emissions Control and Data
470
Scrubber Inlet
473
SO2 360 PPM
NO 260 PPM
NO2 20 PPM
NOx 280 PPM
CO 300 PPM
O2 5.2%
Scrubber Outlet
474
SO2 0.8 PPM
NO 5.0 PPM
NO2 15.0 PPM
NOx 20.0 PPM
CO 300 PPM
O2 6.4%
Pahlmanite Feeder Speed
Increase
Decrease
471
Feeder Speed
472
220 lbs/hr
483
NOx Control
475
476
Manual
Auto
477
Set Point
20.0 PPM
478
SO2 Control
479
480
Manual
Auto
481
Set Point
2.0 PPM
482
Alarms
020 High Inlet Temperature Bag House
F1
F2
F3
F4
F5
F6
F7
F8
F9
F10

Figure 19

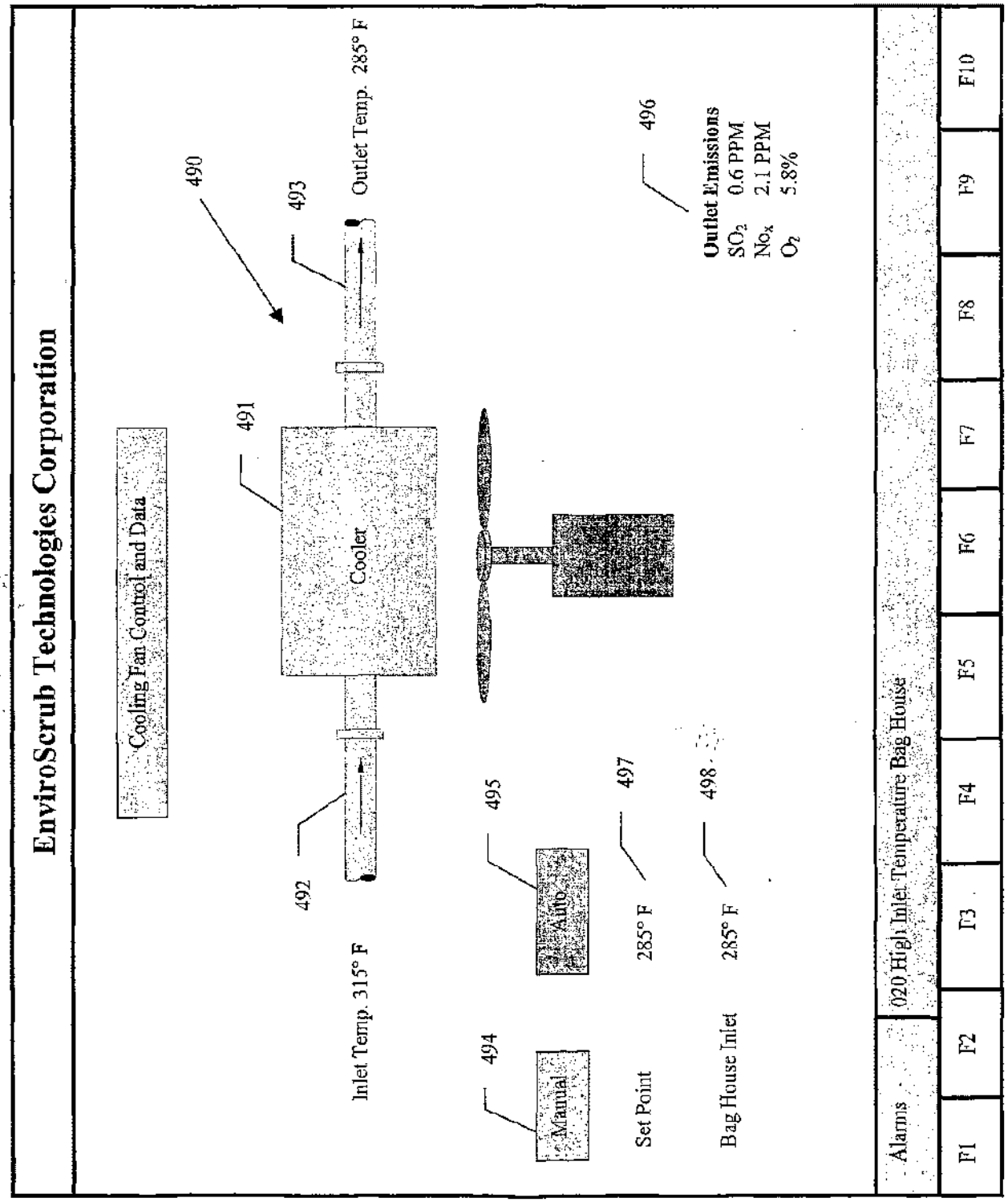

EnviroScrub Technologies Corporation
Cooling Fan Control and Data
490
491
Cooler
492
493
Outlet Temp. 285° F
Inlet Temp. 315° F
494
Manual
495
Auto
496
Outlet Emissions
SO_2 0.6 PPM
No_x 2.1 PPM
O_2 5.8%
497
Set Point
285° F
498
Bag House Inlet
285° F
Alarms
020 High Inlet Temperature Bag House
F1
F2
F3
F4
F5
F6
F7
F8
F9
F10

Figure 20

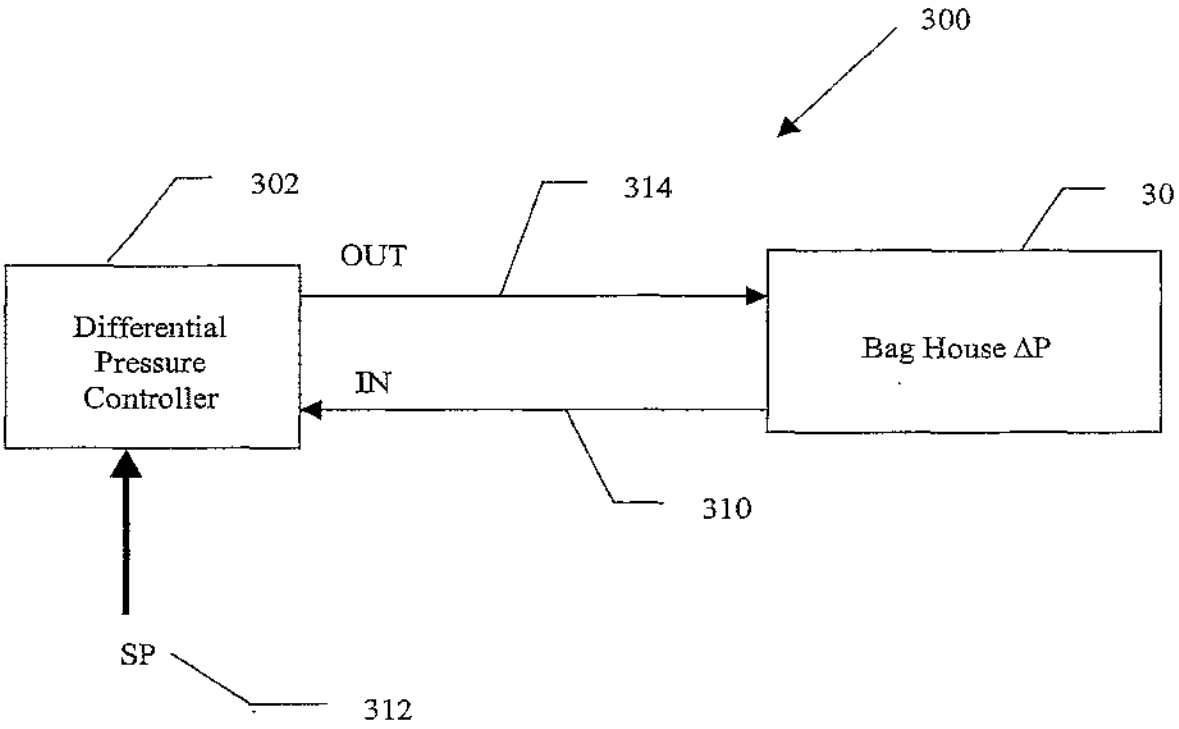

300
302
314
30
OUT
Differential Pressure Controller
Bag House ΔP
IN
310
SP
312

Figure 21

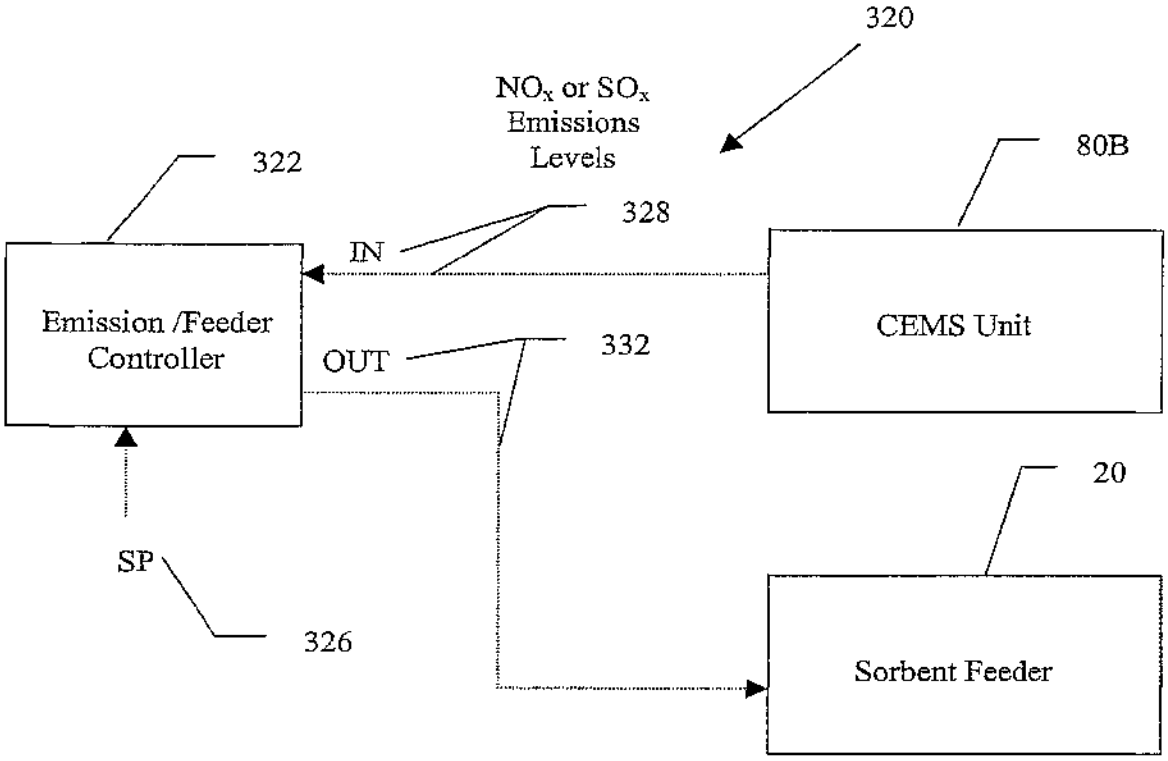

320
NO_x or SO_x Emissions Levels
322
328
80B
IN
Emission /Feeder Controller
CEMS Unit
OUT
332
20
SP
326
Sorbent Feeder

Figure 22

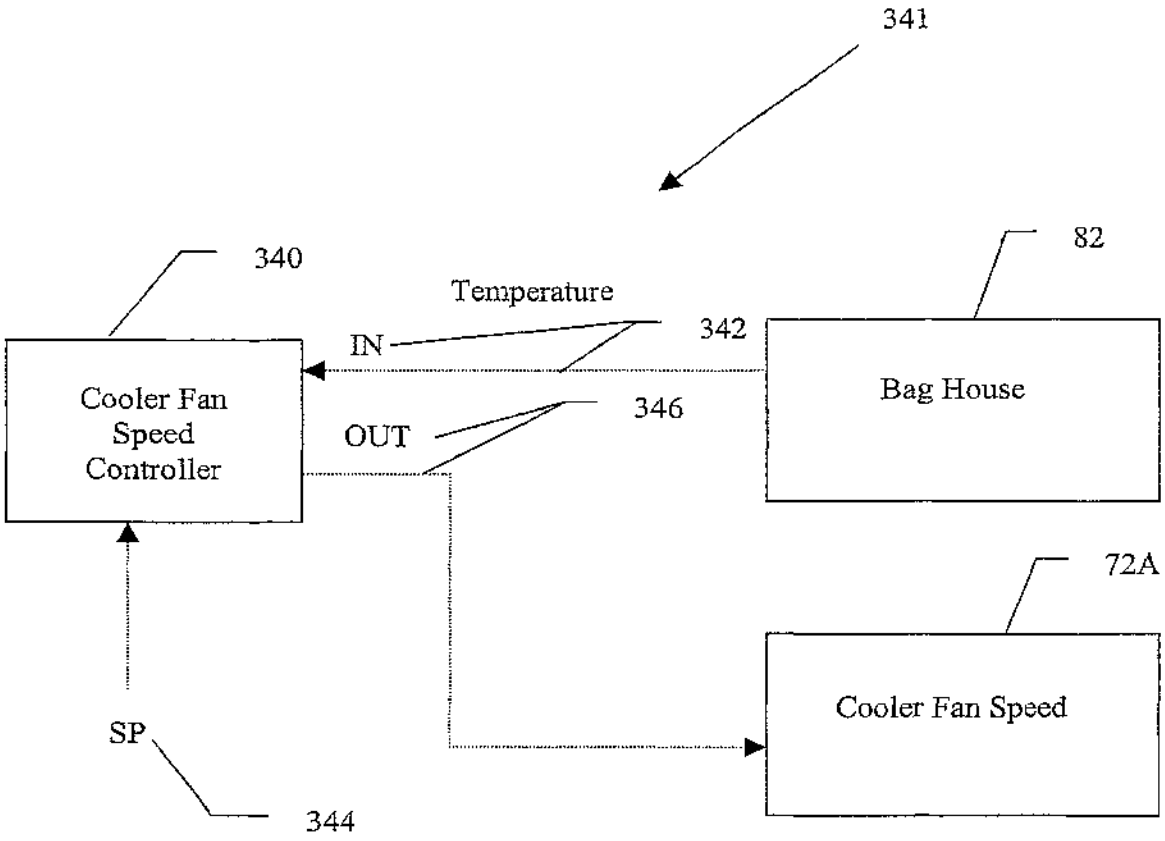

341
340
82
Temperature
IN
342
Cooler Fan Speed Controller
Bag House
OUT
346
72A
Cooler Fan Speed
SP
344

Figure 23

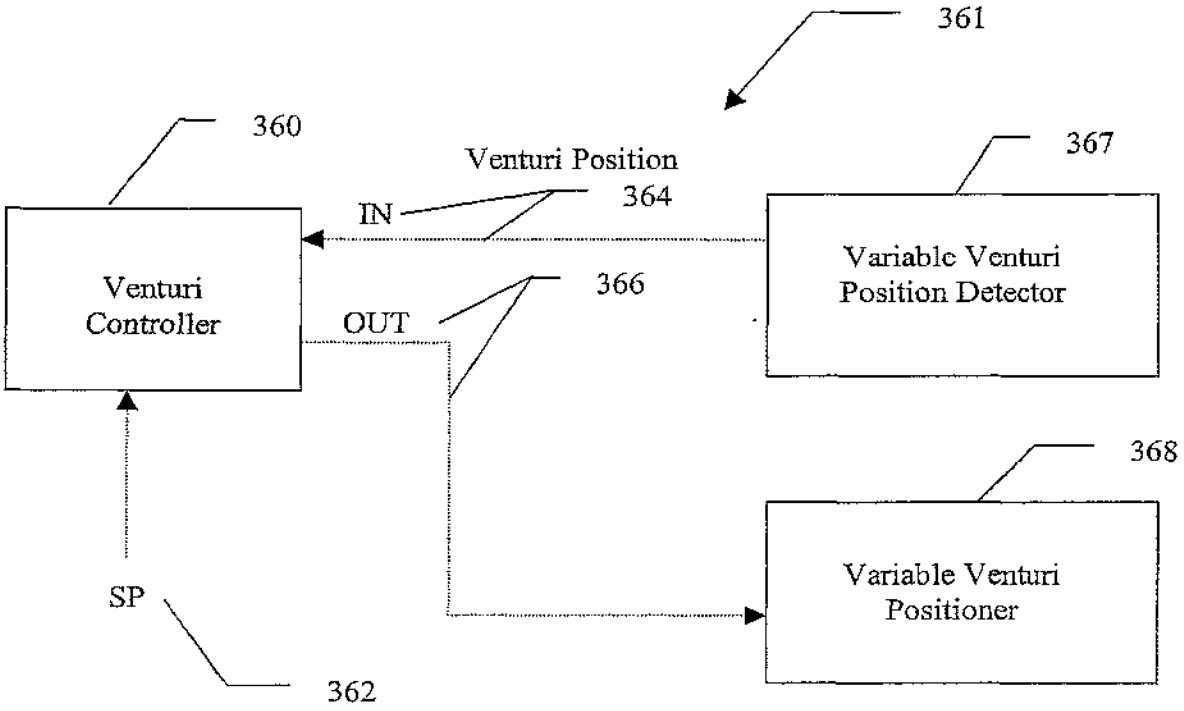

361
360
Venturi Position
367
IN
364
Venturi
Controller
Variable Venturi
Position Detector
366
OUT
368
Variable Venturi
Positioner
SP
362

Figure 24
Software Control Loop for Simultaneous NO_x, SO_x, and ΔP Control
Diagram 3

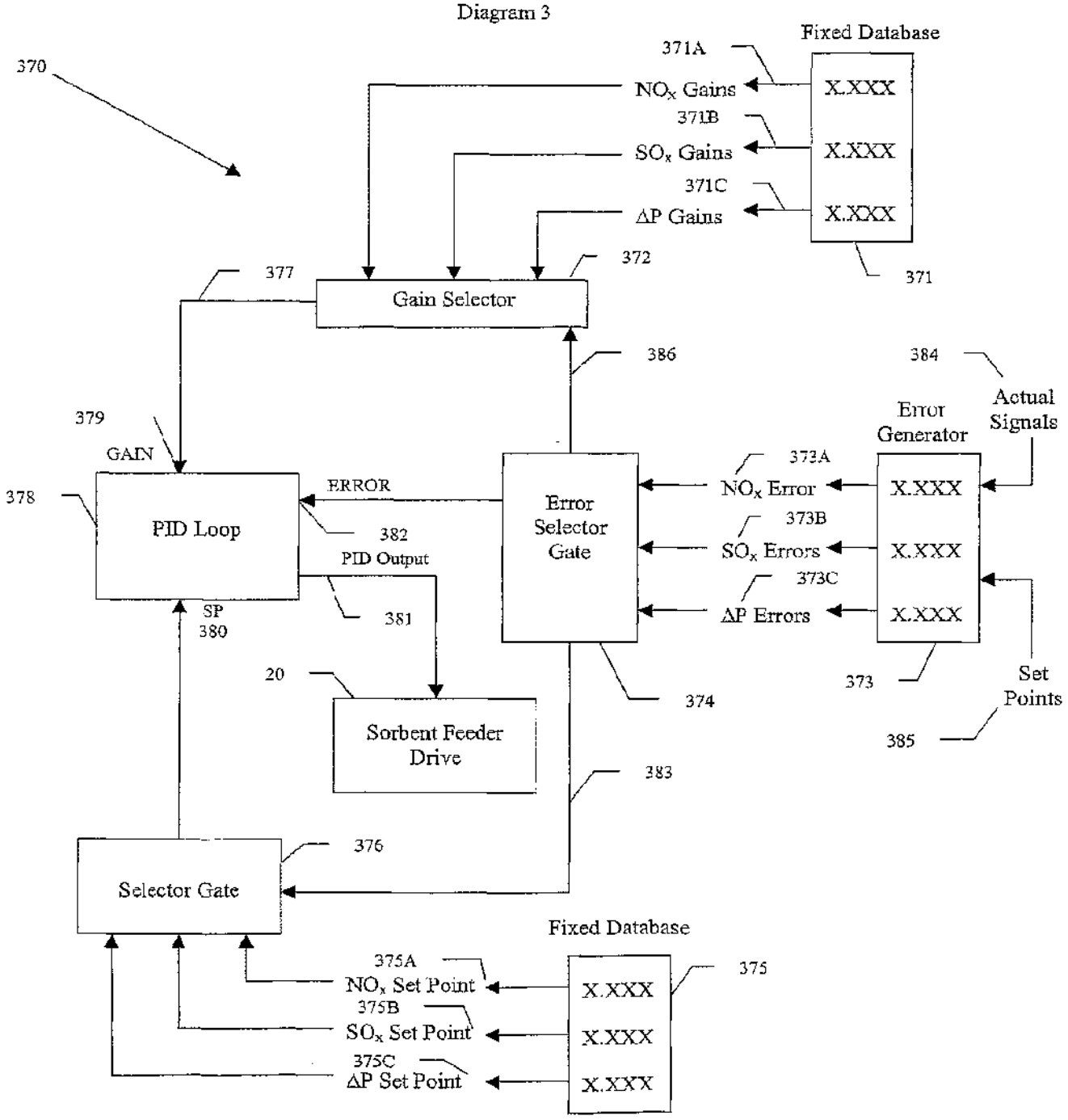
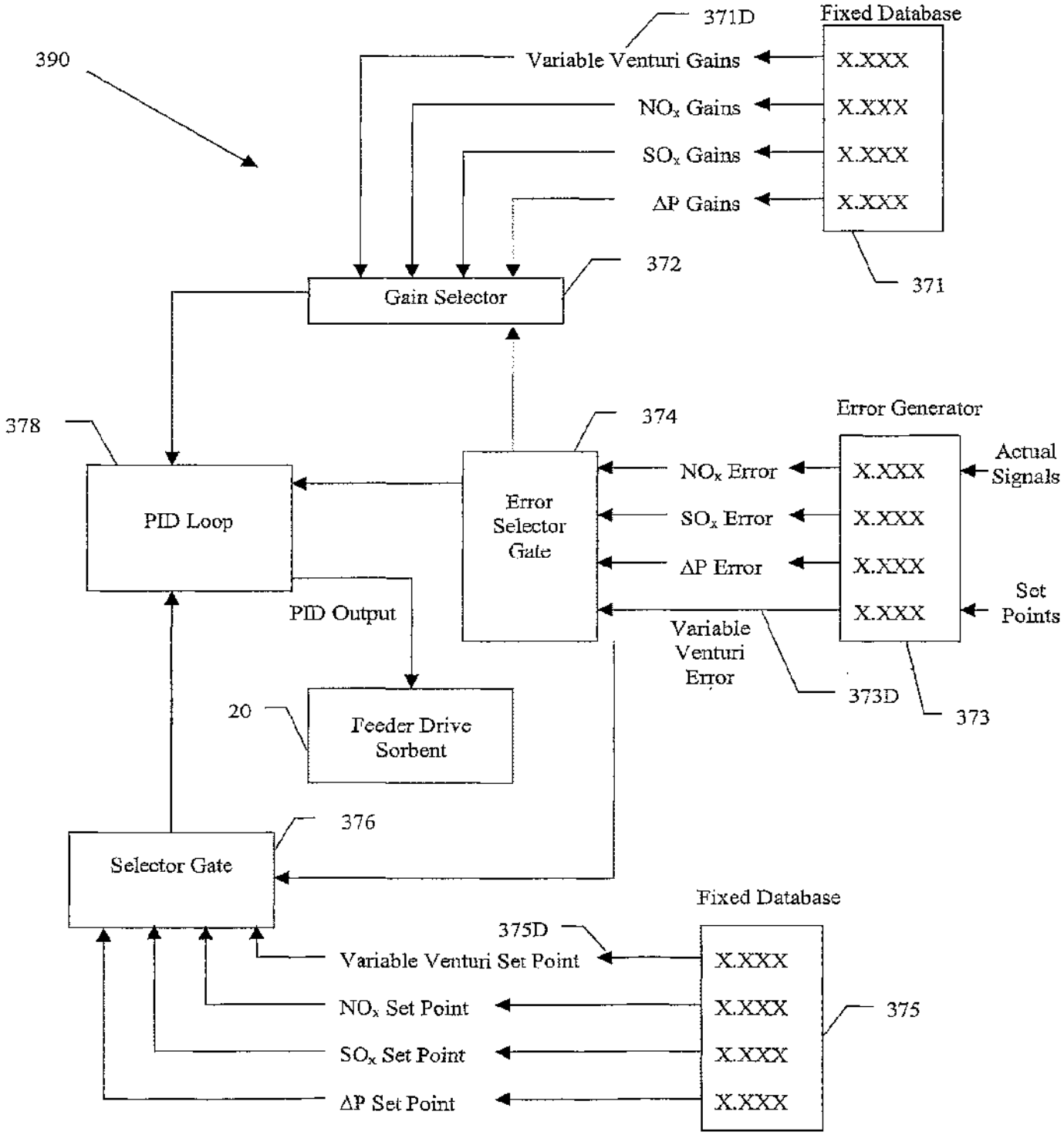
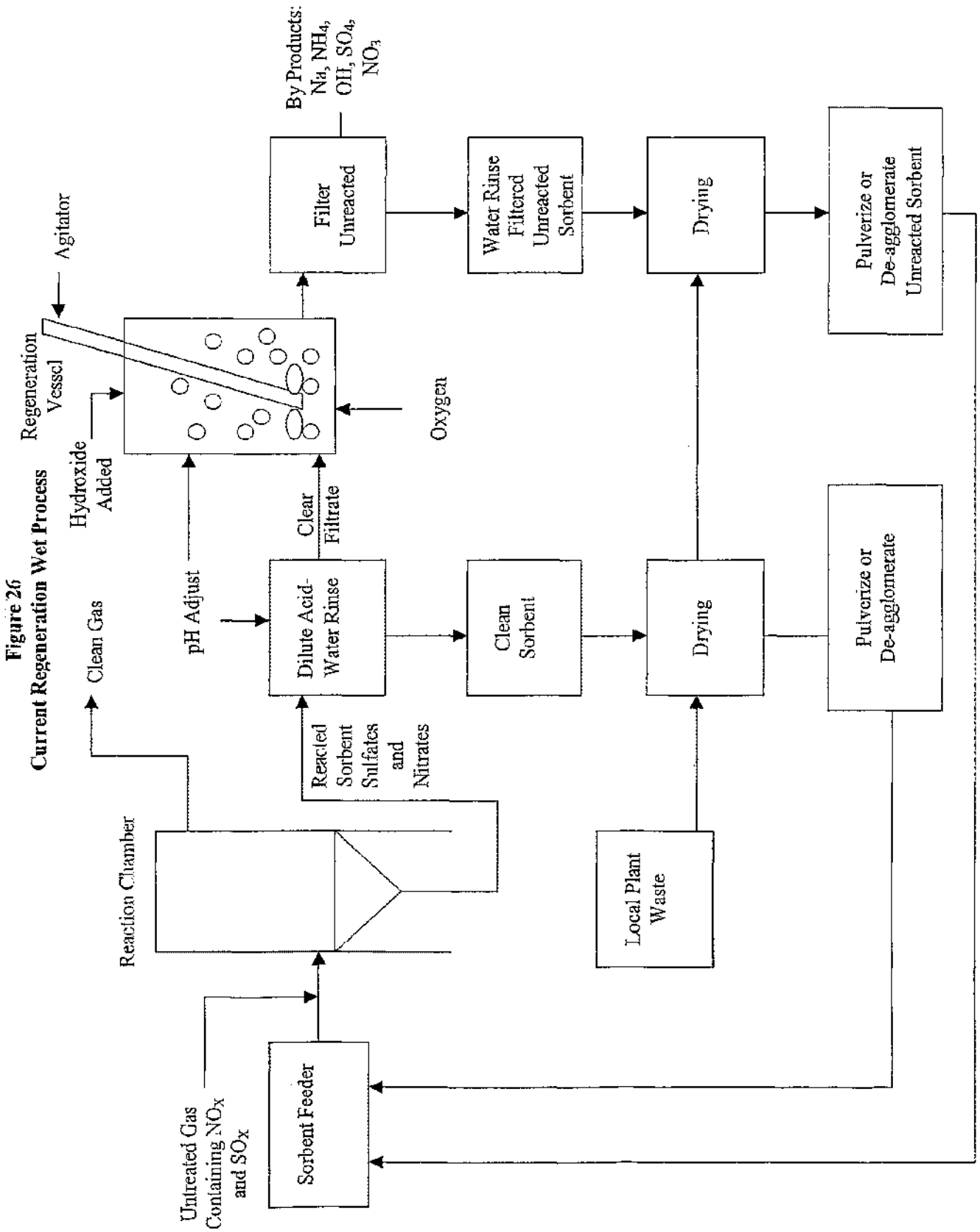


Figure 25
Software Control Loop for Simultaneous NO_x, SO_x, ΔP, and Variable Venturi Position Control
Diagram 6




Figure 26
Current Regeneration Wet Process
Unreated Gas Containing NO_X and SO_X
Sorbent Feeder
Reaction Chamber
Clean Gas
Reacted Sorbent Sulfates and Nitrates
Local Plant Waste
pH Adjust
Dilute Acid-Water Rinse
Clean Sorbent
Drying
Pulverize or De-agglomerate
Hydroxide Added
Clear Filtrate
Oxygen
Regeneration Vessel
Agitator
Filter Unreated
By Products: Na, NH_4, OH, SO_4, NO_3
Water Rinse Filtered Unreacted Sorbent
Drying
Pulverize or De-agglomerate Unreacted Sorbent

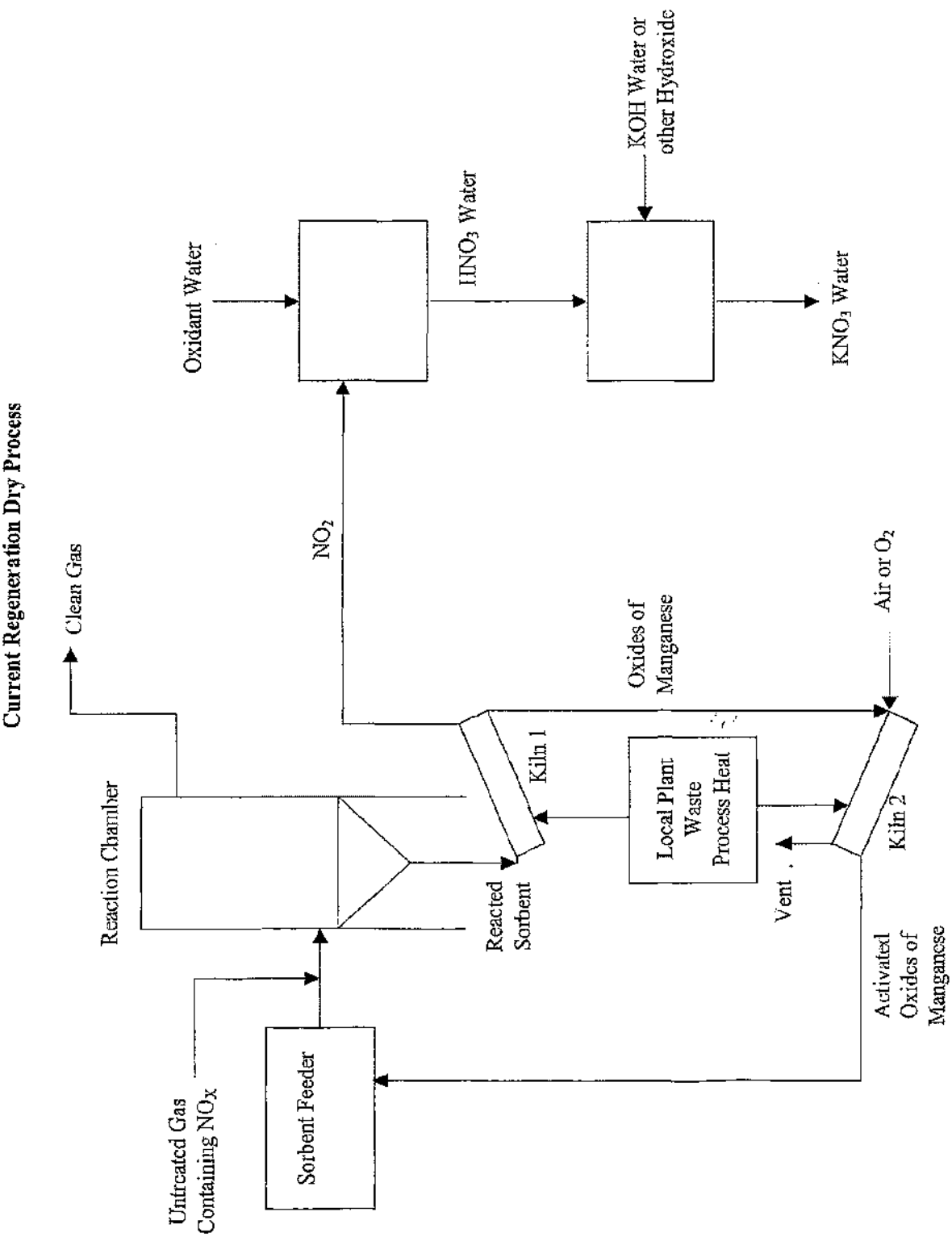
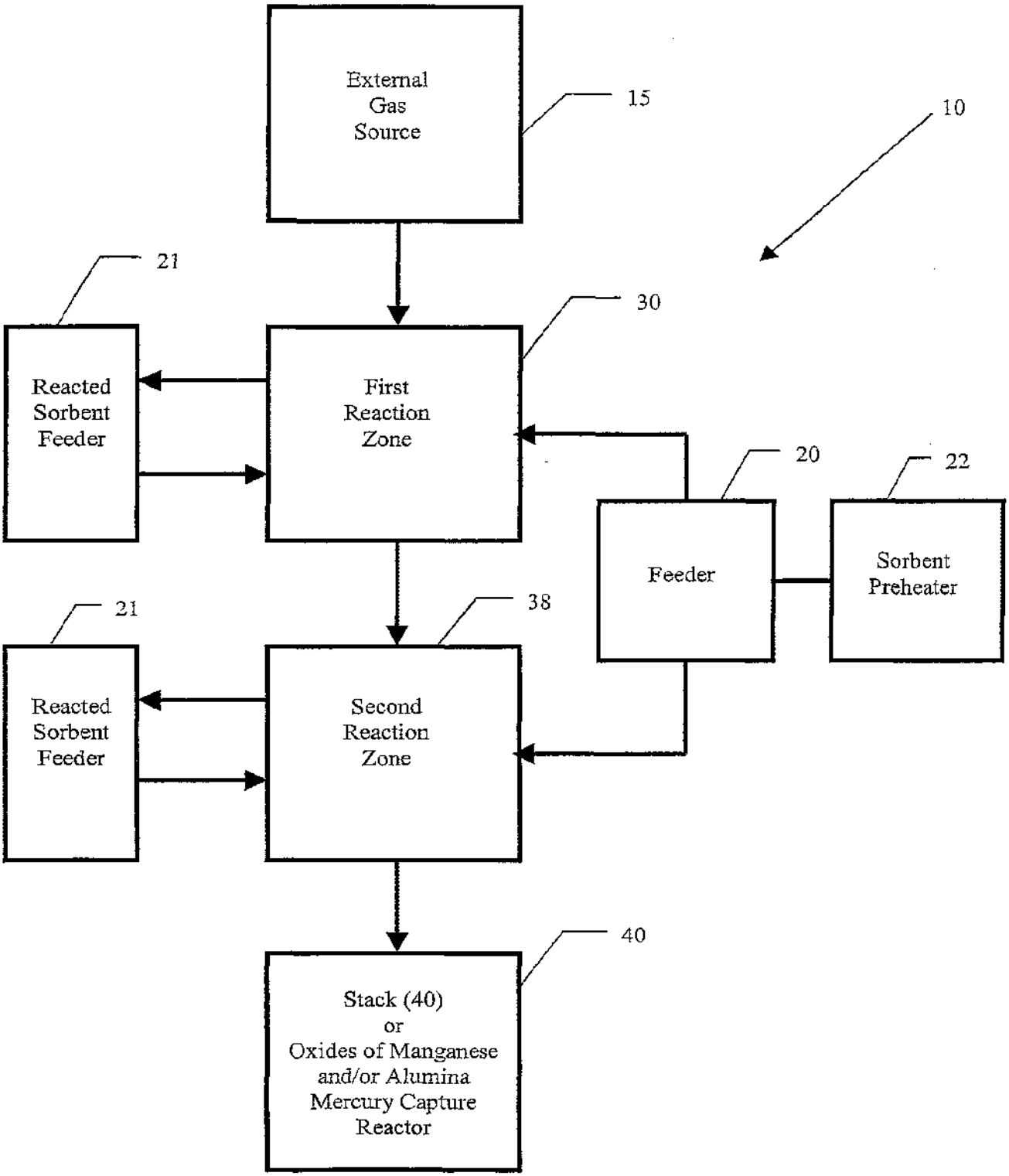
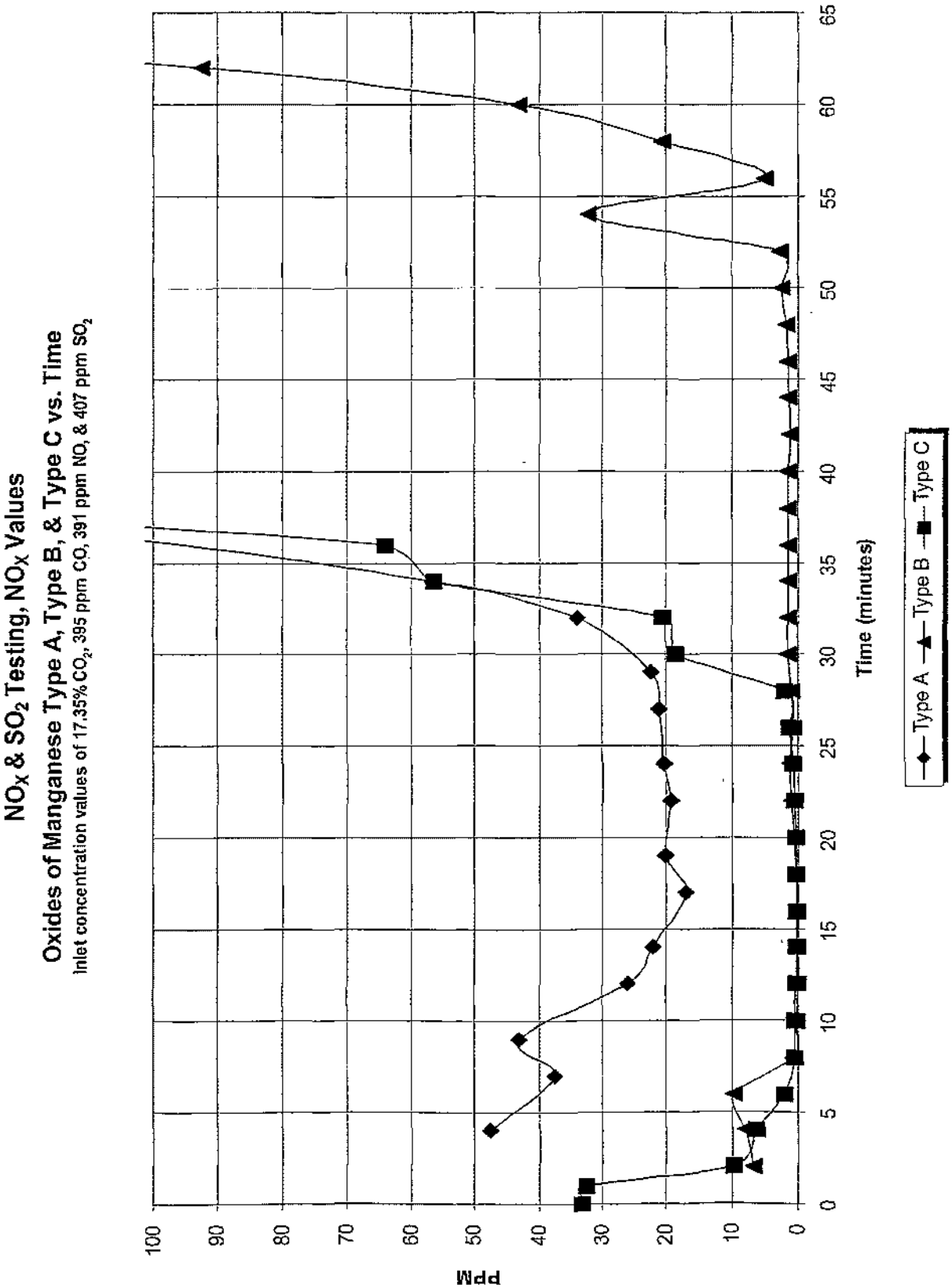
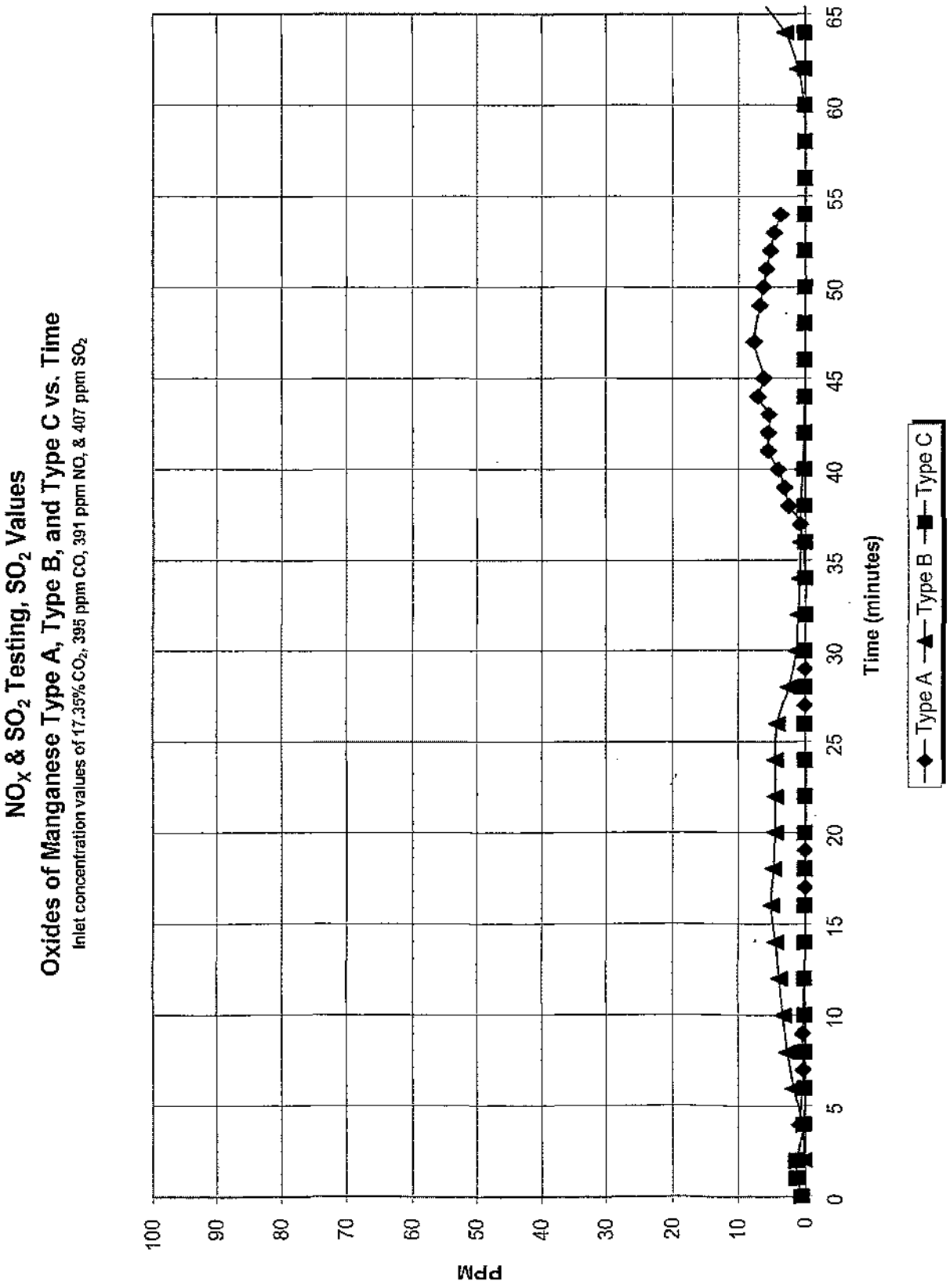


Figure 27
Current Regeneration Dry Process

Figure 28


External Gas Source
15
10
21
30
Reacted Sorbent Feeder
First Reaction Zone
20
22
Feeder
Sorbent Preheater
21
38
Reacted Sorbent Feeder
Second Reaction Zone
40
Stack (40) or Oxides of Manganese and/or Alumina Mercury Capture Reactor


NOX & SO2 Testing, NOX Values
Oxides of Manganese Type A, Type B, & Type C vs. Time
Inlet concentration values of 17.35% CO2, 395 ppm CO, 391 ppm NO, & 407 ppm SO2
ppm
Time (minutes)
Type A
Type B
Type C


NO_X & SO_2 Testing, SO_2 Values
Oxides of Manganese Type A, Type B, and Type C vs. Time
Inlet concentration values of 17.35% CO_2, 395 ppm CO, 391 ppm NO, & 407 ppm SO_2
ppm
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Time (minutes)
Type A
Type B
Type C

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International Bureau

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PCT

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(72) Inventors; and

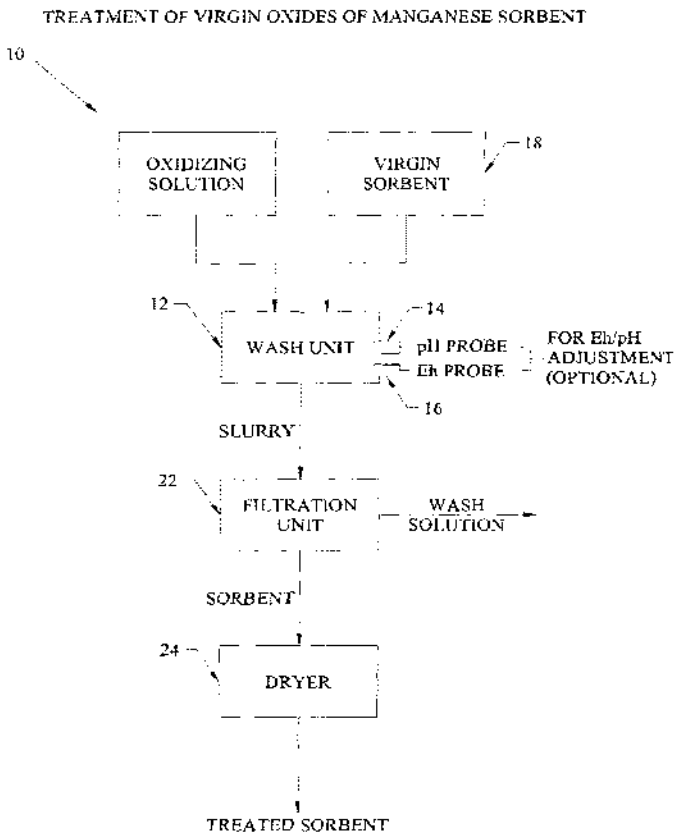
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(54) Title: PRETREATMENT AND REGENERATION OF OXIDES OF MANGANESE



(57) Abstract: The invention relates to systems and processes for treating particulate oxides of manganese useful as oxidizing sorbents for capturing or removing target pollutants from industrial gas streams, including, but not limited to, nitrogen oxides (NO_x), sulfur oxide (SO_x), mercury (Hg), hydrogen sulfide (H_2S), other totally reduced sulfides (TRS), and oxides of carbon (CO and CO_2) gases. Oxides of manganese are washed an aqueous oxidizing solution, which may be adjusted as necessary to maintain the oxidizing solution a desired range of pH (acidity) and Eh (oxidizing potential) within the MnO_2 stability area for aqueous solutions. The resulting treated oxides of manganese are equally or more efficient as sorbents as the oxides of manganese processed with the invention.

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PRETREATMENT AND REGENERATION OF OXIDES OF MANGANESE

Related Applications

This application claims priority to US Provisional Application No. 60/342,587 filed December 21, 2001, which is incorporated herein by reference.

Field of the Invention

The invention relates to systems and processes for treating oxides of manganese that may be utilized as a sorbent for capture and removal of target pollutants from industrial and other gas streams. Further, the invention relates to pollution removal systems incorporating such methods and apparatus and to oxides of manganese, oxides of manganese sorbent particles, and oxides of manganese filter cake formed by the processes of the invention.

Background of the Invention

The element manganese (Mn) may exist in six different valence (oxidation) states. Of particular interest and usefulness in the Pahlman™ systems and processes are those oxides of manganese having valence states of +2, +3, and +4, which correspond to the oxides MnO, Mn_2O_3, and MnO_2. The oxide MnO_4 is probably a solid-solution of both the +2 and +3 states.

A characteristic of most oxides of manganese species is non-stoichiometry; that is, most oxides of manganese molecules or MnO_2 species typically contain on average less than the theoretical number of 2 oxygen atoms, with numbers more typically ranging between 1.5 to 2.0. The non-stoichiometry characteristic is thought to result from solid-solution mixtures of two or more oxide species, and exists in all but the beta (β), or pyrolusite, form of manganese dioxide. Oxides of manganese having the formula MnOX where X is about 1.5 to about 2.0 are particularly suitable for dry removal of target pollutants from gas streams. However, the most active types of oxides of manganese for use as a sorbent for target pollutant removal usually have the formula $MnO_{1.7 \text{ to } 1.95}$, which translates into manganese valence states of +3.4 to +3.9, as opposed to the theoretical +4.0 state. It is unusual for average valence states above about 3.9 to exist in most forms of oxides of manganese. The

formula MnO_2, as used herein, symbolically represents all varieties of manganese dioxide including those with valence states ranging from +3 to +4, or $MnO_{1.5-2.0}$.

Oxides of manganese are known to exhibit several identifiable crystal structures, which result from different assembly combinations of their basic molecular structural units. These basic structural "building block" units are MnO_6 octahedra, which consist of one manganese atom at the geometric center, and one oxygen atom at each of the six apex positions of an octahedral geometrical shape. The octahedra may be joined together along their edges and/or corners, to form "chain" patterns, with void spaces ("tunnels"). Regular (and sometimes irregular) three-dimensional patterns consist of layers of such "chains" and "tunnels" of joined octahedra. These crystalline geometries are identified by characteristic x-ray diffraction (XRD) patterns. Most oxides of manganese are classifiable into one or more of the six fundamental crystal structures, which are called alpha (α), beta (β), gamma (γ), delta (δ), epsilon (ε), and ramsdellite. Certain older literature also included rho (ρ) and lambda (λ) structures, which are now thought obsolete, due partly to improvements in XRD technique. Some (amorphous) forms of MnO_2 exhibit no crystalline structure.

Certain characteristics of oxides of manganese probably arise from the size and shape of voids within these crystalline patterns and from certain elements, and compounds, which may occupy the voids and appear to help prevent collapse of certain structures. Applicants believe that these characteristics in addition to the oxidation state may have and affect upon the loading capacity of oxides of manganese sorbent. Further, many oxides of manganese are hydrous, and include structurally bound water. This bound water may also contribute to chemical reactivity and possibly catalytic behavior of the species.

Some oxides of manganese have the ability to absorb oxygen from gas. Manganous oxide (MnO) will oxidize to MnO_2 in the presence of air, for example. Additionally, the dioxides are themselves oxidizers, they readily exchange oxygen in chemical reactions, and they are known to have catalytic properties. This oxygen exchange ability may be related to proton mobility and lattice defects common within most MnO_2 crystal structures. The oxidizing potential of MnO_2 is advantageously utilized in target pollutant removal in the Pahlman™ and other systems and processes. Target pollutants, such as NO_X and SO_2 gases, mercury (Hg) and other pollutants, require oxidation of the species prior to reaction with MnO_2 sorbent to form reaction products, such as manganese sulfates and nitrates, mercury compounds, and other corresponding reaction products, in order for them to be captured and removed from gas stream.

Manganese compounds are soluble in water in the +2 valence state, but not in the +4 state. Therefore Mn^{+2} compounds, including MnO are readily soluble in aqueous solutions, as opposed to MnO_2. During the formation of reaction products such as manganese nitrates and sulfates, the manganese is reduced from about the +4 state to the +2 state. This property allows the reaction products formed on the surface of oxides of manganese sorbent particles to be readily dissolved and removed from the sorbent particles in aqueous solutions by disassociation into sulfate, nitrate, and Mn^{+2} ions.

Manganese dioxides are divided into three origin-based categories, which are: 1) natural (mineral) manganese dioxide (NMD), 2) chemical manganese dioxide (CMD), and 3) electrolytic manganese dioxide (EMD). As implied, NMD occurs naturally as various minerals, which may be purified by mechanical or chemical means. The most common form of NMD is pyrolusite (β-MnO_2), which is inexpensive, but has rather low chemical activity and therefore low pollutant loading capacity. CMD and EMD varieties are synthetic. EMD is produced primarily for the battery industry, which requires relatively high bulk density (which often results from relatively large, compact particles), relatively high purity, and good electrochemical activity. Though useful as a sorbent, characteristics such as low surface area and large compact particle size make EMD somewhat inferior to CMD for gas removal applications, despite its good electrochemical activity. Chemically synthesized oxides of manganese of all kinds falls into the CMD category and includes chemically treated oxides of manganese. In chemical synthesis, a great deal of control is possible over characteristics such as particle size and shape, porosity, composition, surface area, and bulk density in addition to electrochemical or oxidation potential. It is believed that these characteristic contribute the loading capacity of some oxides of manganese.

EnviroScrub Technologies Corporation has developed pollutant removal systems and processes utilizing dry and wet removal techniques and combinations thereof, incorporating the use of oxides of manganese as a sorbent. These systems and processes, commonly known as Pahlman™ systems and processes are the subject of co-pending U.S. Patent Application Numbers 09/919,600, 09/951,697, 10/044,089 and 10/025,270, the disclosures of which are incorporated herein. High target pollutant removal efficiencies have been obtained utilizing the Pahlman™ systems and processes with oxides of manganese as the sorbent. Due to pollutant loading during the removal process, the Pahlman™ system or some of its system components must be periodically taken off-line so that sorbent may be removed for regeneration and recovery of useful by-products. The frequency of such disruptions and

related downtime could be decreased if it were possible to increase the loading capacity of the sorbent. It would therefore be desirable to enhance the loading capacities of the oxides of manganese in order to extend the period of sorbent use and its loading capacity. Applicants have developed methods of treating virgin oxides of manganese and of recycle processing of loaded oxides of manganese with oxidants or oxidizers that result in treated oxides of manganese having enhanced or increased loading capacity.

Brief Description of the Drawings

Figure 1 is a block flow diagram depicting an embodiment of a treatment system and method of the invention.

Figure 2 is a block flow diagram depicting an embodiment of a treatment system and method of the invention.

Figure 3 is a sorbent loading graph.

Figure 4 is a sorbent loading graph.

Figure 5 is a sorbent loading graph.

Figure 6 is a sorbent loading graph.

Figure 7 is a block flow diagram of a treatment system and method of the invention incorporating a controller.

Figure 8 is a block flow diagram of a embodiment of a treatment system and method of the invention incorporating a controller.

Figure 9 is a Pourbaix diagram for an aqueous solution of 1 mole/liter manganese ion concentration.

Figure 10 is a Pourbaix diagram for an aqueous solution of 10^{-6} mole/liter manganese ion concentration.

Summary of the Invention

The invention relates to systems and processes for treatment of oxides of manganese that may be utilized as a sorbent for removal of target pollutants from a gas stream.

An embodiment of a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprises the steps of washing virgin oxides of manganese in wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area; and filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of

manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

Another embodiment of a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprises the steps of washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area; monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO_2 stability area; and filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese. The monitoring and adjusting step may be carried out by a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area.

An embodiment of a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprises the steps of washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; and removing the pretreated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese.

An embodiment of a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream comprises the steps of washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO_2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; and removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed.

An embodiment of a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system comprises the steps of rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; and removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed.

The above processes may further comprise the steps of drying the filter cake; and comminuting and sizing the dried filter cake to provide oxides of manganese particles. The may alternative further comprise the steps of drying the filter cake; and comminuting and sizing the dried filter cake to provide oxides of manganese particles for introduction into a feeder or reaction chamber of a dry pollution removal system. In a further alternative, they processes may further comprise the steps of drying the filter cake; comminuting and sizing the dried filter cake to provide oxides of manganese particles for introduction into a feeder or reaction chamber of a dry pollution removal system; and introducing the comminuted and sized oxides of manganese particles into the feeder or reaction chamber. In yet a further alternative, the above described processes may further comprise the step of conveying the filter cake to a dryer configured to inject the a wet filter cake or a slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system. In yet another further alternative, the above-described processes may further comprise the steps of conveying the filter cake to a dryer configured to inject the a wet filter cake or a slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system; and injecting the wet filter cake or the slurry into the reaction chamber.

In the above-described processes the aqueous oxidizing solution contains an oxidizer. The oxidizer may be selected from the group consisting of hypochlorites, perchlolates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

13 An embodiment of a system for pretreatment of virgin oxides of manganese comprising a wash unit configured to hold and agitate a slurry of virgin oxides of manganese in an aqueous oxidizing solution, the solution have Eh and pH values within the MnO_2 stability area, the wash unit being optionally equipped with a pH probe, an Eh probe, and a temperature probe, the wash unit being further configured to receive the slurry of virgin oxides of manganese or to individually receive virgin oxides of manganese and the aqueous oxidizing solution; a filtration unit configured to receive the slurry from the wash unit and to filter the slurry to form a filtrate and a pretreated oxides of manganese filter cake; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being optionally equipped with an Eh probe; an oxides of manganese vessel containing a supply of virgin oxides of manganese, the vessel having a feeder configured to feed oxides of manganese directly to the wash unit or, in conjunction with the aqueous oxidizing solution feeder to feed a slurry of virgin oxides of manganese to the wash unit; and a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the wash unit. The system of this embodiment may further comprise a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area.

This embodiment of a system for treatment of virgin or loaded oxides of manganese may further comprise a dryer for drying the filter cake; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the wash unit.

14 Another embodiment of a system for treatment of virgin or loaded oxides of manganese comprising a rapid filtration wash unit, the wash unit being configured to individually receive oxides of manganese and an aqueous oxidizing solution having a Eh and

pH values within the MnO_2 stability area, the wash unit being further configured to rapidly remove the aqueous oxidizing solution from contact with the oxides of manganese forming a filtrate and a treated oxides of manganese filter cake; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being optionally equipped with a probe selected from the group consisting of an Eh probe, a pH probe, a temperature probe, or any combination thereof; an oxides of manganese vessel containing a supply of virgin of loaded oxides of manganese, the vessel having a feeder configured to feed oxides of manganese to the wash unit; optionally, a oxidizer vessel containing a supply of oxidizer, the oxidizer vessel having feeder configured to feed oxidizer to the aqueous oxidizing solution vessel; and optionally, a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the aqueous oxidizing solution vessel. The system of this embodiment may further comprise a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of the temperature, Eh values, and pH values within the aqueous oxidizing solution vessel in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area.

This embodiment of a system for treatment of virgin or loaded oxides of manganese may further comprise a dryer for drying the filter cake; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the aqueous oxidizing solution vessel.

Another embodiment of a system for pretreatment of virgin oxides of manganese comprises a wash unit configured to hold and agitate a slurry of virgin oxides of manganese in an aqueous oxidizing solution, the solution have Eh and pH values within the MnO_2 stability area, the wash unit being equipped with a pH probe, an Eh probe, and a temperature probe, the wash unit being further configured to receive the slurry of virgin oxides of manganese or to individually receive virgin oxides of manganese and the aqueous oxidizing

solution; a filtration unit configured to receive the slurry from the wash unit and to filter the slurry to form a filtrate and a pretreated oxides of manganese filter cake; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being equipped with an Eh probe; an oxides of manganese vessel containing a supply of virgin oxides of manganese, the vessel having a feeder configured to feed oxides of manganese directly to the wash unit or, in conjunction with the aqueous oxidizing solution feeder to feed a slurry of virgin oxides of manganese to the wash unit; a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the wash unit; and a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area, the controller being electronic communication with the probes and feeders of the system.

This embodiment of a for pretreatment of virgin oxides of manganese may further comprise a dryer for drying the filter cake; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the wash unit.

18 Another embodiment of a system for treatment of virgin or loaded oxides of manganese comprises a rapid filtration wash unit, the wash unit being configured to individually receive oxides of manganese and an aqueous oxidizing solution having a Eh and pH values within the MnO_2 stability area, the wash unit being further configured to rapidly remove the aqueous oxidizing solution from contact with the oxides of manganese forming a filtrate and a treated oxides of manganese filter cake; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being equipped with a probe selected from the group

consisting of an Eh probe, a pH probe, a temperature probe, or any combination thereof; an oxides of manganese vessel containing a supply of virgin of loaded oxides of manganese, the vessel having a feeder configured to feed oxides of manganese to the wash unit; a oxidizer vessel containing a supply of oxidizer, the oxidizer vessel having feeder configured to feed oxidizer to the aqueous oxidizing solution vessel; a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the aqueous oxidizing solution vessel; and a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of the temperature, Eh values, and pH values within the aqueous oxidizing solution vessel in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area, the controller being in electronic communication with the probes and feeders of the system.

This embodiment of a system for treatment of virgin or loaded oxides of manganese may further comprise a dryer for drying the filter cake; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the aqueous oxidizing solution vessel.

In the above-described systems the aqueous oxidizing solution contains an oxidizer. The oxidizer may be selected from the group consisting of hypochlorites, perchlolates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

The invention also relates to oxides of manganese, oxides of manganese particles, and oxides of manganese filter cakes formed by the above-described processes.

Oxides of manganese particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprising the steps of washing virgin oxides of manganese in wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area; filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese; drying

the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area; monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO_2 stability area; filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese; drying the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprising the steps of washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; removing the pretreated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese; drying the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese particles may formed by a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream comprising the steps of washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO_2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed; drying the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese sorbent particles may formed by a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface

thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system, comprising the steps of rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed; drying the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese filter cakes particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area; monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO_2 stability area; and filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

Oxides of manganese filter cake may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the step of washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; wherein the oxides of manganese of the pretreated oxides of manganese filter cake have a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese.

Oxides of manganese filter cake formed by a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream comprising the step of washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values

within the MnO_2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; wherein the oxides of manganese of the regenerated oxides of manganese filter cake have a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed.

Oxides of manganese filter cake may be formed by a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system comprising the step of rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; wherein the oxides of manganese in the regenerated oxides of manganese filter cake have a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed.

In the processes for formation of the above-described oxides of manganese particles and oxides of manganese filter cakes, the aqueous oxidizing solution contains an oxidizer. The oxidizer may be selected from the group consisting of hypochlorites, perchlolates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

Detailed Description of Preferred Embodiments

The following definitions will be useful in understanding the invention disclosed herein:

"Reacted" or "loaded," as used interchangeably herein, refers in conjunction with "oxides of manganese" and/or "sorbent" to oxides of manganese or sorbent that has interacted with one or more target pollutants in a gas whether by chemical reaction, adsorption or absorption. The term does not mean that all reactive or active sites of the sorbent have been utilized as all such sites may not actually be utilized.

"Unreacted" or "virgin," as used interchangeably herein, refers in conjunction with "oxides of manganese" and/or "sorbent" to oxides of manganese or sorbent that has not interacted with target pollutants in a gas or gas stream.

"Nitrates of manganese," as used herein, refers to and includes the various forms of manganese nitrate, regardless of chemical formula, that may be formed through the chemical reaction between NO_X and the sorbent and includes hydrated forms as well.

"Sulfates of manganese," as used herein, refers to and includes the various forms of manganese sulfate, regardless of chemical formula that may be formed through the chemical reaction between SO_X and the sorbent and includes hydrated forms as well.

"Target pollutant," as used herein, refers to the pollutant or pollutants that are or are to be captured and removed from a gas stream.

"MnO_2 stability area," as used herein, refers to the region of thermodynamic stability for manganese dioxide delineated by Eh and pH values for aqueous solutions. More specifically, it refers to the region of thermodynamic stability for manganese dioxide delineated by Eh and pH values for aqueous solutions in an electrochemical stability diagram, such as presented by Pourbaix diagrams.

Oxides of manganese may be utilized for various applications. one such application is in the use as a sorbent for removal of target pollutants in gas streams. Examples of target pollutants that may be removed with an oxide of manganese sorbent, include but are not limited to, NO_X, SO_X,, mercury (Hg) and some mercury compounds, H_2S and other totally reduced sulfides (TRS), and oxides of carbon. As previously noted above, certain target pollutant removal systems and processes methods utilizing oxide of manganese sorbents and referred to as Pahlman™ systems and Pahlman™ processes are described and disclosed in co-pending U.S. patent application numbers 09/919,600, 09/951,697, 10/044,089 and 10/025,270, all assigned to EnviroScrub Technologies Corporation, the assignee of this application. The disclosures of these four patent applications are incorporated herein by reference.

Oxides of manganese sorbents are introduced into these and other pollution removal systems and interact with the target pollutants in gas streams routed through the systems as a catalyst, a reactant, an absorbent or an adsorbent.

During such interaction in the process of pollutant removal, the oxidation (or valence) state of the oxides of manganese sorbent is reduced from its original state during reaction with the target pollutants. For example, where the target pollutants are NO_X or SO_X, possibly through overall reactions such as the following:

$SO_2+MnO_2 \rightarrow MnSO_4$ Reaction (1)

$2NO + O_2+MnO_2 \rightarrow Mn(NO_3)_2$ Reaction (2)

In both of the reactions above, manganese (Mn) is reduced from the +4 valence state to +2 valence state during formation of the reaction products shown. It should be noted that the actual reactions may include other steps not shown, and that indicating Reactions 1 and 2 is not in any way intended to limit the scope of the invention, but is used only to illustrate the process.

Additionally, it is believed that reaction products, such as the salts of Reaction (1) and Reaction (2) above, form on the surfaces of the sorbent particles of oxides of manganese. These reactions may extend to some depth inside the sorbent particles. Applicants believe that formation of such reactions products occurs on the surfaces of the oxides of manganese particles, resulting in a layer or coating, which effectively isolates the covered portion of the particle surface and thereby prevents continued rapid reaction with additional target pollutants. Further, the oxidation state and thus the loading capacity of the oxides of manganese below the surface of the reaction product coating may be reduced during the pollutant removal, thus diminishing the loading capacity of sorbent even after the reaction product have been removed or disassociated into an aqueous solution.

Following reaction with the target pollutants, it is desirable for economic reasons to re-use the unreacted portions of the sorbent for subsequent cycles of pollutant gas removal. These unreacted portions may exhibit decreased loading capacity. In order to render reacted oxides of manganese effective for subsequent re-use as a gas sorbent with high removal efficiency, it is necessary to: (1) remove reaction products, such as salts from the sorbent particle surfaces and (2) restore or increase the target pollutant loading capacity of the oxides of manganese sorbent. Applicants have found that washing the loaded oxides of manganese in an aqueous oxidizing solution that has been adjusted to within the MnO_2 stability area can accomplish these requirements. Further, Applicants have found that loading capacity of virgin or unreacted sorbent can be increased by washing with aqueous oxidizing solutions.

Without being bound by theory, Applicants believe that the processing of oxides of manganese according to the invention in aqueous oxidizing solution systems maintained with the MnO_2 stability window may beneficially affect a number of sorbent characteristics. Such characteristics may include particle size and shape, crystalline structure or morphology,

porosity, composition, surface area, bulk density ,electrochemical or oxidation potential or manganese valence states.

Regardless, the increased loading capacity is achieved with aqueous oxidizing solutions. Hypochlorites, such as sodium hypochlorite (NaOCl), have been found to be a suitable oxidizers for use in the aqueous oxidizing solutions, although many other oxidizers may also be suitable for this purpose. Other suitable oxidizers include, but are not limited to chlorates, such as sodium chlorate ($NaClO_3$), perchlorates such as sodium perchlorate (Na_2ClO_4), permanganates, such as potassium permanganate ($KMnO_4$), oxygen (O_2) or air, ozone (O_3), peroxides, such as H_2O_2, and persulfates, such as sodium peroxidisulfate ($Na_2S_2O_8$). The electrochemical potential of the aqueous oxidizing solution, and therefore the effectiveness of the treatment methods of the invention, depends, in part, upon the strength of the oxidizer and/or the concentration of the oxidizer in the solution.

In the treatment methods and systems disclosed herein, the oxidizer used to prepare the aqueous oxidizing solution, must be able to provide the required electrochemical (oxidizing) potential (Eh), within the specified pH range, to provide an Eh-pH combination to achieve stable solution equilibrium, as defined by the MnO_2 stability area as delineated in a Pourbaix diagram, such as those depicted in Figures 9 and 10. In a Pourbaix diagram, the MnO_2 stability area is defined by the thermodynamically stable ranges or boundaries of pH-Eh combinations that promote the existence and formation MnO_2 (Mn having valence state of +4) as the most thermodynamically stable form of manganese in an aqueous solution system. The domain of MnO_2 stability for an aqueous solution varies based upon the various components of the system. For example, changes in dissolved manganese ion concentration, solution temperature, and competing dissolved ions will affect the boundaries of stability for MnO_2. The effects of such changes upon the boundaries of the MnO_2 stability area on a Pourbaix Eh-pH diagram can be determined either by empirical data derived from experimentation or with computer software programs known to those skilled in the art, such as HSC Chemistry distributed by Outokumpu Oy of Finland. Software may also be written to determine the MnO_2 stability area as defined by other diagrams, such as the Latimer Diagram or the Frost Diagram.

In Figure 9, ranges of pH and Eh values for thermodynamically stable aqueous solutions of various manganese compounds are illustrated in graph form for aqueous solution systems at 25° C and a 1mole/liter manganese ion concentration. Figure 10 similarly illustrates ranges of pH and Eh values for aqueous solution systems at 25° C but with a 1.0 x

10^{-6} mole/liter manganese ion concentration. The Pourbaix Window diagrams depicted in Figures 9 and 10 were derived from the diagram presented in Atlas Of Electrochemical Equilibria in Aqueous Solutions," Marcel Pourbaix, pages 286-293, National Association of Corrosion Engineers, Houston, Texas.

The Eh and pH values as plotted on the graphs delineate the boundaries of the MnO_2 stability area for each of the two aqueous solution systems, emphasized with shading in Figures 9 and 10. A comparison of the boundaries of the two shaded areas on Figures 9 and 10 is illustrative of the different stability areas that exist under different system conditions.

Regardless of the specific system conditions, under the thermodynamically stable conditions for MnO_2 at a given pH and corresponding Eh range within the MnO_2 stability area or the given system conditions, the desired manganese valence state (theoretically +4) will exist. Thus, there is no propensity for Mn compounds in the +4 valence state to degrade to +3 or +2 valence states. Applicants have found that oxides of manganese treated in oxidizing solutions maintained within the MnO_2 stability area will exhibit a Mn valence state of close to +4, resulting in a MnO_2 with target pollutant loading capacities equal to and/or greater than (increased) the loading capacities of virgin or loaded oxides of manganese.

From the graph presented in Figure 9 or 10, the thermodynamically stable ranges or boundaries of pH-Eh combinations for the particular aqueous system that will promote the existence and formation of MnO_2 can be identified. Through their understanding of the relationships between these system parameters of the MnO_2 stability area of a Pourbaix Window diagram and application thereof to conditions of a given aqueous system, Applicants are able to treat both virgin and loaded oxides of manganese sorbents so as to yield a treated sorbent, both pretreated and recycled, having equal or increased loading capacity when compared to the untreated sorbent.

Oxidizing solutions having the desired pH-Eh combination can be prepared, maintained or adjusted by increasing or decreasing oxidizer, acid, or base concentrations and/or temperature adjustment, as appropriate, so that the conditions are adjusted to remain within the MnO_2 stability area. With monitoring of Eh and pH data, an operator can make necessary adjustments in order to maintain or return the oxidizing solution to conditions within the MnO_2 stability area. Monitoring and adjusting can also be automated utilizing electronic sensors and controllers.

Virgin (unreacted) oxides of manganese sorbent particles may be treated or pretreated to increase the oxidation state and/or target pollution loading capacity. This can be

accomplished by washing virgin (unreacted) sorbent with a wash solution of volume-to-sample weight ratio (liquid-to-solids ratio) of 2:1 or greater. However, effective treatment can also be accomplished with both lower and higher liquid-to-solids ratios as well. The sorbent powder is added to an aqueous oxidizing solution, for example a hypochlorite solution, stirred or agitated for a time sufficient to achieve an increased oxidation state and/or target pollution loading capacity. The then treated sorbent is separated by filtering, and the wet particles dried, which prepares the sorbent for target pollutant removal.

This method of virgin sorbent treatment may be better understood with reference to Figure 1. Turning to Figure 1 a virgin sorbent pretreatment system 10 is illustrated. The pretreatment system includes a washing unit 12, optionally equipped with pH probe 14 and Eh probe 16. As explained later in the specification, these probes may be utilized to provide information on aqueous solution conditions that may be utilized to provided manual or electronically controlled adjustments to relative to providing and maintaining the desire pH-Eh combination and other operating conditions. For example, temperature probe (not shown) may also optionally be provided. Virgin sorbent from virgin sorbent storage 18 is introduced into wash unit 12 along with an aqueous oxidizing solution prepared to have the desired pH-Eh combination within the MnO_2 stability area. Optionally, adjustments to the slurry pH and Eh can be made using appropriate oxidants for Eh adjustment and mineral acids and bases for pH adjustments.

The solid-liquid mixture or slurry is agitated or stirred and maintained at the desire operating conditions so as to increase the loading capacity and/or the Mn oxidation state. Optionally, adjustments to the slurry pH and Eh can be made using appropriate oxidants for Eh adjustment and mineral acids or bases for pH adjustment, so that the pH/Eh combination of the slurry is maintained within the window of MnO_2 stability for the specific system.

A filtration unit 22 configured for solid-liquid separation is next provided. Suitable filtration units known and readily identified by those skilled in the art may be utilized for filtration unit 22. The slurry from wash unit 12 is conveyed to filtration unit 22 where the treated sorbent is separated from the solution, with the wash solution or filtrate being routed for re-use, other processing or disposal. Since the filtrate may yet contain useful residual oxidizer, it may not be economic or desirable to dispose of the solution after a single use. However, after multiple uses, the solution may contain an accumulation of undesired constituents, such as contaminants and debris, that may be present in a load of virgin sorbent. Such undesired constituents may impact the efficiency or continued usefulness of the filtrate

for subsequent sorbent pretreatment. At that juncture the filtrate may be disposed of or otherwise processed to recover useful values.

In any event, the treated sorbent that has been separated from the slurry is in the form of a wet sorbent cake and may be dried prior to use in a pollutant removal system such as the Pahlman™ system if the sorbent is to be fed dry into the removal system. In some removal systems the sorbent may be fed as a slurry or even as a wet sorbent cake and for such removal systems a drying step would not be required. However, where drying is required or desired prior to introduction into a pollution removal system, the wet sorbent cake is routed to a dryer 24. A variety of dryers known to those skilled in the art may be utilized for this purpose, such as a rotary kiln, heat exchanger, oven, or other suitable dryers. After drying the treated sorbent may require comminution and possible sieving to reduce the sorbent particles to the desired size. Further, the sorbent dryer 24 may be a standard cake or slurry drying system known to those skilled in the art of drying, which could include a fluidized bed dryer or a spray dryer, configured or designed to inject the wet cake or slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system. Whether dried and comminuted or routed to a cake or slurry drying system, the resulting sorbent having increased loading capacity is ready for use in a pollution removal system

Loaded (reacted) sorbent requires a different treatment in order to prepare it for reuse for target pollutant removal. Specifically, applicants have found it advantageous to rapidly remove the aqueous oxidizing solution from contact with the loaded sorbent being treated during washing once dissolved reaction products, such as soluble salts, have disassociated into solution. Applicants believe that such rapid removal of soluble salts is necessary in order to prevent possible re-deposition of a reaction product coating or layer, through precipitation of reaction products, e.g., sulfate and nitrate compounds or their derivatives, upon the washed oxides of manganese sorbent particles. Such coatings are believed to be detrimental to target pollutant removal efficiency of the sorbent. In order to prevent re-deposition of such coatings or layer, the washing or rinsing equipment is configured to prevent buildup of high dissolved salt concentrations and avoids prolonged sorbent contact with the wash solutions used.

Prolonged sorbent-solution contact should be avoided for another reason. As the reaction products are dissolved into solution, the acidity of the wash solution has been observed to increase, perhaps having a pH as low as 2.0-4.0, as a result of sulfate and nitrate salts, for example, combining with wash solution to form weak acids. Such pH shifts during

washing can and oxidizing of loaded sorbent can take the oxidizing solution outside of the MnO_2 stability area At the lower pH ranges, as illustrated in the Pourbaix Window diagram of Figure 9, an upward, sometimes significant, Eh adjustment would be required to remain within the MnO_2 stability area. Base could also be added to accomplish the desired adjustment; however, this will be ineffective if the oxidizer has been depleted, requiring oxidizer addition. As some oxidizers or oxidants are inexpensive, such Eh adjustment can be uneconomic. However, if not otherwise made, a treated sorbent with a lower valance state and/or loading capacity would result. Through avoidance of prolonged contact potentially, costly Eh adjustments and pH adjustments can be avoided or minimized and a treated sorbent with increased loading capacity can be obtained.

Rapid filtration can be accomplished by various methods such as vacuum or pressure filtration. On the laboratory scale, rapid filtration can be accomplished by placing the loaded oxides of manganese sorbent to be washed on a filter media, using an apparatus such as a Beuchner funnel, and maintaining a vacuum to the filter while applying the wash solution onto the loaded oxides of manganese sorbent. This results in rapid filtration of wash solutions through the sorbent, accompanied by rapid transport of dissolved salts away from the washed sorbent.

Loaded oxides of manganese sorbent samples are washed with an oxidizing wash solution of volume-to-sample weight ratio (liquid-to-solids ratio) of between 2:1 and 50:1 or greater, preferably 25:1 to 35:1. Within these liquid-to-solid ratios and with rapid filtration, effective dissolution and rapid removal of reaction products can be achieved, resulting in a treated or recycle processed (sometimes referred to as regenerated) sorbent having an increased oxidation state and/or target pollution loading capacity.

The system and method of recycle processing of loaded sorbent can be understood with reference to Figure 2. Turning to Figure 2 a loaded sorbent treatment or recycle processing system 30 is illustrated. The system 30 includes a combination rapid filtration wash unit 32. The wash unit 32 is configured to receive loaded sorbent from loaded sorbent storage 34 and to aqueous oxidizing solution. The wash unit 32 is further configured and operated so as to avoid and pooling of oxidizing solution or creation of a liquefied slurry or other conditions that would lead to prolonged solid-liquid contact such that the solution no longer remains within the MnO_2 stability area. Devices such as moving belt filters presses, filter presses, and filter drum presses or pressurized or vacuum filters or other such devices

known to those skilled in the art for rapid filtration washing can be used for rapid filtration wash unit 32.

Loaded sorbent is introduced into rapid-wash filtration unit 32 from loaded sorbent storage 34. An aqueous oxidizing solution prepared to have the desired pH-Eh combination within the MnO_2 stability area is then passed over and through the loaded sorbent with rapid filtration. The aqueous oxidizing solution may be monitored and adjusted prior to application to the loaded sorbent and the Eh and pH of the filtrate may be monitored. However, monitoring is not really required as long as there is no pooling so as to cause undesirable prolonged solid-liquid contact. Once the load sorbent had been washed for a time sufficient to restore or increase the loading capacity and/or Mn oxidation state, solution is no longer applied and the wet sorbent cake is routed to dryer 36. The same types and variety of dryers suitable as dryer 24 in the virgin sorbent pretreatment system 10 are suitable for use as dryer 36 in the loaded sorbent treatment system 30. And similarly, the selection will depend upon whether the recycle processed sorbent is to be introduced into a pollutant removal system dry or as a wet sorbent cake. If to be introduced dry, with comminution and possibly sieving, as necessary, the treated or recycle processed loaded sorbent is ready for re-introduction into a pollutant removal system.

It should be noted that the embodiment of the system of the invention in Figure 2 may be utilized for treatment of virgin oxides of manganese as well, even though prolonged liquid-solid contact need not be avoided for pretreatment. Thus, virgin sorbent may be treated in the system depicted in either Figure 1 or Figure 2 and by the same method as loaded sorbent.

Respectively, Figures 7 and 8 illustrate embodiments of the invention incorporating electronic controller to provide integrated simultaneous monitoring and adjustment of operational parameters for treatment of oxides of manganese with option feed back loop for checking the loading capacity of the treated sorbent.

With reference to Figure 7, the pretreatment system 40, illustrated in block flow, has a wash unit 42, a filtration unit 44, and a dryer 46. Wash unit 42 is equipped with temperature probe 47A, pH probe 47B and Eh probe 47C which are in electronic communication with a controller 50. A vessel 52 containing oxidizing solution is configured to feed oxidizing solution to wash unit 42. Virgin sorbent vessel 53 containing virgin sorbent is configured to feed virgin sorbent to wash unit 42. Acid and/or base vessel 54 is configured to feed acid and or base to wash unit 42. The feeders (not shown) of vessels 52, 53 and 54 are in electronic

communication with the controller 50. The controller is also in electronic communication with the Eh probe 55 with which the oxidizing solution vessel 53 is equipped. As illustrated treated sorbent from dryer 46 is routed to reaction chamber 56. Alternatively, sorbent from dryer 46 may be routed for storage or to a sorbent feeder prior to introduction to the reaction chamber 56. Reaction chamber 56 represents a pollution removal system or a reaction zone of a pollution removal system such as a Pahlman™ dry removal system described in co-pending U.S. patent application numbers 09/919,600, 09/951,697, 10/044,089 and 10/025,270 or any other pollution control system that utilizes oxides of manganese as a sorbent for removal of target pollutants from gas streams. Reaction chamber 56 is equipped with optional target pollutant concentration readers or continuous emission monitors (CEMS) for NO_X and SO_X readers 57A and 57B in electronic communication with controller 50.

The controller 50 interfaces with probes 47A-47C, readers 57A, 57B and the feeders of the vessels 52-54 for measurement and adjustment of operational parameters with in the pretreatment system. These parameters are important in determining the proper Eh of the aqueous oxidizing solution prior to addition to the washing unit 42 and the conditions in the washing unit 42 when the virgin sorbent is added. Eh probe 55 is in communication with controller 50 to adjust the Eh of oxidizing solution vessel 52. The controller 50 adds oxidant to vessel 52 until the desired Eh reading is abtained prior to addition to the wash unit 42. The temperature, pH, and Eh of the washing unit are monitored and adjusted so as to maintain conditions within the MnO_2 stability area.

The controller 50 contains a programmable logic controller (PLC) and other hardware components necessary for the operation of the controller such as a power supply, input and output nodules that would communicate with the probes 47A-47C and/or readers 57A, 57B, and the feeders of the vessels 52-54 . The controller 50 receives inputs from the various probes and readers and converts them into ladder logic language that would be used by an internal proportional integral derivative (PID) loop to individually and simultaneously monitor system operational parameters and to reconcile the inputs with predetermined or computer generated calculated set points for the operational parameters, such as temperature, and Eh and pH levels. As determined by computer logic, the controller 50 will send an output as necessary to any of the feeders of vessels 52-53 signaling a feeder to cycle on or to change feeder rate so as to maintain or adjust system operational parameters to within the MnO_2 stability area. The controller 50 may also contain an Ethernet card or other component that allows onsite or offsite remote display and operator interface and control as needed.

The controller 50 would be given a start command and direct the feeders of vessels 52 and 53 to inject, respectively, a predetermined amounts of virgin sorbent and oxidizing solution into the washing unit 42. The controller would signal the feed of a predetermined amount of oxidant into the aqueous oxidizing solution vessel checking and or adjusting the Eh and/or pH of the solution prior to feeding into the washing unit. The Eh of the oxidizing solution in vessel 52 may be adjusted by addition of an oxidizer in sufficient quantity as to raise the Eh to the desired level from an oxidizer vessel, not shown in Figure 7, containing a supply of oxidizer. As determined by programmed controller logic, the controller 50 would also check, based on inputs received from the probes 47A-47C and/or adjust the conditions of the washing unit by adjusting the temperature utilizing a heater or heat exchanger (not shown in Figure 7) to increase or decrease solution temperature; the pH, if needed, by increasing or decreasing the rate of base or acid feed; and the Eh, if needed, by increasing or decreasing the oxidizer concentration of the aqueous oxidizing solution. An optional, final quality control loop may be provided utilizing the readers 57A, 57B checking the loading performance of the treated sorbent by sending, for example, SOx and NOx readings back to the controller 50. As determined by controller logic, the controller 50 would then adjust the washing unit parameters, if needed, to provide treated oxides of manganese having increased loading capacity as compared to the untreated virgin sorbent contained in vessel 53. The same controller may also be used to control the entire operation of both the reaction chamber 56 and the pretreatment system 40, or separate controllers may be provided.

With reference to Figure 8, a recycle processing or regeneration system 60, for treating loaded sorbent is illustrated as a block flow diagram. The regeneration system 60 has a rapid filtration wash unit 62 from which treated sorbent is routed to dryer 64. The filtrate from wash unit 62 is directed for disposal or for other processing to recover useful values therein. Loaded sorbent vessel 66 is configured to feed loaded sorbent to wash unit 62. An oxidizing solution vessel 68 containing oxidizing solution is configured to feed oxidizing solution to wash unit 62. The feeders (not shown) of vessels 66, 68 are in electronic communication with the controller 70. Vessel 68 is equipped with an Eh probe 72A and pH probe 72B which are also in electronic communication with the controller 70. As illustrated, treated sorbent from the dryer 64 is routed to a reaction chamber 56. It being understood that, as in pretreatment system of Figure 7, the treated sorbent may be routed to a sorbent feeder or to a sorbent storage bin. Similarly, optional readers 57A, 57B are in electronic

communication with controller 70, providing a optional control loop to check loading performance of treated sorbent.

The controller 70 interfaces with the Eh probe 72A, pH probe 72B, temperature probe 72C, the readers 57A, 57B, and the feeders of the vessels 66, 68 to monitor and adjust the operational parameters of pH, Eh and temperature within the regeneration system 60. Additionally, the controller 70 interfaces with a vessel (not shown in Figure 8) and the feeder thereof to provide acid or base as necessary to the aqueous oxidizing solution. It is important to determine and adjust, as necessary, the operational parameters prior to introducing the oxidizing solution into wash unit 62 in order to assure that conditions of the oxidizing solution are within the MnO_2 stability area.

The controller 70 contains a programmable logic controller (PLC) and other components that would be necessary for the operation of the controller such as a power supply, input and output modules that would communicate with the probes 72A, 72B, 72C, the readers 57A, 57B and the feeders that supply the loaded sorbent, the aqueous oxidizing solution, and acid or base. The controller 70 receives inputs from the various probes and readers and convert them into ladder logic language that would be used by the internal proportional integral derivative (PID) loop to individually or simultaneously monitor system operational parameters and to reconcile the inputs with predetermined or computer generated calculated set points for the operational parameters. The controller 70 may also contain an Ethernet card or other component that allows onsite or offsite remote display and operator interface and control as needed. Such integrated control of the regeneration system allows a practical alternative to manual adjustments by an operator and lends itself to automation of the regeneration system even from remote locations.

The controller 70 would be given a start command and signal the feeders of the vessels 66, 68, simultaneously or in desired sequence, to inject a predetermined amount of loaded sorbent and oxidizing solution into rapid filtration wash unit 62. In order to maintain conditions of the solution within the MnO_2 stability area, the controller 70 would, as necessary, signal feed of a predetermined amount of oxidizer, acid or base into the aqueous oxidizing solution in vessel 68, regularly monitoring and/or adjusting the Eh and/or pH of the solution prior to being fed into the washing unit. As determined by the controller logic, the controller 70 would also check, based on inputs received from the probes 72A, 72B, 72C, and/or adjust the conditions of the aqueous oxidizing solution in vessel 68 by adjusting the temperature utilizing a heater or heat exchanger (not shown in Figure 8) to increase or

decrease solution temperature; the pH, if needed, by increasing or decreasing the rate of base or acid feed; and the Eh, if needed, by increasing or decreasing the oxidizer concentration of the aqueous oxidizing solution.

As in the pretreatment system, an optional, final quality control loop may be provided utilizing the readers 57A, 57B, checking the loading performance of the treated sorbent by sending, for example, SOx and NOx readings back to the controller 70. As determined by controller logic, the controller 70 would then adjust oxidizing solution parameters, if needed, to provide treated oxides of manganese having increased loading capacity as compared to the untreated loaded sorbent contained in vessel 66. The same controller may also be used to control the entire operation of both the reaction chamber 56 and the treatment system 40, or separate controllers may be provided.

Applicants conducted a series of lab-scale tests utilizing a live slipstream of an actual exhaust gas from a coal-fired combustion source in order to demonstrate the increased loaded capacity achieved with the invention. A glass reactor designed to mimic the gas-solid interactions known to be present in the reaction zones of a Pahlman™ dry target pollutant removal system was utilized for the tests. The glass reactor was a vertically positioned Pyrex™ glass cylinder having an internal diameter of 2 inches and a length of approximately 18 inches. For each test run, 50.0 grams of oxides of manganese were suspended in the reactor using a permeable fritted glass filter positioned approximately 4 inches from the bottom of the reactor, allowing for flow of the gas stream through the reactor while keeping the oxides of manganese suspended. The test reactor was insulated and configured with thermocouples for temperature readings and heating elements for temperature control to maintain a temperature set point, which in the purposes of the conducted testes was 250°F.

A NOx and SO_2 laden gas stream was pumped into the bottom of the test reactor at a flow rate which provided adequate fluidization of the bed of sorbent to promote optimal gas/solids contact. The reactor was heated during the testing to 250°F and the gas flow rate was metered at a constant 6.5 liters per minute (lpm). The slipstream of actual exhaust gas was from a 570 MW tangentially-fired coal-burning boiler operating on Powder River Basin (PRB) western coal.

The composition of the exhaust gas was measured both on the inlet and outlet of the test reactor with appropriate gas analyzers, as one skilled in the art would employ and for the test run examples presented found to be within the following ranges: Oxygen (O_2) 6-7%, carbon dioxide (CO_2) 10-12%, oxides of nitrogen (NOx) 190-250ppm, sulfur dioxide (SO_2)

400-500ppm. The composition of the inlet gas to the test reactor varied slightly from test to test, therefore the data was normalized and presented as pounds (lbs) of NOx or SO_2 into and out of the test reactor. The extent of NOx and SO_2 loading was then calculated to determine the effectiveness of the aqueous oxidizing rinse. The slipstream was passed through the fluidized bed of oxides of manganese, where the flow carried a portion of the sorbent up onto the filter, thus creating a filter cake, which mimics a bag house reaction chamber of a Pahlman™ dry target pollutant removal system.

SO_2 and NO_X concentrations were measured continuously alternating from the reactor inlet and outlet utilizing a continuous emissions monitoring system (CEMS). SO_2 concentrations were measured utilizing a Bovar Western Research model 921NMP spectrophotometric instrument and NO_X concentrations were measured utilizing a Thermo Electron model 42H chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C. Inlet gas temperature was 250° F, with a differential pressure across the permeable fritted glass filter was 2.00" of WC. Figures 3 and 4 show the results of comparative test runs conducted utilizing 50g of each of virgin EMD type oxides of manganese sorbent, to provide a baseline, and treated virgin EMD type oxides of manganese sorbent prepared according to the invention. The treated virgin EMD type oxides of manganese sorbent sample was prepared by first treating with an aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl). The measured pH and Eh values of the starting aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl) were 8.5 and 900mV respectively, which provided a solution within the MnO_2 stability area. A quantity of virgin EMD type oxides of manganese sorbent (75.3g) was then added to a mixing beaker of 151g of the aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl). The slurry was then continually stirred for a period of 15 minutes while recording data on the changing pH and Eh of the solution. The starting pH of 8.5 quickly dropped to 6.2 within the first minute of mixing and after 15 minutes had dropped to 6.1. The Eh which started at 900mV rose to 1040mV within the first minute of mixing then started slowly dropping in about even increments to a finial value of 885mV after 15 minutes. The slurry was then placed in a paper filter to separate the solids from the filtrate. The now treated EMD type oxides of manganese sorbent was then placed in a drying oven and dried for 5 hrs at 185°F (85°C). The dried sorbent was then gently deagglomerated and 50g were then placed in the laboratory test reactor for subsequent target pollutant loading, the measured data points

are plotted and identified in Figures 3 and 4 as "Virgin Sorbent Following Treatment". Along with the treated virgin EMD type sorbent loading rates, data points from untreated virgin EMD type oxides of manganese sorbent are alos plotted in Figure 3 and 4 as "Virgin Sorbent Baseline" to provide a baseline for loading capacity comparison.

Figure 3 shows the NOx loading curves. Looking at the virgin sorbent baseline, the virgin EMD type sorbent was at least achieving 90% NOx removal on a ppm basis for 24 minutes, during which time an accumulative total of 158 x 10^{-6} pounds of NOx entered into the laboratory test reactor with only 5.6 x 10^{-6} pounds of NOx exiting the reactor, for a total of 152.4 x 10^{-6} pounds of NOx being captured by the virgin EMD type oxides of manganese sorbent. The treated virgin EMD type sorbent is shown to exhibit substantially improved loading rates. NOx removal time at a NO_X removal rate of at least 90% was increased to 47 minutes. For comparison, an accumulative total of 331 x 10^{-6} pounds of NOx entered the laboratory test reactor with only 6.1 x 10^{-6} pounds of NOx exiting the reactor for a total of 324.9 x 10^{-6} pounds of NOx being captured by the treated virgin EMD type oxides of manganese sorbent

Figure 4 shows the SO_2 loading curves. Looking at the virgin sorbent baseline, the virgin EMD type sorbent was at least achieving 99% SO_2 removal on a ppm basis for 24 minutes, during which time an accumulative total of 548 x 10^{-6} pounds of SO_2 entered into the laboratory test reactor with only 1.9 x 10^{-6} pounds of SO_2 exiting the reactor, for a total of 546.1 x 10^{-6} pounds of SO_2 being captured by the virgin EMD type oxides of manganese sorbent. The treated virgin EMD type sorbent is shown to exhibit substantially improved loading rates. SO_2 removal time a a removal rate of at least 99% was increased to 61 minutes. For comparison, an accumulative total of 1266 x 10^{-6} pounds of SO_2 entered the laboratory test reactor with only 0.9 x 10^{-6} pounds of SO_2 exiting the reactor, for a total of 1265.1 x 10^{-6} pounds of SO_2 being captured by the treated virgin EMD type oxides of manganese sorbent.

Figures 5 and 6 show the results of comparative test runs conducted utilizing 50g of each of virgin EMD type oxides of manganese sorbent, to provide a baseline, and treated loaded EMD type oxides of manganese sorbent prepared according to the invention. The treated loaded EMD type sorbent sample was first treated with an aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl). The measured pH and Eh values of the starting aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl) were 8.9 and 900mV respectively, which provided a solution within the MnO_2 stability area. A quantity of loaded

EMD type oxides of manganese sorbent (98.8g) was evenly distributed on moistened filter paper, which was placed in a Beuchner funnel. After applying vacuum, a first quantity of 1650 ml of aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl) was evenly applied to the loaded EMD type sorbent surface at a rate such that no solution pooling was allowed to take place. The filtrate was then collected and the pH and Eh was measured to be 2.8 and 1070mV respectively. A second quantity of 1650 ml of an aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl) was again evenly applied to the loaded sorbent surface at a rate such that no solution pooling was allowed to take place. The second filtrate was then found to have a pH of 2.8 and an Eh of 1100mV. The now treated EMD type oxides of manganese sorbent was then placed in a drying oven and dried for 2 hrs at 185°F (85°C). The dried sorbent was then gently deagglomerated and 50g were then placed in the laboratory test reactor for subsequent target pollutant loading, the measured data points are plotted and identified in Figures 5 and 6 as "Loaded Sorbent Following Treatment." The data points from untreated virgin EMD type oxides of manganese sorbent are plotted in Figure 5 and 6 as "Virgin Sorbent Baseline" to provide a baseline for loading capacity comparison.

Figure 5 shows the NOx loading curves. Looking at the virgin sorbent baseline, the EMD type sorbent was at least achieving 90% NOx removal on a ppm basis for 24 minutes, during which time an accumulative total of 158 x 10^{-6} pounds of NOx entered into the laboratory test reactor with only 5.6 x 10^{-6} pounds of NOx exiting the reactor, for a total of 152.4 x 10^{-6} pounds of NOx being captured by the virgin EMD type oxides of manganese sorbent. The loaded EMD type sorbent following treatment is shown to exhibit substantially improved loading rates. NOx removal time at a removal rate of at least 90% was increased to 32 minutes. For comparison, an accumulative total of 222 x 10^{-6} pounds of NOx entered the laboratory test reactor with 8.4 x 10^{-6} pounds of NOx exiting the reactor, for a total of 213.6 x 10^{-6} pounds of NOx being captured by the treated loaded EMD type oxides of manganese sorbent.

Figure 6 shows the SO_2 loading curves. Looking at the virgin sorbent baseline, the EMD type sorbent was at least achieving 99% SO_2 removal on a ppm basis for 24 minutes, during which time an accumulative total of 548 x 10^{-6} pounds of SO_2 entered into the laboratory test reactor with only 1.9 x 10^{-6} pounds of SO_2 exiting the reactor, for a total of 546.1 x 10^{-6} pounds of SO_2 being captured by the virgin EMD type oxides of manganese sorbent. The treated loaded EMD type sorbent is shown to exhibit substantially improved

loading rates. SO_2 removal time at a rate of at least 99% was increased to 47 minutes. For comparison, an accumulative total of 901 x 10^{-6} pounds of SO_2 entered the laboratory test reactor with only 3.2 x 10^{-6} pounds of SO_2 exiting the reactor, for a total of 897.8 x 10^{-6} pounds of SO_2 being captured by the treated loaded EMD type oxides of manganese sorbent.

The data from the lab-scale tests presented in Figure 3-6 illustrate the increased loading capacity that is achievable with the invention.

While exemplary embodiments of this invention and methods of practicing the same have been illustrated and described, it should be understood that various changes, adaptations, and modifications might be made therein without departing from the spirit of the invention and the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area ; and

b. filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

2. A process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area ;

b. monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO_2 stability area; and

c. filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

3. A process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; and

b. removing the pretreated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese.

4. A process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream, comprising the steps of:

a. washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO_2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; and

b. removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed.

5. A process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system, comprising the steps of :

a. rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area; and

b. removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed.

6. The process of any one of claims 1 to 5, further comprising the steps of:
drying the filter cake; and
comminuting and sizing the dried filter cake to provide oxides of manganese particles.

7. The process of any one of claims 1 to 5, further comprising the steps of:
drying the filter cake;

comminuting and sizing the dried filter cake to provide oxides of manganese particles for introduction into a feeder or reaction chamber of a dry pollution removal system.

8. The process of any one of claims 1 to 5, further comprising the steps of:

drying the filter cake;

comminuting and sizing the dried filter cake to provide oxides of manganese particles for introduction into a feeder or reaction chamber of a dry pollution removal system; and

introducing the comminuted and sized oxides of manganese particles into the feeder or reaction chamber.

9. The process of any one of claims 1-5, further comprising the step of:

conveying the filter cake to a dryer configured to inject the a wet filter cake or a slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system.

10. The process of any one of claims 1-5, further comprising the steps of:

conveying the filter cake to a dryer configured to inject the a wet filter cake or a slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system; and

injecting the wet filter cake or the slurry into the reaction chamber.

11. The process of claim 2, wherein the monitoring and adjusting step is carried out by a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area.

12. The process of anyone of claims 1-5, , wherein the aqueous oxidizing solution contains an oxidizer selected from the group consisting of hypochlorites, chlorates, perchlorates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

13. A system for pretreatment of virgin oxides of manganese, comprising:

a. wash unit configured to hold and agitate a slurry of virgin oxides of manganese in an aqueous oxidizing solution, the solution have Eh and pH values within the MnO_2 stability area, the wash unit being optionally equipped with a pH probe, an Eh probe, and a temperature probe, the wash unit being further configured to receive the slurry of virgin oxides of manganese or to individually receive virgin oxides of manganese and the aqueous oxidizing solution;

b. a filtration unit configured to receive the slurry from the wash unit and to filter the slurry to form a filtrate and a pretreated oxides of manganese filter cake;

c. an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being optionally equipped with an Eh probe;

d. an oxides of manganese vessel containing a supply of virgin oxides of manganese, the vessel having a feeder configured to feed oxides of manganese directly to the wash unit or, in conjunction with the aqueous oxidizing solution feeder to feed a slurry of virgin oxides of manganese to the wash unit; and

e. a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the wash unit.

14. A system for treatment of virgin or loaded oxides of manganese, comprising:

a. a rapid filtration wash unit, the wash unit being configured to individually receive oxides of manganese and an aqueous oxidizing solution having a Eh and pH values within the MnO_2 stability area, the wash unit being further configured to rapidly remove the aqueous oxidizing solution from contact with the oxides of manganese forming a filtrate and a treated oxides of manganese filter cake;

b. an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being optionally equipped with a probe selected from the group consisting of an Eh probe, a pH probe, a temperature probe, or any combination thereof;

c. an oxides of manganese vessel containing a supply of virgin or loaded oxides of manganese, the vessel having a feeder configured to feed oxides of manganese to the wash unit; and

d. optionally, a oxidizer vessel containing a supply of oxidizer, the oxidizer vessel having feeder configured to feed oxidizer to the aqueous oxidizing solution vessel; and

e. optionally, a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the aqueous oxidizing solution vessel.

15. The system of claim 13, further comprising

a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area.

16. The system of claim 14, further comprising

a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of the temperature, Eh values, and pH values within the aqueous oxidizing solution vessel in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area.

17. A system for pretreatment of virgin oxides of manganese, comprising:

a. a wash unit configured to hold and agitate a slurry of virgin oxides of manganese in an aqueous oxidizing solution, the solution have Eh and pH values within the MnO_2 stability area, the wash unit being equipped with a pH probe, an Eh probe, and a temperature probe, the wash unit being further configured to receive the slurry of virgin oxides of manganese or to individually receive virgin oxides of manganese and the aqueous oxidizing solution;

b. a filtration unit configured to receive the slurry from the wash unit and to filter the slurry to form a filtrate and a pretreated oxides of manganese filter cake;

c. an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having

a feeder configured to feed aqueous oxidizing solution to the wash unit and being equipped with an Eh probe;

d. an oxides of manganese vessel containing a supply of virgin oxides of manganese, the vessel having a feeder configured to feed oxides of manganese directly to the wash unit or, in conjunction with the aqueous oxidizing solution feeder to feed a slurry of virgin oxides of manganese to the wash unit;

e. a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the wash unit;

f. a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area, the controller being electronic communication with the probes and feeders of the system..

18. A system for treatment of virgin or loaded oxides of manganese, comprising:

a. a rapid filtration wash unit, the wash unit being configured to individually receive oxides of manganese and an aqueous oxidizing solution having a Eh and pH values within the MnO_2 stability area, the wash unit being further configured to rapidly remove the aqueous oxidizing solution from contact with the oxides of manganese forming a filtrate and a treated oxides of manganese filter cake;

b. an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being equipped with a probe selected from the group consisting of an Eh probe, a pH probe, a temperature probe, or any combination thereof;

c. an oxides of manganese vessel containing a supply of virgin or loaded oxides of manganese, the vessel having a feeder configured to feed oxides of manganese to the wash unit;

d. a oxidizer vessel containing a supply of oxidizer, the oxidizer vessel having feeder configured to feed oxidizer to the aqueous oxidizing solution vessel;

e. a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the aqueous oxidizing solution vessel; and

f. a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of the temperature, Eh values, and pH values within the aqueous oxidizing solution vessel in order to maintain conditions of the aqueous oxidizing solution within the MnO_2 stability area, the controller being in electronic communication with the probes and feeders of the system.

19. The system of any one of claims 13, 14, 17, or 18, wherein the aqueous oxidizing solution contains an oxidizer selected from the group consisting of hypochlorites, chlorates, perchlorates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

20. The system of claim 15, further comprising,

a dryer for drying the filter cake;

a device for comminuting and sizing the dried filter cake to form oxides of manganese particles;

a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the wash unit.

21. The system of claim 16, further comprising:

a dryer for drying the filter cake;

a device for comminuting and sizing the dried filter cake to form oxides of manganese particles;

a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the aqueous oxidizing solution vessel.

22. The system of claim 17, further comprising,

a dryer for drying the filter cake;

a device for comminuting and sizing the dried filter cake to form oxides of manganese particles;

a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the wash unit.

23. The system of claim 18, further comprising:

a dryer for drying the filter cake;

a device for comminuting and sizing the dried filter cake to form oxides of manganese particles;

a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the aqueous oxidizing solution vessel.

24. Oxides of manganese particles formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area ;

b. filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese;

c. drying the filter cake; and

d. comminuting and sizing the dried filter cake to form oxides of manganese particles.

25. Oxides of manganese particles formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area ;

b. monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO_2 stability area;

c. filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese;

d. drying the filter cake; and

e. comminuting and sizing the dried filter cake to form oxides of manganese particles.

26. Oxides of manganese particles formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area;

b. removing the pretreated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese;

c. drying the filter cake; and

d. comminuting and sizing the dried filter cake to form oxides of manganese particles.

27. Oxides of manganese particles formed by a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream, comprising the steps of:

a. washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO_2 stability area to form a filtrate and a regenerated oxides of manganese filter cake;

b. removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed;

c. drying the filter cake; and

d. comminuting and sizing the dried filter cake to form oxides of manganese particles.

28. Oxides of manganese sorbent particles formed by a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system, comprising the steps of:

a. rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to

form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area;

b. removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed;

c. drying the filter cake; and

d. comminuting and sizing the dried filter cake to form oxides of manganese particles.

29. The oxides of manganese particles formed by the process of anyone of claims 24-28, wherein the aqueous oxidizing solution contains an oxidizer selected from the group consisting of hypochlorites, chlorates, perchlorates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

30. Oxides of manganese filter cakes particles formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of:

a. washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO_2 stability area ;

b. monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO_2 stability area; and

c. filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

31. Oxides of manganese filter cake formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the step of:

washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area;

wherein the oxides of manganese of the pretreated oxides of manganese filter cake have a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese.

32. Oxides of manganese filter cake formed by a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream, comprising the step of:

washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO_2 stability area to form a filtrate and a regenerated oxides of manganese filter cake;

wherein the oxides of manganese of the regenerated oxides of manganese filter cake have a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed.

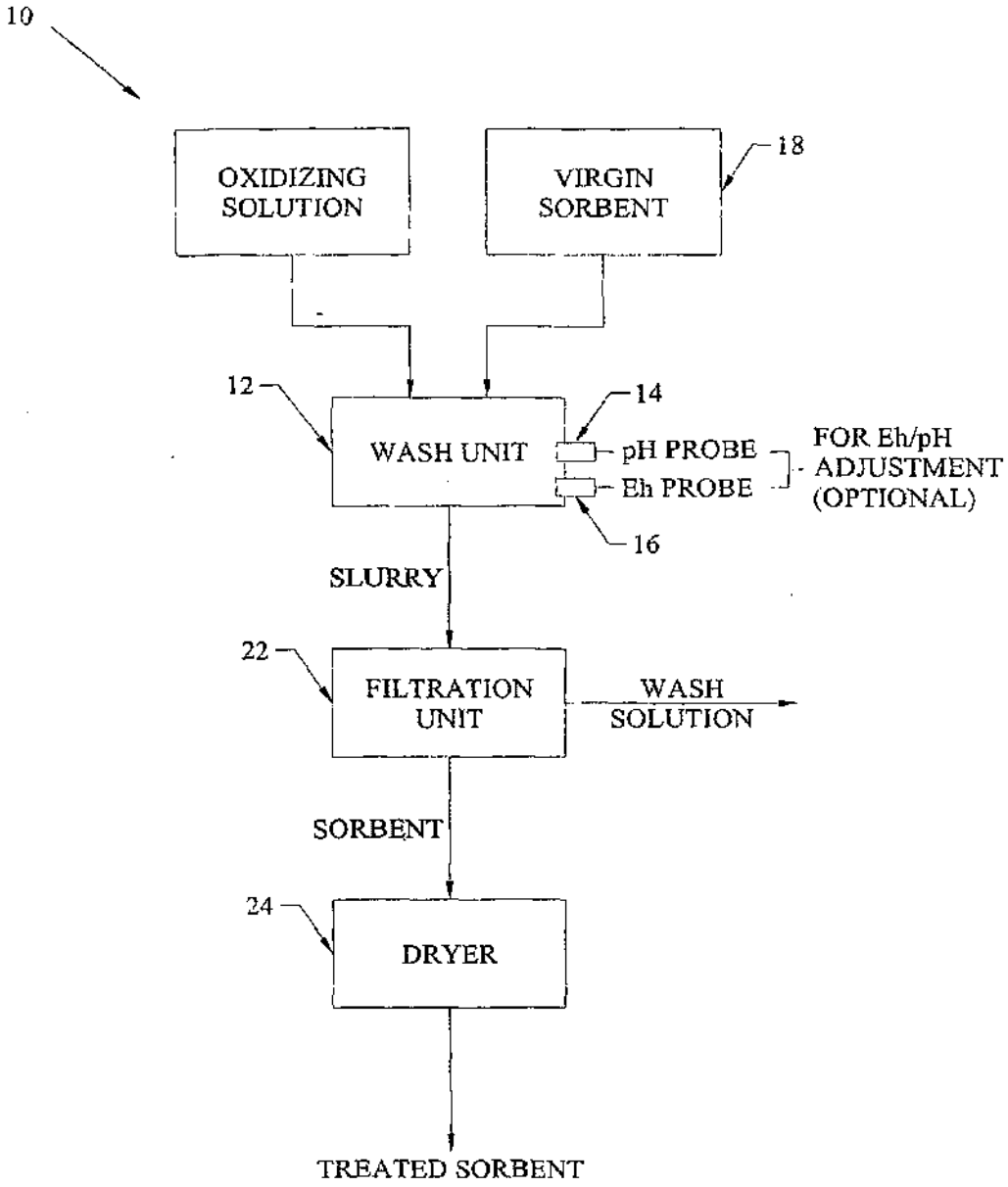
33. Oxides of manganese filter cake formed by a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system, comprising the step of:

rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the MnO_2 stability area;

wherein the oxides of manganese in the regenerated oxides of manganese filter cake have a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed.

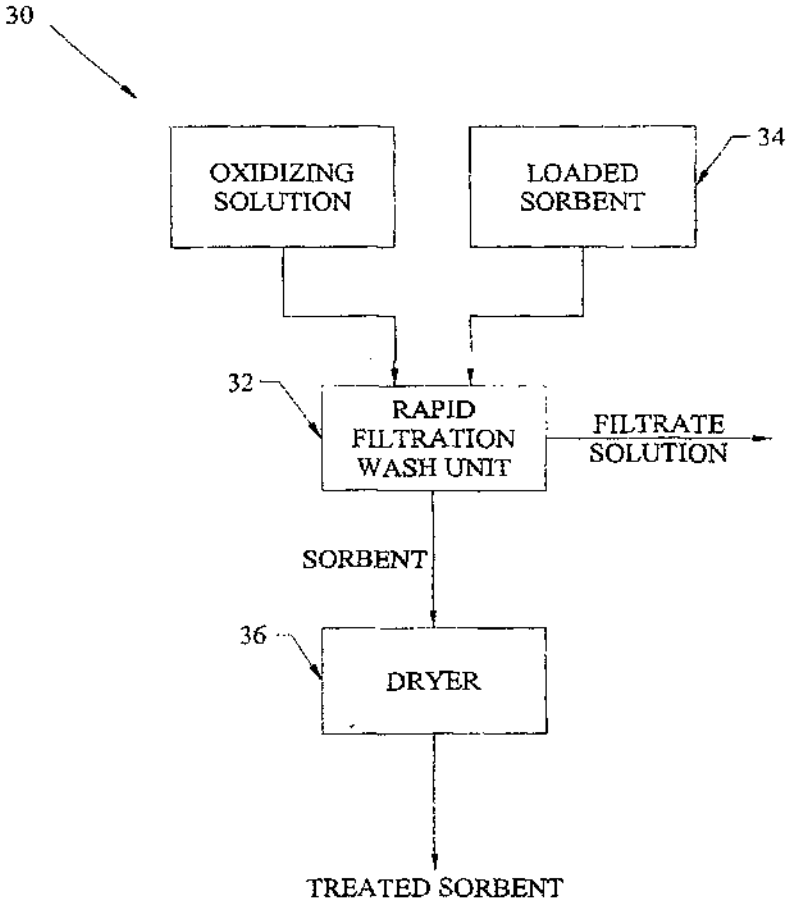
34. The filter cakes of anyone of claims 30-33, wherein the aqueous oxidizing solution contains an oxidizer selected from the group consisting of hypochlorites, chlorates, perchlorates, permanganates, oxygen (O_2), air, ozone, peroxides, persulfates, and combinations thereof.

FIGURE 1
TREATMENT OF VIRGIN OXIDES OF MANGANESE SORBENT



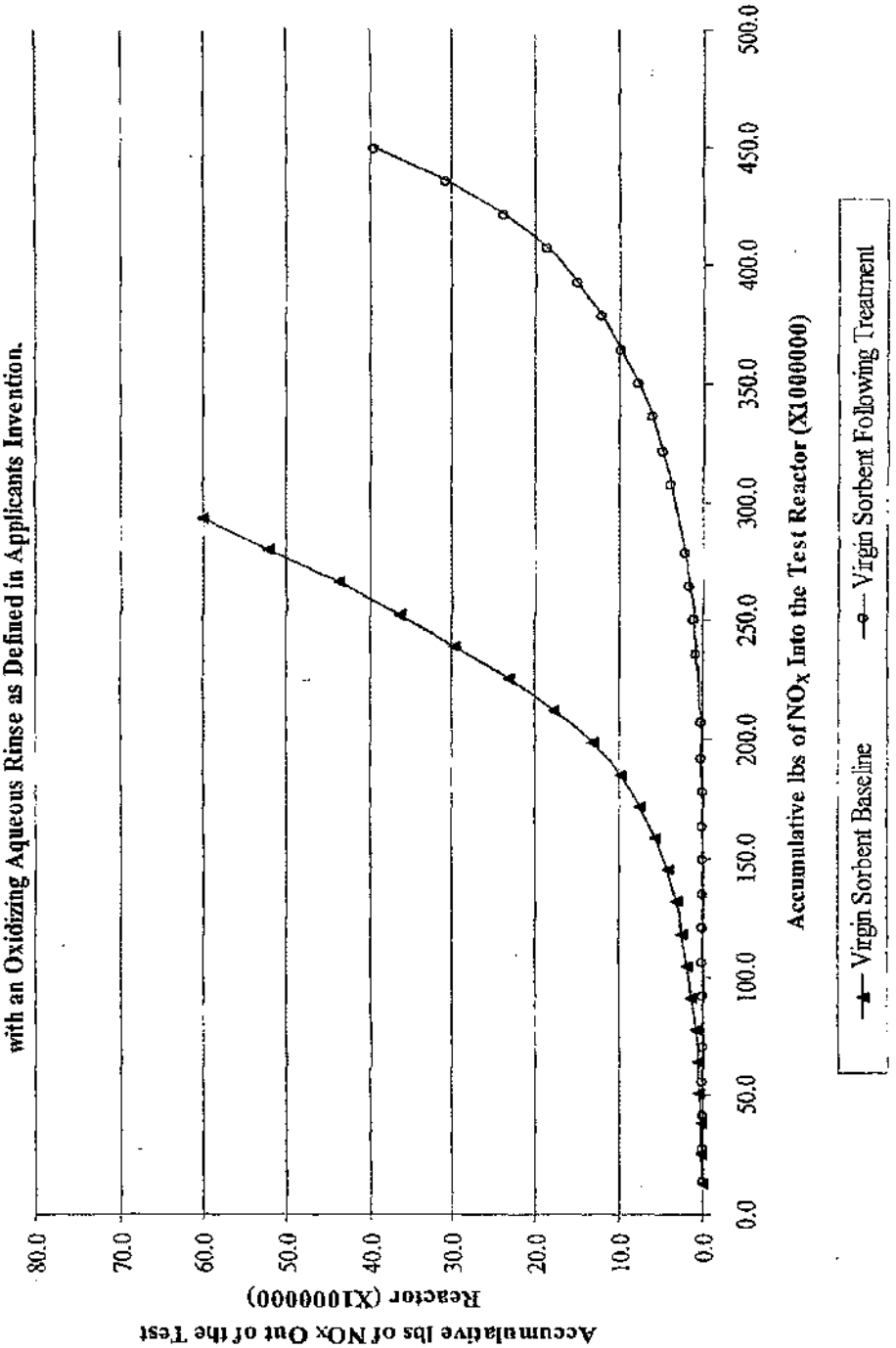
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FIGURE 2
TREATMENT OF LOADED OXIDES OF MANGANESE SORBENT



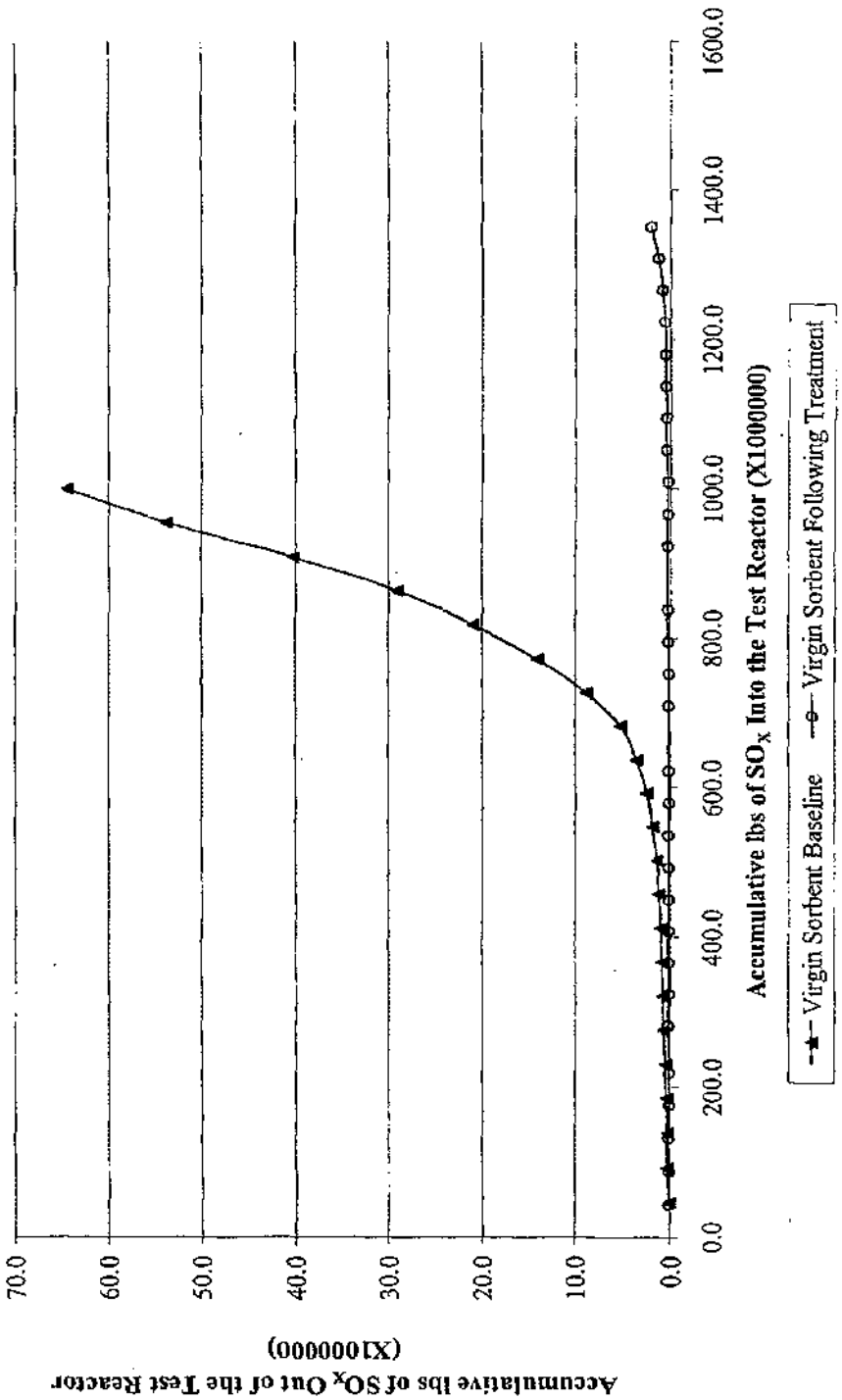
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Figure 3
NO_X Loading of Virgin Unreacted Oxides of Manganese Sorbent Following Treatment with an Oxidizing Aqueous Rinse as Defined in Applicants Invention.



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Figure 4
SO_X Loading of Virgin Unreacted Oxides of Manganese Sorbent Following Treatment with an Oxidizing Aqueous Rinse as Defined in Applicants Invention.



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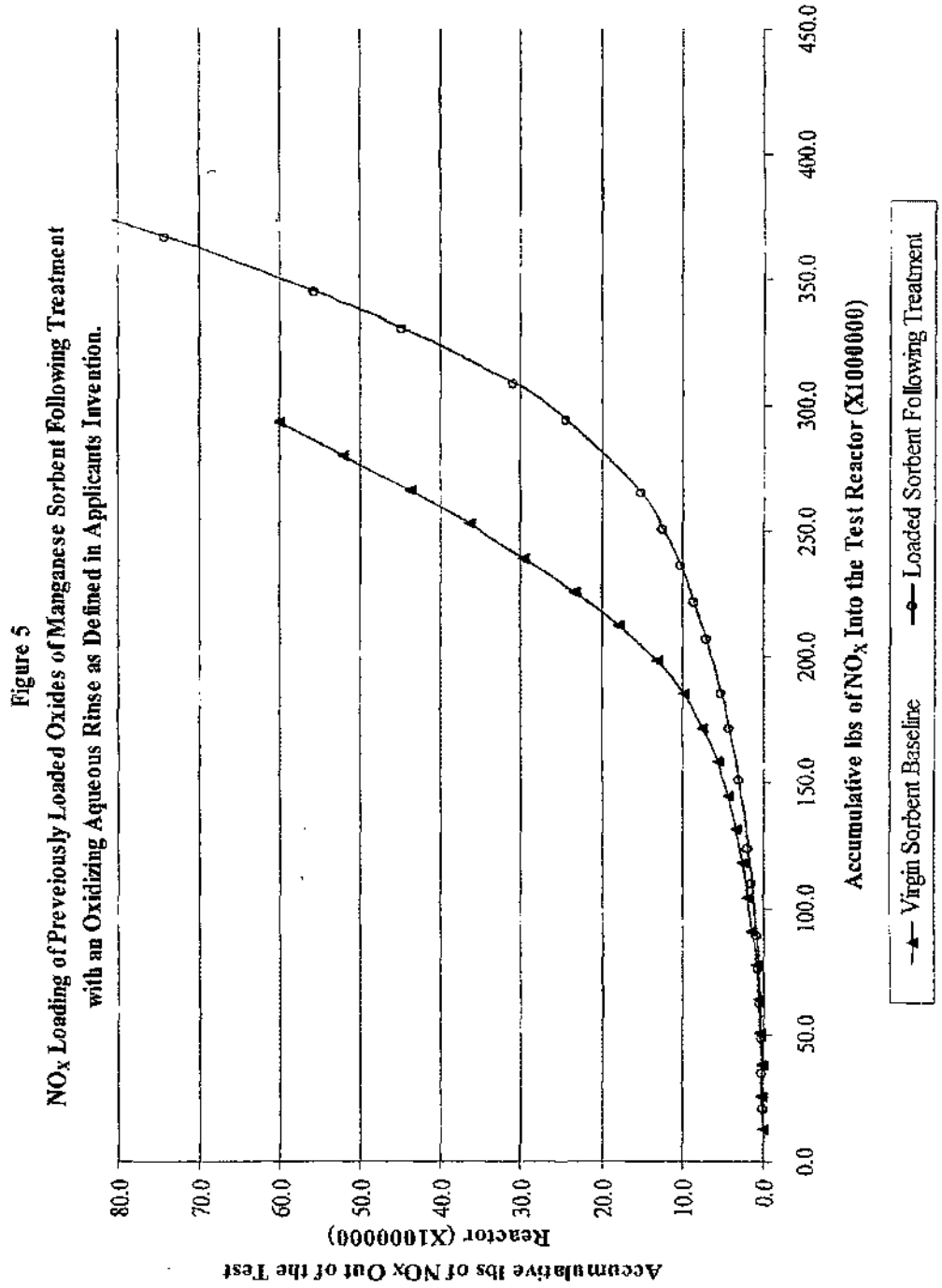
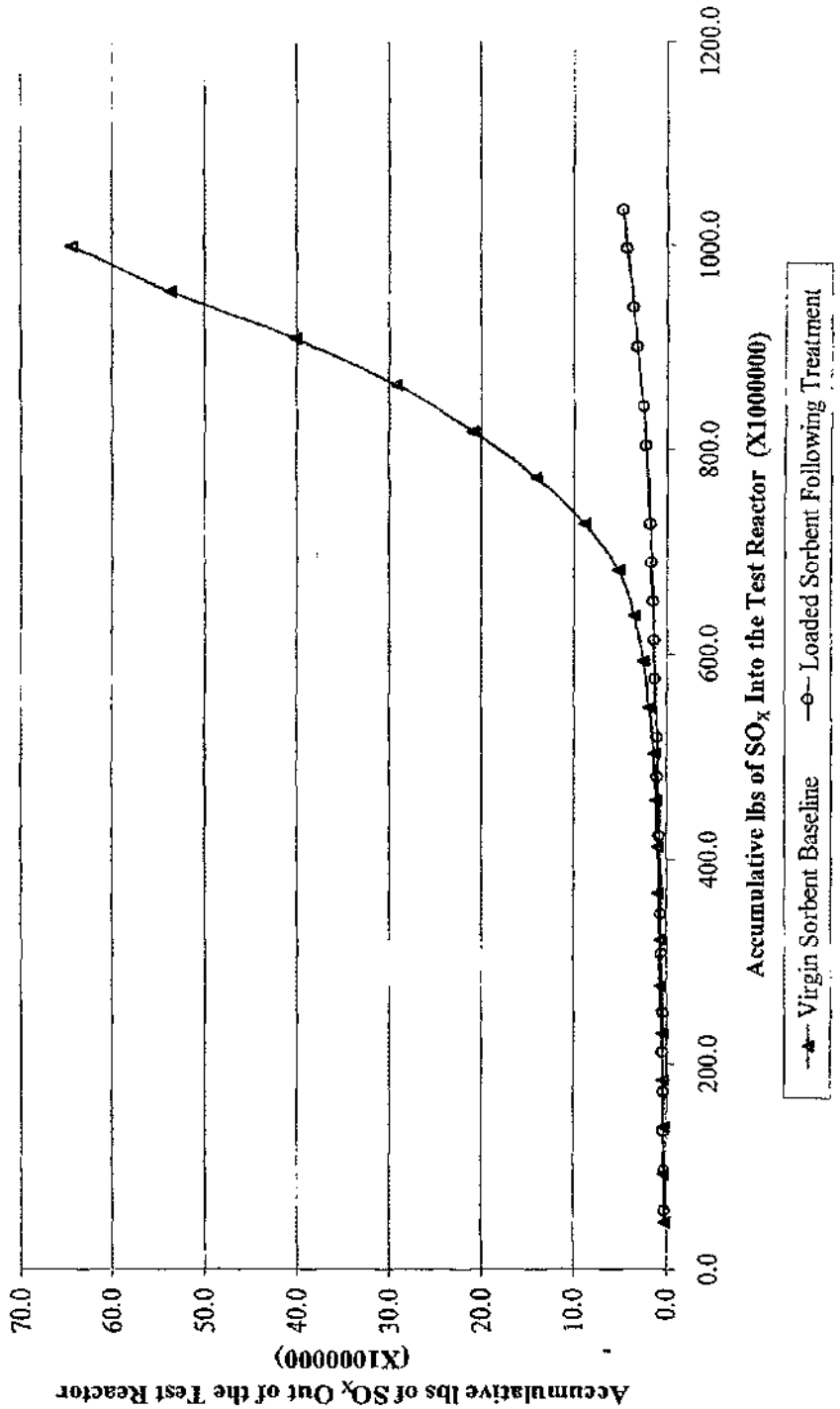


Figure 5
NO_X Loading of Preveiously Loaded Oxides of Manganese Sorbent Following Treatment with an Oxidizing Aqueous Rinse as Defined in Applicants Invention.

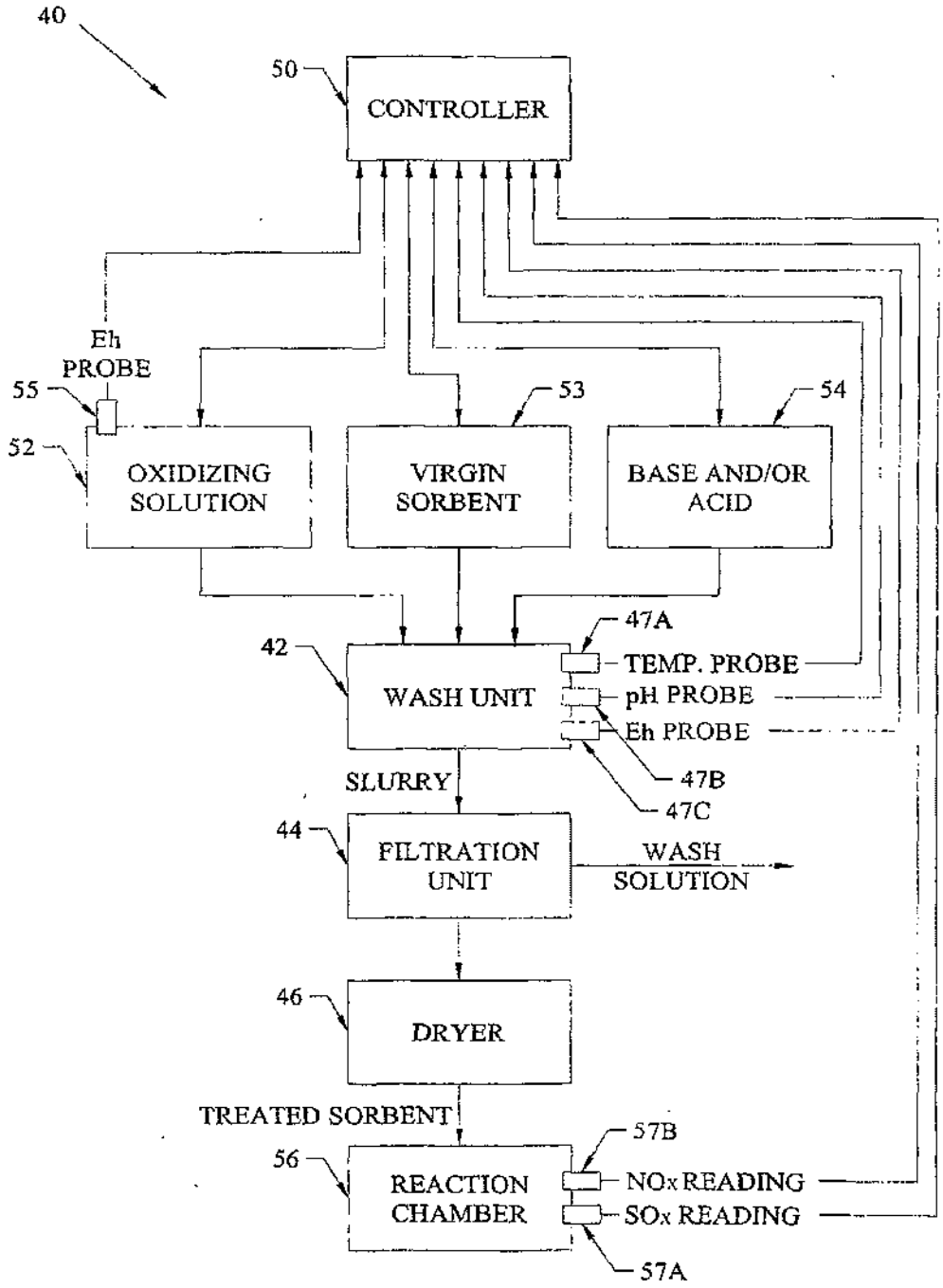
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Figure 6
SO_X Loading of Preveciously Loaded Oxides of Manganese Sorbent Following Treatment with an Oxidizing Aqueous Rinse as Defined in Applicants Invention.



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FIGURE 7
TREATMENT OF VIRGIN OXIDES OF MANGANESE SORBENT



8/10
FIGURE 8
TREATMENT OF LOADED OXIDES OF MANGANESE SORBENT

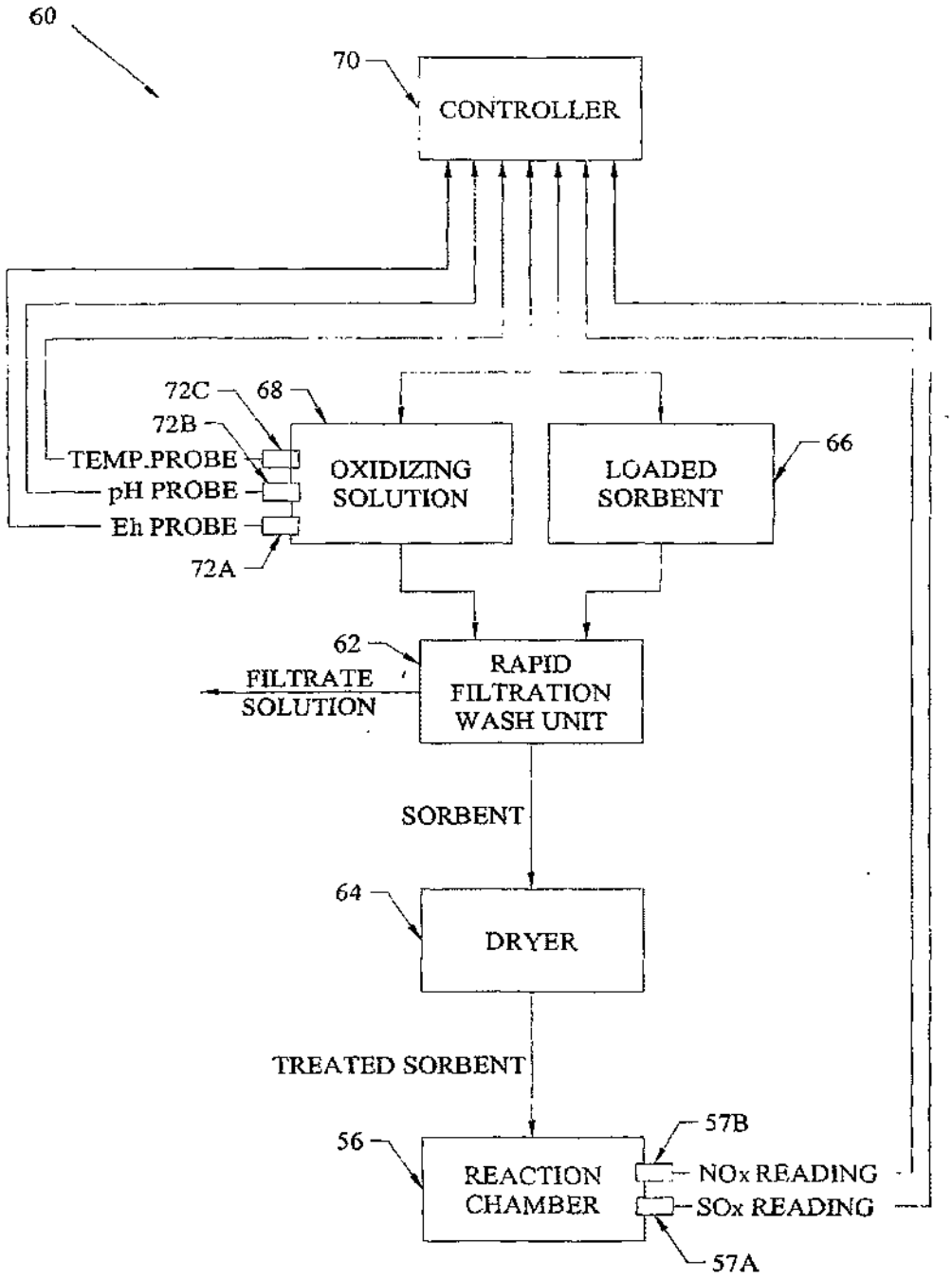


FIGURE 9
POURBAIX DIAGRAM AT 25° C WITH $1x10^0$ DISSOLVED MANGANESE CONCENTRATOIN

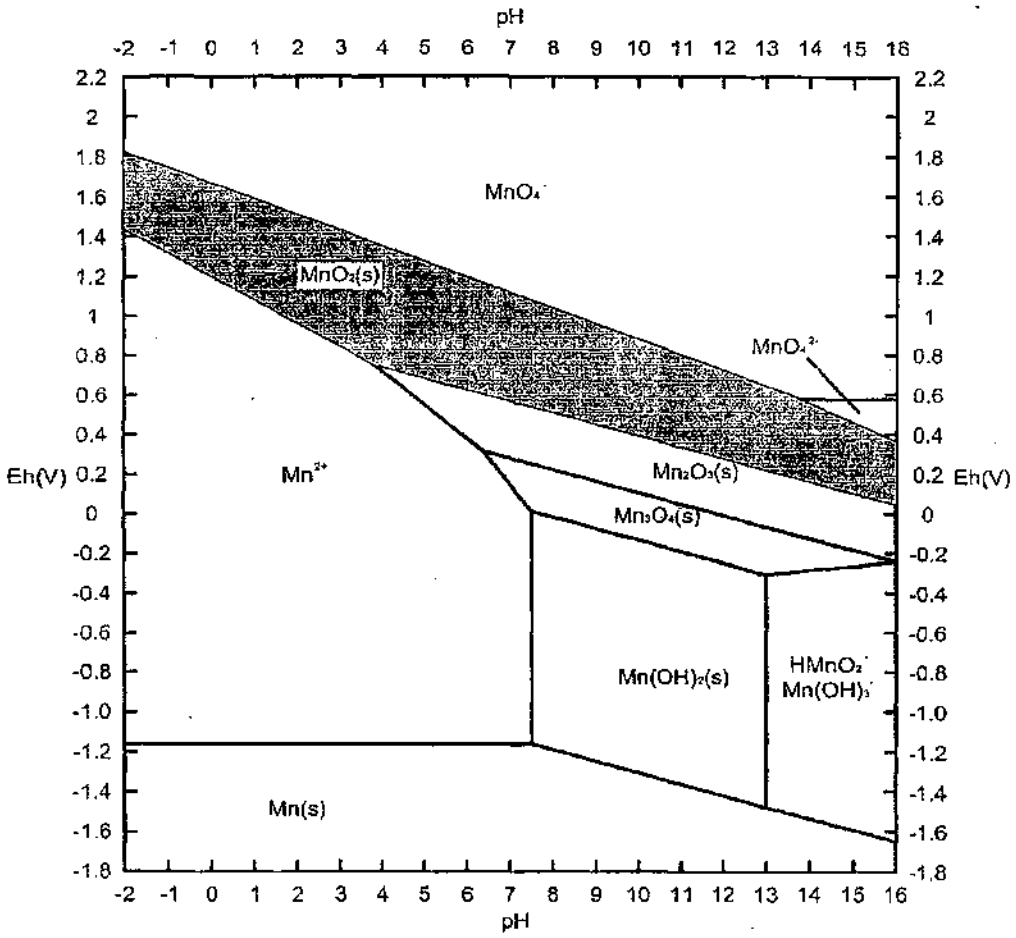
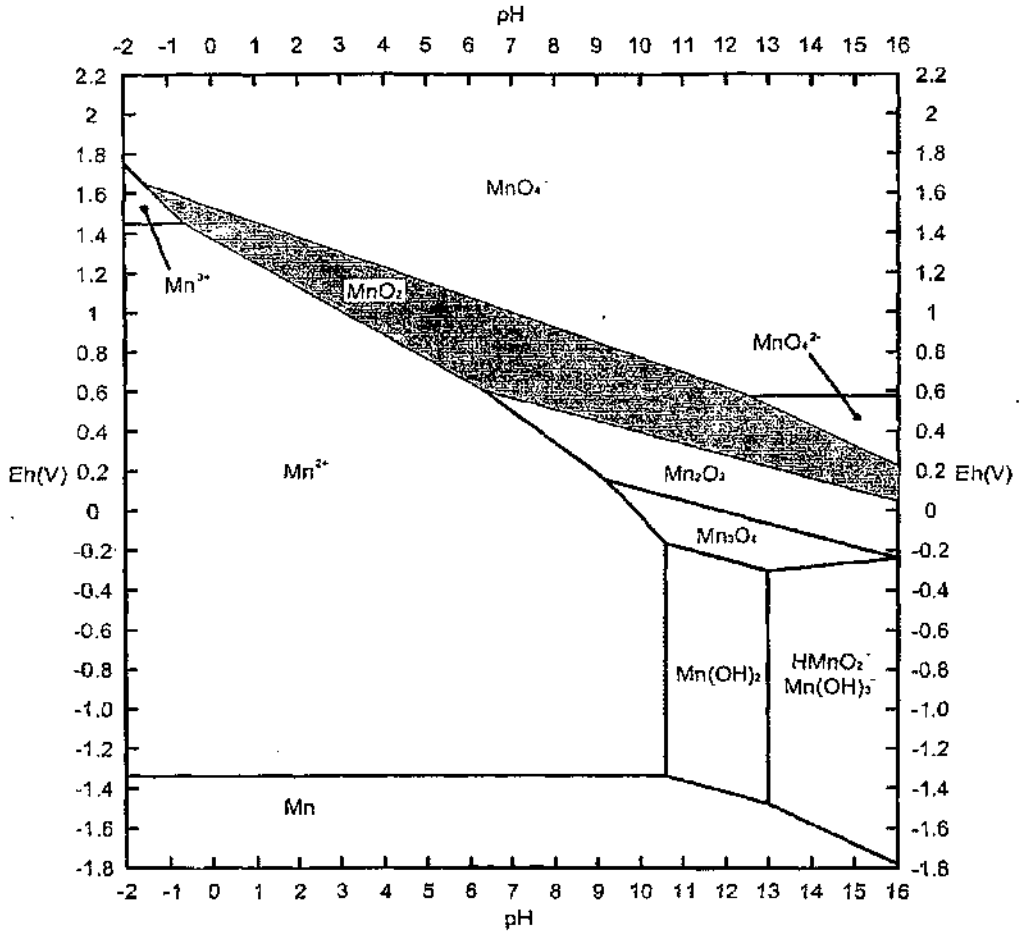


FIGURE 10
POURBAIX DIAGRAM AT 25° C WITH $1x10^{-6}$ DISSOLVED MANGANESE CONCENTRATION



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/41276

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J20/06 B01J20/34 B01J23/34

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 7 B01J

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, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 552 734 A (IANNICELLI JOSEPH ET AL) 12 November 1985 (1985-11-12) column 4, line 7 -column 9, line 65; claims; figures; examples	1-34
X	US 5 366 710 A (CHOU CHARLES C ET AL) 22 November 1994 (1994-11-22) column 2, line 53 -column 5, line 68; claims; figures; examples; tables	1-34
X	US 4 164 545 A (SCOTT RICHARD L) 14 August 1979 (1979-08-14) column 1, line 8 -column 4, line 39; claims; figures; examples; tables	1-34

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in 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
13 June 2003	27/06/2003

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, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	de Cauwer, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/41276

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 923 688 A (IANNICELLI JOSEPH) 8 May 1990 (1990-05-08) column 2, line 67 -column 8, line 45; claims; figures; examples	1-34
P,X	WO 02 28513 A (ENVIROSCRUB TECHNOLOGIES CORP) 11 April 2002 (2002-04-11) the whole document	1-34
P,X	WO 02 09852 A (ENVIROSCRUB TECHNOLOGIES CORP ;PAHLMAN KATHLEEN S HF (US); AXEN ST) 7 February 2002 (2002-02-07) the whole document	1-34

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/41276

Box I Observations where certain claims were found unsearchable (Continuation of item 1 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:
see FURTHER INFORMATION sheet PCT/ISA/210

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 II Observations where unity of invention is lacking (Continuation of item 2 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 an additional fee, this Authority did not invite payment of any additional fee.

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.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

In view of the large number and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise), namely a process for the (pre)treatment of oxides of manganese, a system therefore and the products thereof as described in the lab-scale test on page 25 to 29.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/41276

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4552734	A	12-11-1985	CA	1216732 A1	20-01-1987
			DK	410584 A	09-03-1985
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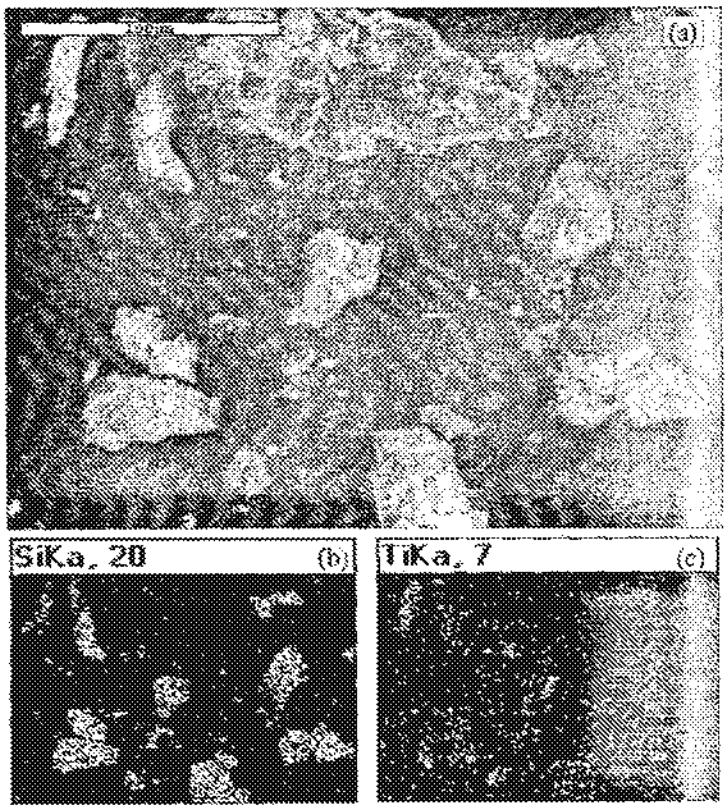
(72) Inventors; and
(75) Inventors/Applicants (*for US only*): MAZYCK, David, W. [US/US]; 9505 NW 4th Place, Gainesville, FL 32607 (US). WU, Chang-Yu [US/US]; 5400 NW 39th Avenue, Apt. L108, Gainesville, FL 32606 (US). PITONIAK, Erik, R. [US/US]; 117 NW 15th Street, Gainesville, FL 32603 (US). POWERS, Kevin, W. [US/US]; 5007 NW 75th Lane, Gainesville, FL 32653 (US). LONDEREE, Danielle, J. [US/US]; 281 SE 18th Avenue, Deerfield Beach, FL 33441 (US).

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, 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, NA, NI, NO, NZ, OM, PG,

[Continued on next page]

(54) Title: METHOD AND A COMPOSITE FOR MERCURY CAPTURE FROM FLUID STREAMS



(57) Abstract: A method for removing mercury from a fluid stream includes the steps of providing a porous composite material comprising a substrate and a plurality of catalyst and/or photocatalyst particles, and contacting substrate with a fluid stream. The porous composite material adsorbs and/or then oxidizes or reduces metallic species including elemental mercury. A fossil fuel fired power plant can include an emission control device comprising the porous composite material to filter flue gas to and thereby minimize mercury emissions into the environment.

WO 2004/089501 A2

PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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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.

METHOD AND A COMPOSITE FOR MERCURY CAPTURE FROM FLUID STREAMS

[01] This application claims benefit under 35 U.S.C. § 119(e) to U.S. Provisional Application Serial No. 60/452,572, filed March 6, 2003, the disclosure of which is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[02] The U.S. Government has certain rights to the invention based on Environmental Protection Agency Grant/Contract No. R-82960201 and National Aeronautics and Space Administration Grant/Contract No. NCC 9-110, both with the University of Florida.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[03] This invention is directed to methods and composite materials for purifying fluid streams. For example, fields of the invention include flue gases emitted from combustion sources (e.g., coal-fired power plants, waste-to-energy facilities, medicinal and similar incinerators, and industrial manufactures) and for purifying ground, surface, and/or industrially processed waters. More particularly, the invention relates to removal of mercury and other contaminants from a fluid stream by adsorption and either subsequent or continuous catalytic and photocatalytic oxidation using catalyst and photocatalyst impregnated or doped sorbents (e.g., silica-gels).

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2. Description of the Related Prior Art

[04] Mercury emission from combustion sources is a significant environmental concern. When mercury is released into the atmosphere, it can be transported by wind and then through direct deposition can accumulate in surface waters. In the water, biological processes can transform mercury (typically elemental mercury) into methylmercury, which is highly toxic and can bioaccumulate in fish. Therefore, preventing the release of mercury into the environment is very important.

[05] The largest emitters of mercury are coal-fired electric utility plants, which account for an estimated more than 90% of all anthropogenic mercury emissions. Mercury is also listed as one of the 189 hazardous air pollutants (HAPs) in the 1990 Clean Air Act Amendments (CAAA). Regulations are being set for future emission standards for combustion sources to be implemented as early as 2007.

[06] The unique feature of mercury emission that differs from other toxic metals results from mercury's $5d^{10}6s^2$ closed shell electronic structure that is isoelectronic to He ($1s^2$), and is accordingly highly stable in its elemental state. As a result, unlike other toxic metals, the dominant form of mercury in combustion exhaust is elemental mercury (Hg^0) vapor, unless chlorine is present. Since Hg^0 is insoluble, gas removal devices, such as scrubbers, are also ineffective for its removal. Similarly, particulate removal devices (e.g., baghouses and electrostatic precipitators) are also highly ineffective.

[07] In recent years, numerous studies for enhanced mercury removal from combustion sources have been undertaken. Generally the methods used in these studies were based on either adsorption or oxidation. Currently, the maximum available control technology (MACT) for mercury is powdered activated carbon injection. However, its predicted use is limited because of questionable costs, presently low capacity, low applicable temperature

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range, and problems associated with collection and regeneration of the carbon. This approach has been estimated to cost about $2-5 billion annually to implement in U.S. coal-fired power plants.

[08] In addition to activated carbon, calcium-based sorbents such as hydrated lime have also been considered. However, calcium-based sorbents provide poor efficiency for mercury removal unless they are modified with fly ash. Studies have also been carried out using zeolite and bentonite, but they have demonstrated very low capacity for mercury.

[09] The use of an advanced oxidation process has also been investigated for mercury removal. Heterogeneous photocatalysis is one such method that utilizes a semiconductor in the oxidation and mineralization of pollutants, either in the air phase or water phase. When the surface of the photocatalyst absorbs a specific amount of energy (usually a photon), an electron from the valence band is promoted to the conduction band, thereby leaving a positive charged "hole" in the valence band. Reactions with these electron-hole pairs result in the formation of hydroxyl radicals (OH), which are very reactive oxidizing species. Titanium dioxide (TiO_2) is one such semiconductor/catalyst that can be activated when irradiated by UV light.

[10] Wu et al. (*Env. Eng. Sci.* 1998;15(2):137-148) and Lee et al. (*AIChE J* 2001;47:954-961) used TiO_2 nano-aerosols generated in-situ in combustion systems to effectively transform elemental mercury into mercuric oxide. This process was reported to have high efficiency, but a major limitation related to separation and regeneration of the mercuric oxide-loaded TiO_2 aerosols.

[11] Therefore, an economical solution that can more efficiently capture mercury compared to the technologies discussed above offers the potential to significantly decrease the estimated costs to meet pending regulations. In addition, the solution should be

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engineered such that it could be easily implemented in existing coal-fired power plants and similar installations. Not to be bound by theory, but a viable location for the technology derived herein would be to insert the technology between the electrostatic precipitator or baghouse and the effluent stack for coal-fired power plants, although the technology is not limited to this location. In addition, it is conceivable to micronize (create a fine powder with diameters less than 45 μm) and inject the material in to a flue duct.

SUMMARY OF THE INVENTION

[12] In accordance with the present invention, there is provided a method and composite for removing mercury from a fluid stream, the method including the steps of contacting a composite material comprising a substrate and catalyst particles with a fluid stream. The composite material adsorbs and oxidizes the mercury.

[13] Preferably, the catalyst particles are located on the substrate surface and/or contained in the substrate. The composite material may be a sorbent and, if so, is preferably a gel, more preferably, a xerogel.

[14] The method of the invention preferably includes the step of irradiating the composite material with radiation, preferably radiation having a wavelength of from about 160 to about 680 nm. The substrate is preferably transparent to radiation and, for example, may be porous silica, and the catalyst may comprise TiO_2. Preferably, the sorbent is a material having a surface area (BET) of about 1 to about 1500 m^2/g, preferably about 200 to about 900 m^2/g. The catalyst is preferably present in the composite material in an amount of from about 0.1 wt% to about 100 wt%.

[15] The method of the present invention also preferably comprises the step of regenerating the composite. The regeneration may be either chemical or thermal regeneration.

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[16] The present invention also relates to a composite, the composite including a sorbent and mercuric oxide and preferably further including a catalyst. If a catalyst is present, it may be present in an amount of about 0.1 wt% to about 100 wt%. The catalyst is preferably a photocatalyst, more preferably, TiO_2. The sorbent is preferably a gel, more preferably, a xerogel. The sorbent is preferably silica, and preferably has a surface area (BET) of from about 1 to about 1500 m^2/g, preferably about 200 to about 900 m^2/g. The composite preferably contains the mercuric oxide in an amount of from about 0.1 wt% to about 100 wt%, more preferably about 0.1 wt% to about 10 wt%.

BRIEF DESCRIPTION OF THE DRAWINGS

[17] A fuller understanding of the present invention and the features and benefits thereof will be accomplished upon review of the following detailed description together with the accompanying drawings, in which:

[18] FIG. 1 (a)-(c) illustrate scanning electron microscope (SEM) and energy dispersive spectrometry (EDS) analyses of crushed composite pellets including a SEM image, Si mapping and Ti mapping, respectively.

[19] FIG. 2 illustrates a schematic of an exemplary photocatalytic adsorption packed bed reactor based system for mercury vapor removal equipped with a source of mercury vapor and an analyzer for measuring mercury concentrations.

[20] FIG. 3 illustrates dimensionless outlet mercury concentration (C/Co) as a function of time (13 wt% TiO_2 loading, relative humidity of 70% and residence time of 0.29 sec).

[21] FIG. 4 illustrates mercury removal efficiencies for various TiO_2 loadings (15% relative humidity, 0.35 sec residence time).

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[22] FIG. 5 illustrates mercury removal efficiencies for various residence times (13 wt% TiO_2, 70% relative humidity).

[23] FIG. 6 illustrates mercury removal by adsorption alone and then removal by adsorption and irradiation (10% relative humidity, 12 wt% TiO_2 loading)

[24] FIG. 7 illustrates mercury removal via simultaneous adsorption and UV irradiation (70% relative humidity, 12 wt% TiO_2 loading)

DETAILED DESCRIPTION OF THE INVENTION

[25] The invention includes a new method and composite that can remove mercury from a fluid stream. Specifically, the invention is targeted to remove mercury via adsorption and/or either simultaneous or subsequent oxidation. Adsorption on the composite material allows mercury to be concentrated while exposure to radiation ensures the oxidation of the adsorbate(s). Intermittent UV light exposure can be used with the invention which minimizes energy consumption of the process if so desired. High efficiency, large capacity and the ability to recover mercury are advantageous features of the invention.

[26] As used herein, the term "mercury" refers to all forms of mercury including oxidized states (e.g., HgO, HgCl, $HgCl_2$) and elemental mercury (Hg^0). As used herein, the term, "impregnated" refers to the incorporation of a material (e.g., a photocatalyst) within the porous network of a sorbent, and may be either attached to the surface of the pores and/or a part of the crystalline network. Also, as used herein, the term "doping" refers to the addition of a material such that it is fixed to the sorbent internal or external surface and is accessible to the fluid stream. Further, as used herein, the term "sorbent" refers to an amorphous or crystalline solid that is capable of accumulating contaminants on or within the porous network of the sorbent.

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[27] The porous composite material preferably consists of a high surface area substrate material. For example, a silica-gel impregnated with photocatalyst particles, such as TiO_2, herein referred as a "SiO_2-TiO_2 composite gel". The SiO_2-TiO_2 composite gel can provide a surface area of about a few m^2/g to 1500 m^2/g. The gel is preferably a xerogel, defined as a gel that is obtained by evaporation of the liquid component at ambient pressure and temperatures below the critical temperature of the liquid. However, other gel forms may be used with the invention. Other suitable substrates include activated carbon, ceramics, metal silicates, alumina, zeolites, and the like as well as nonporous substrates such as silica/glass beads, stainless steel, and the like.

[28] The mercury deposited on the composite following irradiation has been identified as mercuric oxide. Very high Hg removal efficiency (at least about 99%) can be achieved with continuous irradiation. It has also been observed that photocatalytic oxidation "activates" the adsorbent, thus enhancing the subsequent adsorption capacity of the composite material when UV irradiation is not applied.

[29] The capacity of the porous composite material can be further increased by optimizing the mass transfer of mercury from the bulk fluid phase to the adsorption sites. For example, one could manipulate the gels pore size distribution or decrease the pellet size from the current 5 x 3 mm size tested herein. If desired, by rinsing the composite pellets with a suitable acid, such as H_2SO_4 and/or HNO_3, adsorbed mercury can be separated from the pellets that permit the adsorption sites on the composite to be regenerated. More efficient regeneration might be obtained by thermal treatment of the mercury at elevated temperatures such as about 200°F to about 1000°F.

[30] Photocatalyst particle (e.g. TiO_2) loading at all levels has been found to enhance mercury removal. Optimal loading is a function of sorbent porosity, surface area,

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transparency to UV light, permeability, adsorption characteristics, granular size, and other physical and chemical characteristics. In the preferred embodiment a TiO2 loading of between10 and 13 wt% has been shown to give optimum performance.

[31] In a preferred embodiment, the SiO_2-TiO_2 composite gel is formed using a sol-gel method. However, other methods to form the composite will be apparent to those skilled in the art. The basic formula uses specific volumetric ratios of various acids, water, silica alkoxide (silica precursor) or sodium silicate, with or without, various cosolvents. During formulation, during gelation, or post gelation the silica is doped, for example, with a commercially available photocatalyst, such as titanium dioxide. Preferably, the titania percentage varies from about 0.5% to about 15% on a wt/wt basis, but TiO_2 loadings up to 100 wt% can be incorporated. Mixed alkoxide synthesis can also be used to form a composite gel of SiO_2 and TiO_2 with a more homogeneous distribution of TiO_2. Various synthesis and aging steps can produce composites with pore sizes ranging from < 10 angstroms to >50 nm or as large as desired. Preferably, the pore sizes are greater than about 30 angstroms and less than about 320 angstroms, more preferably between about 60 and 200 angstroms, and most preferably between about 100 and 140 angstroms. In addition, surface treatments can be used to enhance Hg adsorption. When the solution becomes viscous during the gelation step, it may then be transferred into a mold in order to create a pellet of a desired size. After gelation, the composite may then be aged for varying lengths of time to increase its strength. After aging, the pellets may then be removed from their mold, rinsed with water, and then placed in another container for additional heat treatments. In the preferred embodiment, the pellets are placed in an oven and the temperature may then be ramped from room temperature to 103°C and kept constant for 18 hours, resulting in vaporization of the liquid within the porous silica matrix to form a xerogel. The temperature may then be

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ramped to 180°C and kept constant for 6 hours. Additional curing at higher temperatures can also be achieved (up to 600°C) for strengthening of the gel. The resultant average pore size of the gel can range from a pore size of about 30 angstroms to a pore size of between about 100 to about 200 angstroms, depending on the initial formula. The pellets can then be used in a packed-column.

[32] This indicates only one exemplary composite formulation. A wide variety of formulations, catalysts, aging and drying parameters can be used to derive the optimum pore size, pellet/particle size, surface area, surface adsorption characteristics, reduction efficiency, permeability, temperature stability and regeneration characteristics. Alternatively, the sorbent can be synthesized in bulk and crushed or ground and screened to produce granular particles of the optimum size range for various applications.

[33] A significant difference between the composites described herein and other composites for mercury removal is the use of a UV transparent substrate material such as silica. Porous silica is a good adsorbent medium that is also substantially optically transparent to UV light, which allows the penetration of UV light through its matrix to activate the intermixed photocatalyst particles, such as titanium dioxide. Preferably, the photocatalyst particles are provided both on the surface of and within the silica matrix allowing oxidation to occur on both external and internal surfaces within the porous silica structure.

[34] A wide variety of photocatalysts can be used with the invention. The sol-gel process is not limited to the use of titanium dioxide, but other catalysts such as HgO, ZnO, V_2O_5, SnO_2 or even modified TiO_2 catalysts coated with platinum or other conductive materials can also be used. In addition, the composites can be made into any shape convenient for use, such as spheres, cylinders, or other shapes.

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EXAMPLES

[35] The present invention is further illustrated by the following examples which include demonstrations of the superior performance of the advanced porous composite material for elemental mercury removal. The examples are provided for illustration only and are not to be construed as limiting the scope or content of the invention in any way.

EXAMPLE 1

Synthesis of silica-titania composite

[36] The silica-titania composites were made by a sol-gel method using nitric acid and hydrofluoric acid as catalysts to increase the hydrolysis and condensation rates, thereby decreasing the gelation time. The basic formula used to create gels with a pore size of roughly 150 Å is as follows: 25 mL water, 50 mL ethanol, 35 mL TEOS (tetraethylorthosilicate), 4 mL nitric acid (1N), and 4 mL HF (3%). Of course, one of ordinary skill in the art will recognize that silicon alkoxides, sodium silicate, colloidal silicas, slip casting or traditional ceramic techniques are suitable for use with the invention.

[37] The chemicals were reagent grade and were added individually, in no particular order, to a polymethylpentene container. During this time, a known mass of Degussa (Dusseldorf, Germany) P25 TiO_2 was added to the batch and the percentage of titania recorded is given as a percent by weight of silica. A magnetic stir plate provided sufficient mixing, but care should be used to insure that the TiO_2 is well dispersed in the sol and that the homogeneous distribution of TiO_2 is maintained throughout the gelation process. The solution (including the P25) was pipeted into polystyrene 96-well assay plates before complete gelation. The volume added to each well was approximately 0.3 ml. After gelation, the plates were then covered with lids and wrapped in foil to prevent premature evaporation. Next, the sample was aged at room temperature for two days, then at 65°C for two days.

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[38] After aging, the pellets were removed from the container, rinsed with deionized water to remove any residual acid or ethanol, and placed in a Teflon container for the next series of heat treatments. A small hole in the lid of the container allowed slow and uniform drying of the gel. The pellets were then placed in an oven and the temperature was ramped from room temperature to 103°C (2°/min) and kept constant for 18 hours, resulting in the vaporization of liquid solution within the silica network. Next, the temperature was ramped to 180°C (2°/min) for removal of physically adsorbed water and hardening of the gel, where it was kept constant for 6 hours and then was slowly decreased back to room temperature over a 90 minute period. The resultant size of an individual cylindrical pellet after drying was approximately 5 mm in length with a diameter of 3 mm.

[39] The BET (Brunauer, Emmett, and Teller equation) surface area and pore volume analyses were performed on a Quantachrome NOVA 1200 Gas Sorption Analyzer (Boynton Beach, FL). The samples were outgassed at 110°C for approximately 24 hours and analyzed using nitrogen adsorption. The average pore size was calculated from the total pore volume and the surface area. Pore size distribution curves were also attained to provide additional information on pore morphology. Scanning Electron Microscopy (SEM) (JSM-6400, JEOL USA, Inc.) with Energy Dispersive Spectroscopy (EDS) detector (Tracor System II, Oxford Instruments, Inc.) was used for morphology and surface elemental analysis. The silica-titania gel composites had specific surface areas on the order of 200 to 300 m^2/g, pore volumes around 1 cc/g, and average pore diameters of about 150 angstroms. The synthesized pellets had a white color due to the presence of TiO_2. The addition of TiO_2 in the range studied did not seem to significantly affect the surface area. The pore volume within the loading range was roughly 1.0 cc/g and had negligible differences among the various pellets. Concerning pore size, the average pore diameter (pore volume/surface area) averaged 150 angstroms.

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The SEM image of crushed fresh pellet (13 wt% loading) is shown in FIG. 1(a). The corresponding EDS elemental mappings of Si and Ti are shown in FIG. 1(b) and FIG. 1(c), respectively. FIG. 1(c) shows TiO_2 was well distributed in the SiO_2 matrix although some agglomerated TiO_2 can also be seen.

EXAMPLE 2

Mercury Removal Characterization/Methodology

[40] Silica-Titania Composite Gel formed using the synthesis method described above was tested in a packed bed reactor system to characterize the mechanisms and efficiency for mercury vapor removal. The reactor system including a supply of mercury vapor and a Hg analyzer is shown in Figure 2. The flow-rate of mercury-laden air was 0.67 liters/min with a residence time in the reactor of 0.29 seconds. The initial mercury concentration for experiments ranged from 7 to 150 ppb. Mercury vapor laden air was introduced into the system by passing purified air above liquid mercury held in a reservoir. To study the effects of moisture on the system, water vapor was introduced by bubbling water using purified air. The mercury concentration of the mixture was measured by a UV mercury analyzer (VM 3000, Mercury Instruments or Zeeman RA-915 mercury analyzer). The air carrying the designated level of mercury concentration and humidity flowed downward through the packed-bed reactor from the top in order to minimize the chance of selective flow or channeling through the reactor.

[41] A stainless steel mesh (64 *um* opening) was used to hold the pellets. A UV lamp (4W) was placed at the center of the packed-bed reactor, and the pellets were randomly packed around the lamp. Between 5 and 10 grams of pellets were used in the experiments. The cross-sectional area of the reactor was 26.5 cm^2. After flowing through the reactor, dilution air was introduced to dilute the mercury concentration to the appropriate range for

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measurement. The air was then passed through a carbon trap before it was exhausted into a hood while a slit of the air was directed to the mercury analyzer for measurement. Purge air was used to flush mercury out of the system after each experiment.

[42] After the experiment, the composite pellet was analyzed by BET again to examine if there was any significant change in surface area. The amount of total mercury adsorbed on pellets was determined following a hot acid digestion (HNO_3:H_2SO_4 mixture; 7:3) of 25 mg of pellets/10 ml of solution. Samples were brought to a refluxing boil on a hot plate for 4 hours. After cooling, 0.1 ml of concentrated HCl was added to the samples, and the final volume adjusted to 50 ml by dilution with Nanopure® water. Mercury concentration was then measured by Inductively Coupled Plasma spectroscopy (ICP) to determine the capacity.

EXAMPLE 3
Mercury Removal Rate as a Function of Adsorption and Oxidation

[43] FIG. 3 shows the dimensionless outlet mercury concentration (C/Co) for the UV on/off cycles as a function of time. The inlet concentration was regularly checked to ensure it stayed at the designated level. As shown, the outlet concentration in the first cycle increased to 68% after 15 minutes, proving that the high surface area silica gel was capable of adsorbing mercury. The breakthrough time was short due to the small bed height used, but it can be easily made larger by using a longer bed.

[44] After 15 minutes of adsorption, the UV-light was turned on. The outlet concentration quickly dropped down to 0% in less than 2 minutes, demonstrating highly effective photocatalytic oxidation. During this oxidation period, effluent mercury stayed at this low level. After 6 minutes of UV exposure, the UV light was turned off to start the second cycle. The outlet concentration remained at a low concentration for a short period of time and then increased in a similar pattern observed in the previous cycle. Comparison of the end of the

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first cycle before the UV light was turned on and the beginning of the second cycle indicates that photocatalysis oxidized the previously adsorbed mercury and "reactivated" the silica gel. Otherwise, the mercury concentration initially measured in the second cycle would be the final level detected from the previous cycle (i.e. 68%).

[45] The other unexpected phenomenon demonstrated was that oxidation cycles improved adsorption for the next cycle. In other words, by comparing the mercury outlet concentrations of the respective cycles, a decreasing trend was observed.

[46] In a related experiment, the time to reach 20% exhaustion (i.e., 20% of the sorbent's capacity utilized) for each cycle for 10 grams of pellets was measured. As can be seen from Table 1, the pellets performed better with each successive cycle.

Table 1: Time for Reaching 20% Exhaustion by Adsorption in the Various Cycles

Cycle No.	1	2	3	4	5	6
Time (min)	1	2.1	3.2	6	7.2	9.3

[47] Thus, Table 1 clearly shows the increase in time with each cycle to reach 20% exhaustion (e.g. 1 min in the first cycle and 2.1 minutes in the second cycle). This breakthrough profile became stable after a few cycles.

EXAMPLE 4
TiO_2 Loading

[48] An increase in TiO_2 loading to a certain extent is expected to yield higher mercury removal efficiencies by providing more active sites for photocatalytic oxidation. However, higher loadings (i.e., greater wt% ratio) may interfere with the adsorption or hinder UV transparency, therefore reducing the effectiveness. Measured efficiencies for various TiO_2 loadings are shown in FIG. 4. The efficiencies of photocatalytic oxidation, adsorption at 5 minutes and at 15 minutes are both reported.

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[49] When the UV light was on, mercury removal was 100%. In looking at adsorption, the 2.8% impregnated silica-gel clearly had a lower capacity than the other two loadings. This deficiency may be due to the photocatalytic "activation" discussed in the previous section. The 2.8% TiO_2 loading may not be enough to provide the necessary OH radicals for activation, thus resulting in a lower adsorption capacity. Comparing the 13% and 18% data, the 13% provided a slightly better performance but the difference did not appear to be significant.

[50] For optimum system performance, TiO_2 particles should be dispersed. Agglomeration appears to yield less effective use of TiO_2 for this purpose. The experimental results suggest that 13% loading to be the optimal based on the current doping methodology.

EXAMPLE 5
Residence Time

[51] Flow rate is another important operating parameter that generally determines the mercury removal efficiency in the system. The flow rate controls the residence time of the mercury containing gas in the reactor and therefore the effectiveness of adsorption and reaction can me impacted. In addition, by varying the flow rate, the rate limiting mechanism can be identified. The removal efficiency as a function of residence time is shown in FIG. 5.

[52] As the residence time decreased from 0.78 to 0.16 s, adsorption was greatly impacted. The removal efficiency drastically decreased when the residence time decreased. Compared to adsorption, the removal efficiency by photocatalytic oxidation only decreased slightly, although it was much more affected at the smallest residence time. While short residence time reduces the performance of the system regardless of whether adsorption or oxidation is the main removal mechanism, the results clearly indicate that adsorption is the rate limiting factor.

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EXAMPLE 6

Continuous UV versus Cyclic Operation

[53] An alternative to exposing the silica-gels to intermittent UV is to maintain an environment of constant irradiation. FIG. 6 demonstrates that once UV was applied to the system, the effluent mercury concentration returned to zero and remained there for the duration of the experiment. Similarly, FIG. 7 demonstrates that if the system is irradiated from the beginning, other than the fluctuation in effluent mercury concentration in the beginning of the experiment, the effluent concentration remained at zero for the duration of the experiment. Similar experiments were carried out for almost 500 hours with the same results. Furthermore, silica impregnated with HgO with and without TiO_2 performed similarly in the presence and absence of UV light.

[54] It is to be understood that while the invention has been described in conjunction with the preferred specific embodiments thereof, that the foregoing description as well as the examples which follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

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WHAT IS CLAIMED IS:

1. A method for removing mercury from a fluid stream, comprising the steps of: providing a composite material comprising a substrate and catalyst particles; and contacting a fluid stream with said composite, wherein said composite adsorbs and/or oxidizes said mercury.

2. The method of Claim 1, wherein said catalyst particles are on the substrate surface and/or contained in the substrate.

3. The method of Claim 1, wherein said composite material is a sorbent.

4. The method of Claim 3, wherein said sorbent is a gel.

5. The method of Claim 4, wherein said gel is a xerogel.

6. The method of Claim 1, further comprising the step of irradiating said composite material with radiation.

7. The method of Claim 6, wherein said radiation has a wavelength of from about 160 to about 680 nm.

8. The method of Claim 1, wherein said substrate is transparent to radiation.

9. The method of Claim 8, wherein said substrate comprises porous silica.

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10. The method of Claim 9, wherein said catalyst comprises TiO_2.

11. The method of Claim 3, wherein said sorbent has a surface area (*BET*) of about 1 to about 1500 m^2/g.

12. The method of Claim 1, wherein said catalyst is present in said composite material in an amount of from about 0.1 to about 100 wt%.

13. The method of Claim 1, further comprising the step of regenerating the composite.

14. The method of Claim 13, wherein said regeneration step comprises chemical or thermal regeneration.

15. A composite, comprising a sorbent and mercuric oxide.

16. The composite of Claim 15, further comprising a catalyst.

17. The composite of Claim 16, wherein said catalyst is present in said composite in an amount of about 0.1 to about 100 wt%.

18. The composite of Claim 16, wherein said catalyst is a photocatalyst.

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19. The composite of Claim 18, wherein said photocatalyst is TiO_2.

20. The composite of Claim 15, wherein said sorbent is a gel.

21. The composite of Claim 20, wherein said gel is a xerogel.

22. The composite of Claim 15, wherein said sorbent is silica.

23. The composite of Claim 15, wherein said sorbent has a surface area (BET) of from about 1 to about 1500 m^2/g.

24. The composite of Claim 15 , wherein said mercuric oxide is present in said composite in an amount of from about 0.1 to about 100 wt% .

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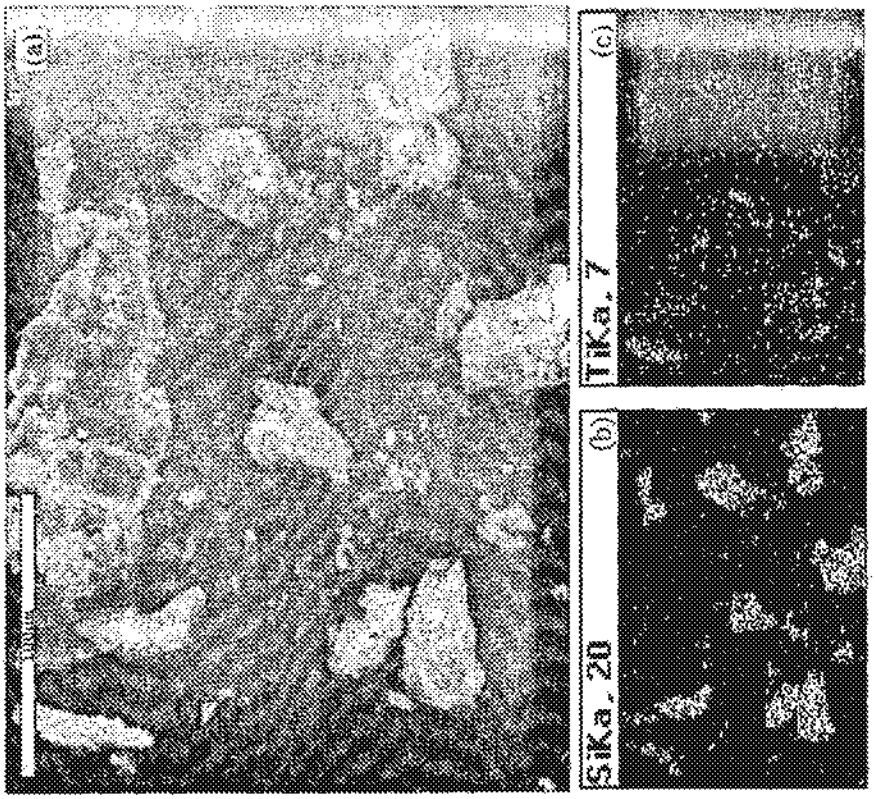


FIG 1

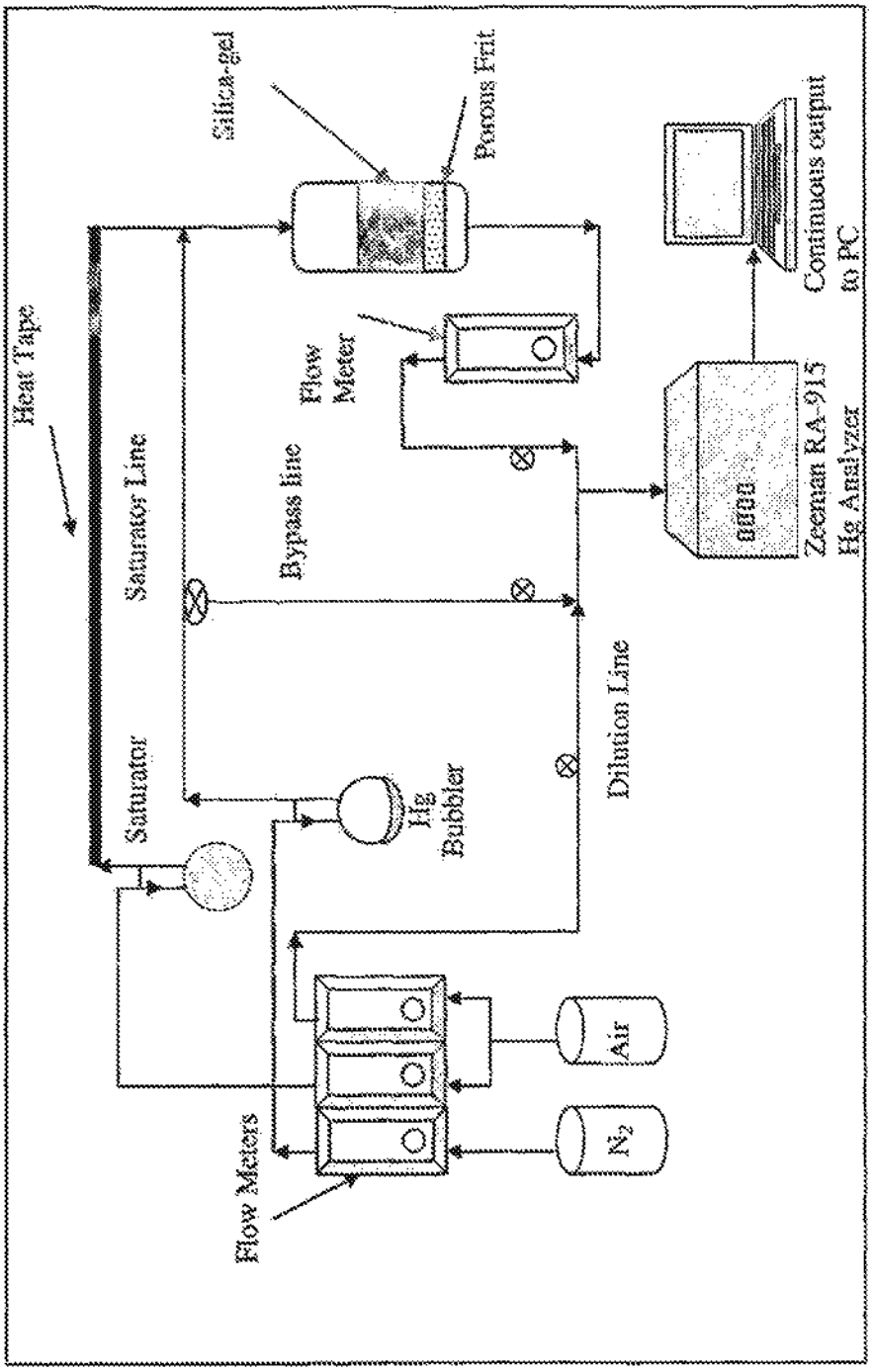

Silica-gel
Porous Frit
Heat Tape
Saturator Line
Flow Meter
Bypass line
Continuous output to PC
Zeeman RA-915 Hg Analyzer
Saturator
Hg Bubbler
Dilution Line
Air
N_2
Flow Meters

FIG 2

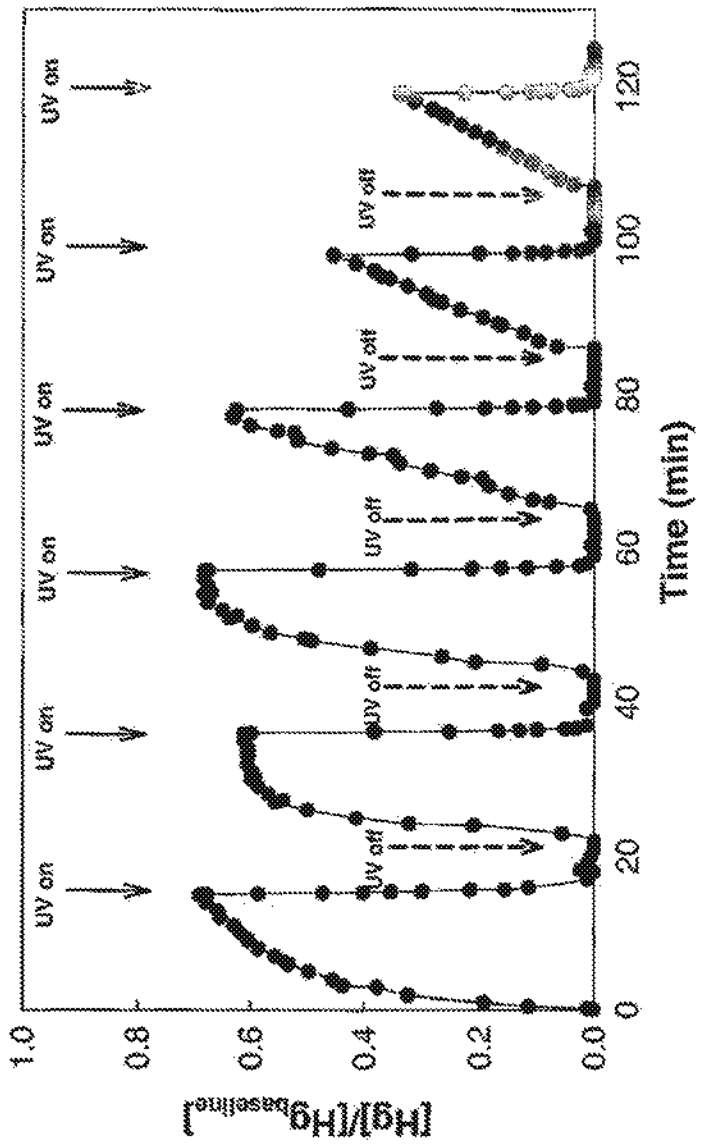

UV on
UV off
[Hg]/[Hg$_{baseline}$]
Time (min)
0.0
0.2
0.4
0.6
0.8
1.0
0
20
40
60
80
100
120

FIG 3

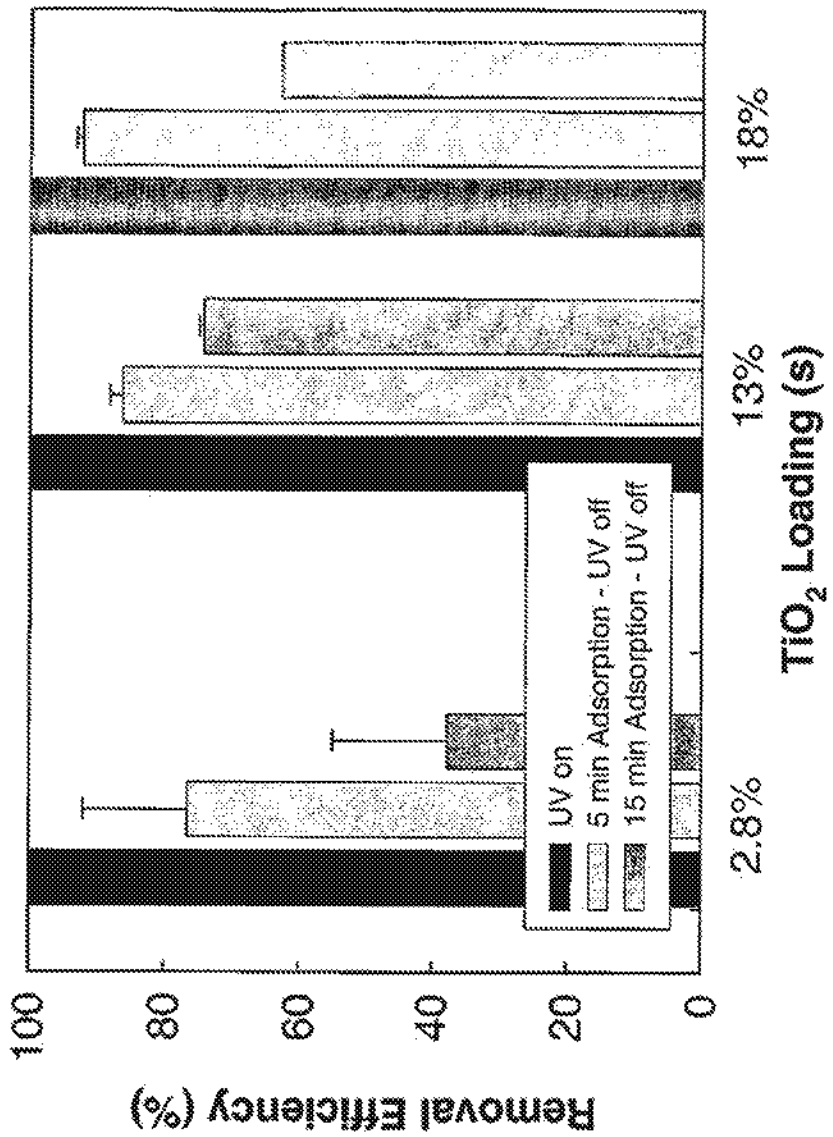

Removal Efficiency (%)
100
80
60
40
20
0
UV on
5 min Adsorption - UV off
15 min Adsorption - UV off
2.8%
13%
18%
TiO2 Loading (s)

FIG 4

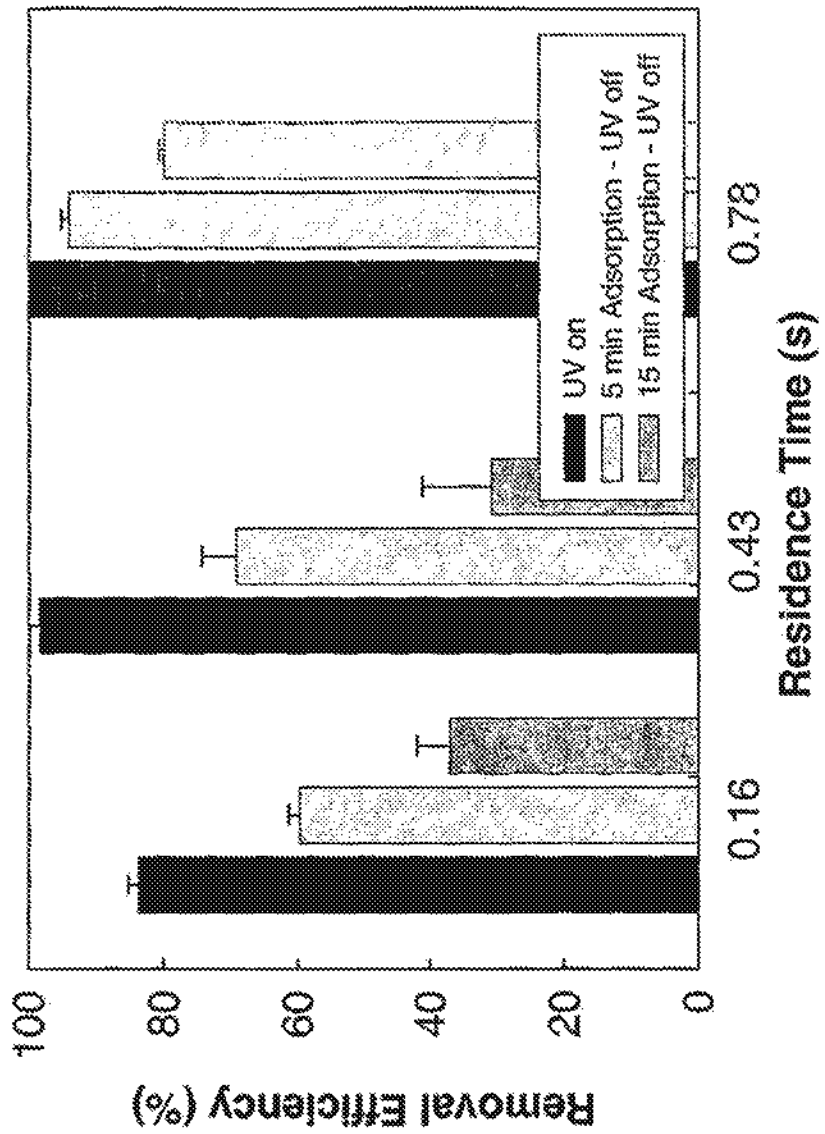

Removal Efficiency (%)
100
80
60
40
20
0
0.16
0.43
0.78
Residence Time (s)
UV on
5 min Adsorption - UV off
15 min Adsorption - UV off

FIG 5

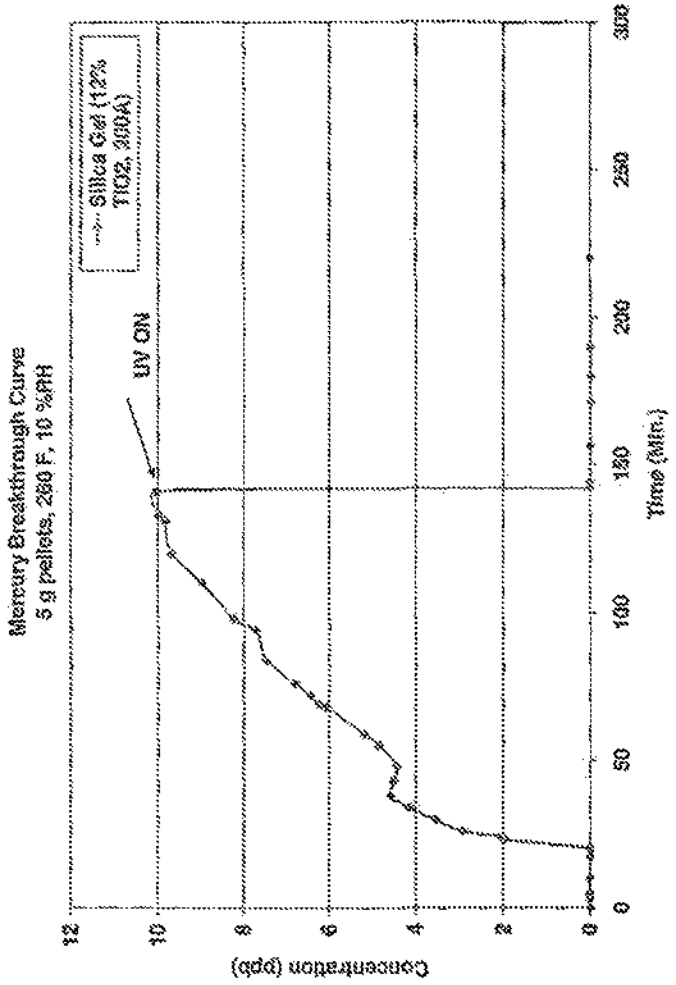

Mercury Breakthrough Curve
5 g pellets, 260 F, 10 %RH
UV ON
Silica Gel (12% TiO2, 2004)
Concentration (ppb)
Time (Min.)
0
2
4
6
8
10
12
0
50
100
150
200
250
300

FIG 6

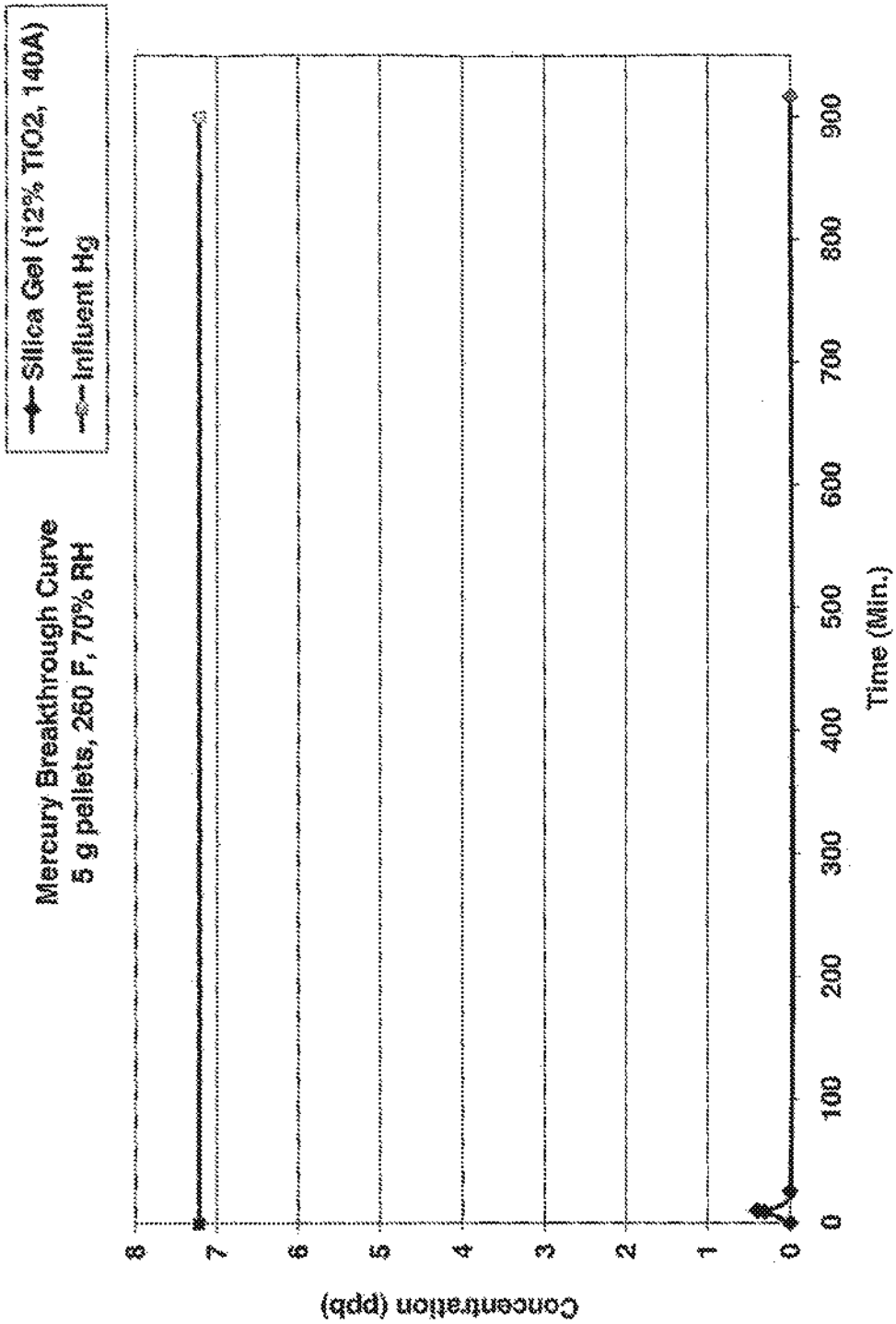

Mercury Breakthrough Curve
5 g pellets, 260 F, 70% RH
Silica Gel (12% TiO2, 140A)
Influent Hg
Concentration (ppb)
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
700
800
900
Time (Min.)

FIG 7

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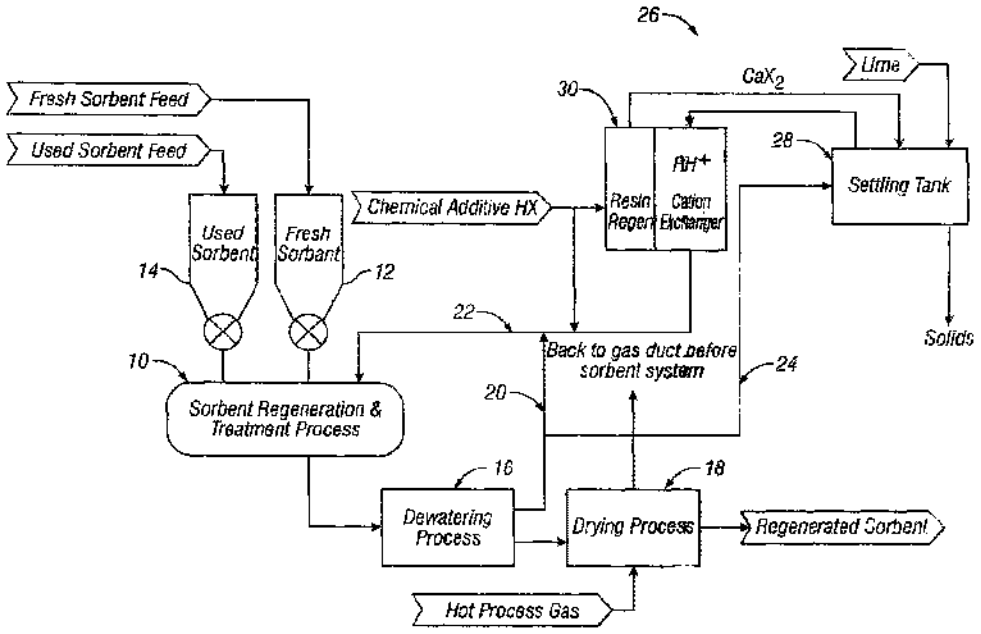
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[Continued on next page]

(54) Title: PROCESS FOR REGENERATING A SPENT SORBENT



(57) Abstract: A method and apparatus is provided for regenerating a sorbent that has been poisoned by components derived from flue gas. The sorbent is treated with an agent to remove the poisoning components and introduce a promoting agent into the sorbent. The method and apparatus can also be used to enhance the effectiveness of a new sorbent.

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PCT PATENT APPLICATION FOR:

PROCESS FOR REGENERATING A SPENT SORBENT

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FIELD OF THE INVENTION

[01] This invention relates to the removal of mercury and other pollutant species from flue gas streams generated during the burning of fossil fuels. In particular, this invention is drawn to a process and system for regenerating spent sorbents, or enhancing fresh sorbents.

BACKGROUND OF THE INVENTION

[02] Burning fossil fuels such as coal generates a flue gas that contains contaminants including mercury and other trace elements. In addition, the flue gas contains oxides of sulfur and nitrogen (acid gas emissions) and particulates whose release to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. In the example of mercury, mercury is generated in its' elemental form during combustion. Downstream of the boiler, in the ducts and stack of the combustion system, part of the elemental mercury is oxidized. The amount of mercury oxidized depends on the amount of hydrochloric acid (HCl) and other gases present in the flue gas. The amount of mercury in a gas stream varies

with different coal, but a typical concentration of mercury in the stream of combustion gas is about 5 parts per billion (ppb). As a result, several pounds of mercury per day may be emitted in some utilities.

[03] Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. In these types of mercury control methods, the mercury contacts the sorbent and attaches to its surface, where it can be collected along with the fly ash in a baghouse or electrostatic precipitator (ESP). One disadvantage in these prior art systems is that sorbents are used only once and discarded. The sorbents are are not regenerated and reused. These prior art techniques also create solid waste disposal problems, and the spent sorbent may contaminate the collected ash for use in various applications.

[04] Another type of mercury control method uses carbon beds for mercury capture in flue gas. In these types of systems, spent sorbent is typically burned and not regenerated. Some prior art systems employ a recirculating carbon bed, where mercury is removed along with acid gases (as ammonium salts) and the carbon is regenerated at high temperatures where ammonium sulfate is decomposed to SO_2 and N_2, and mercury desorbs from the sorbent. Attrition of the sorbent results in a significant sorbent cost in this type of control method.

[05] Another type of mercury control method involves injecting manganese oxide sorbent particles in a flue gas stream. For example, US Patent 6,579,507 describes such a method. In this patent, regeneration is claimed by removal of spent oxide

particles from the reaction zone and rinsing with dilute aqueous acid. One problem with manganese oxide sorbents is that, while they do oxidize and remove elemental mercury from flue gas, the reaction rates are far slower than those with activated carbons. This means that the MnO_2 sorbent can not handle high flow rates of flue gas compared with the injected carbon sorbents. Also, the acid wash of the MnO_2 sorbent does not restore the sorbent to its full original activity. In the described MnO_2 sorbent system, the purpose of the acid wash treatment is to actually remove the poisoned and spent manganese from the surface of the sorbent as soluble salts, which destroys a portion of the sorbent. The soluble salts contaminate the wash solution, and it is difficult to economically separate and recover the manganese and mercury.

[06] Of interest in designing a mercury control process is to use the sorbent downstream of a particulate control device so the sorbent is not highly diluted with the ash particles. The sorbent could then be more easily regenerated and recycled. The prior art discusses several examples of this type of configuration and sorbent processing.

[07] U.S. Pat. No. 5,607,496 teaches the oxidation of mercury on a metal oxide sorbent bed and subsequent absorption to a sorbent. The sorbent bed follows the particulate removal equipment and thus the gas still contains the SO_X and NO_X, which react with the metal oxide sorbent to form metal sulfates, that poison the bed. High temperatures are proposed to regenerate the bed. However, mercury is only partially removed from the sorbent at temperatures up to 500 degrees C. Also, the sorbents do not work effectively after regeneration. The cause may be that manganese sulfate

formed during the sorption cycle does not completely decompose back to an active manganese oxide form. US Patent 6,383,981 describes a fixed MnO_2 or Fe_2O_3 bed for removal of mercury from a hydrocarbon stream, but no regeneration method is included.

[08] US Patent 6,596,661 describes the regeneration of a plate or honeycomb material composed of transition metal oxides that was used for sorption of mercury in flue gas. The claimed process involves heating the sorbent in a reducing gas stream to remove poisons, followed by impregnation with a poly functional complex-forming reagent containing the catalyst active component to restore mercury capture capacity. The first of these steps can remove the mercury, but it is unclear whether it actually removes the sulfate poison. The second of these steps is rather expensive, because one is actually reconstituting the reagent on the sorbent.

[09] Other types of mercury control methods using porous beds containing a mercury oxidizing reagent on a solid support for removal of mercury from gas streams are described in several patents. For example, US Patent 1,984,164 describes the use of activated carbon or other solid impregnated with a halogen for removing mercury from air. The impregnation method is not specified. No regeneration is claimed.

[10] Examples include peroxomonosulfate (for example, US Patent 4,786,483), triiodide or other mixed halogens (for example, US Patents 3,194,629 and 3,662,523), and sulfur (for example, US Patents 3,194,629; 4,101,631, 4,708,853, and 6,258,334). In these examples, the reagent material is destroyed either by reaction with the flue

gas during sorption or by attempts to regenerate the sorbent. Therefore, these sorbents are not regenerated, except by reimpregnation of the expensive reagent. Amalgamating noble metals (gold, silver) on a suitable support can be regenerated by microwave heating (for example, US Patent 6,136,072), but are expensive and not especially active for sorption in flue gas.

SUMMARY OF THE INVENTION

[11] An apparatus and method is provided for regenerating used sorbents by exposing used sorbents to a solution to remove contaminants collected on the sorbent. An apparatus and method is also provided for enhancing the effectiveness of a sorbent by exposing the sorbent to a solution that increases the sorbent effectiveness. In one example, the solution used is an aqueous acidic solution.

[12] Other features and advantages of the present invention will be apparent from the accompanying drawings and from the detailed description that follows below.

BRIEF DESCRIPTION OF THE DRAWINGS

[13] The present invention is illustrated by way of example and not limitation in the figures of the accompanying drawings, in which like references indicate similar elements and in which:

[14] FIG. 1 is a block diagram illustrating one example of the application of the sorbent regeneration technology of the present invention.

[15] FIG. 2 is a block diagram illustrating another example of the application of the sorbent regeneration technology of the present invention.

[16] FIG. 3 is a block diagram illustrating a process for enhancing the effectiveness of a sorbent.

DETAILED DESCRIPTION

[17] The present invention relates to the process for the removal of mercury and other pollutant species from flue gas streams generated during the burning of fossil fuels, such as in a coal-fired utility. This removal process utilizes a sorbent to remove pollutants from the flue gas stream, which is at the same time interacting with other flue gas components that result in poisoning or deactivating the sorbent and reducing its capacity or reaction rates with the pollutant species. The present invention provides a cost effective way to capture the pollutants by utilizing a process to regenerate the reactivity and capacity of the sorbent.

[18] Generally, a process of the present invention includes washing a used sorbent with agents selected to remove the anions that collect on the sorbent during exposure to flue gas and which poison the binding sites for mercury or other contaminants. The process also impregnates the sorbent with agents that promote the chemisorption of mercury and other contaminants in the next service cycle of the sorbent. This is achieved by the fact that, following or during the removal of the sulfate or other contaminants, the sorbent is washed with a reagent that restores mercury or other contaminant sorption effectiveness of the sorbent.

[19] In some examples, the invention applies to regeneration of a sorbent in a powdered form that has been injected into a flue gas stream after particulates have been removed, and have been collected on a filtration device or ESP device. Examples of the composition of sorbents include activated carbon, a metal oxide or metal oxides, a precious metal, or a composite of any of these. In one example using activated carbon, the sorbent may take the form of powdered, granulated, or fibrous carbon. Other examples are also possible. In other examples, sorbent is used with a sorbent bed, rather than being injected. A sorbent bed may be a fixed bed, traveling bed, or a travelling fiber filter. In either type, the poisoning contaminants from the flue gas are removed and a promoting agent added to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier more expensive art of adding a reagent (such as peroxide, gold, triiodide, etc.) to the sorbent.

[20] To help understand the present invention, it helps to understand how a sorbent loses its ability to absorb contaminants. Reactions between acidic components generated from flue gas poison the basic binding sites on the sorbent for oxidized mercury, which is a Lewis acid. Binding of other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants that may also be Lewis acids, would suffer from loss of the intrinsic carbon basic sites.

[21] To achieve the regeneration effect, it is necessary to remove the contaminant species that occupy the basic binding sites on the sorbent. Typically, there are several acid species that occupy these sites far exceeding the number of bound mercury ions.

The most serious competitor for the binding sites is sulfuric acid, formed from the SO_2 and SO_3 in the flue gas. The sulfate formed by reaction of the sulfuric acid with the basic sorbent site can be removed from the sorbent by washing with aqueous hydrochloric acid (HCl) or excess of chloride ion to exchange the sulfate or hydrogen sulfate ions. Washing with an acid or salt solution is more effective than washing with water since the anions exchange the sulfate bound to the sorbent sites. Other acids or reagents will also exchange these ions. Washing with hydrochloric acid and/or other acids also has the effect of promoting the subsequent oxidation of elcmentary mercury when the sorbent is returned to service. Adding the proton from the acid to a basic carbene site on the carbon edge structure forms a carbocation that accept electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface.

[22] There are several solutions that can be used with the present invention to regenerate and/or enhance a sorbent. In a first example, the solution includes one or more inorganic acids such as hydrochloric acid (HCl), hydrobromic acid (HBr), and hydroiodic acid (HI). In another example, the solution includes one or more salt solutions. The salt solution may include a halide salt, containing an associated cation, such as ammonium, sodium, potassium, iron, aluminum, boron, zinc, manganese, magnesium, calcium. In another example, the solution includes an organic acid, such as citric acid, tartaric acid, oxalic acid, malonic acid, maleic acid, formic acid, and acetic acid. In another example, the solution includes an organic salt solution. An organic salt solution may include at least one anion from at least one of citric acid, tartaric acid, oxalic acid, malonic acid, maleic acid, formic acid, and acetic acid, and

at least one associated cation, such as ammonium, sodium, potassium, iron, aluminum, boron, zinc, manganese, magnesium, or calcium.

[23] In another example, the solution includes a compound comprised of a halogen combined with a Group V or Group VI element such as phosphorus, oxygen, sulfur, selenium, nitrogen, etc.. In one example, the compound includes one or more of thionyl chloride, sulfuryl chloride, phosphorus trichloride, phosphorus oxychloride, hypochlorous acid, and chlorine. In another example, the compund includes one or more of thionyl bromide, sulfuryl bromide, phosphorus tribromide, phosphorus oxybromide, hypobromous acid, and bromine.

[24] In another example, water can be used to wash much of the sulfuric acid and sulfates off a carbon sorbent. However this treatment may only be effective in restoring the activity of the sorbent for capture of elementary mercury if halogens are already incorporated into the carbon during a pretreatment or during a previous regeneration cycling of the carbon, which was carried out with a hydrohalide acid (HX).

[25] The present invention may also include washing the recovered powdered sorbent or the bed material in a solution of the contaminant removal agent, for example, an acid reagent. Washing with the reagents will exchange the flue-gas derived sulfate ions and other contaminants from the binding sites on the sorbent. the invention may also include the impregnation of agents into the sorbent to promote sorption activity. This may be accomplished using promoters such as a protonic hydro halide acid HX or Lewis acid MeX_n. These reagents enhance metal oxidation activity

by creating cationic character on the carbon edge structure that attracts mercury atoms and extracts electrons from said mercury atom. A similar mechanism applies to oxidation and capture of reduced arsenic and other pollutant species. In another example, the invention may use a reagent that promotes oxidation via chlorination of a sorbent surface, such as $SOCl_2$, SO_2Cl_2, PCl_3, $POCl_3$, HOCl, NaOCl, Cl_2, and corresponding bromine (or other halide) reagents. These reagents can be liquid, vapor or solution reagents, depending on their stability.

[26] The slurry of treated sorbent particles is subjected to a dewatering step (for example, centrifugal-based, gravity-based, or filtration-based methods) to remove the sorbent particles from the aqueous acid. Finally, the sorbent is further dried via a mild thermal treatment before returning to service. There are several reasons for dewatering the sorbent. By improving flow characteristics, this step will make the powdered or moving particle sorbent easier to handle during duct injection or in a contactor unit. Moisture may also block the pores preventing gas phase diffusion of elemental mercury, or may promote the sorption and subsequent oxidation of SO_2 to sulfuric acid.

[27] In another example, the water produced in the dewatering step may be treated in a settling basin with a Ca or Mg salt to produce insoluble Ca or Mg SO4, or other insoluble salt of the contaminant, which is removed as a sludge or solid. Examples of suitable Ca or Mg salts include lime, halide, or solutions spent from the resin regeneration step. The treated water may also be further subjected to treatment with a cation exchange resin in the proton form to remove any excess of Ca or Mg in the

water from the settling basin and replace it with hydrogen ions. The resulting solution is then fundamentally what is required of the carbon regeneration step (exchange out the contaminant and add the promoter acid). In this process, the spent cation exchange resin from the process is treated with a protonic acid, such as HCl, to regenerate the resin in the proton form and produce a soluble Ca or Mg salt. This process may include the addition of the Ca and Mg brine from the resin regenerating unit to the settling tank to aid the precipitation of the insoluble Ca or Mg salt of the contaminant. The process may also include the addition of acid or salt to the recycled water from the resin treatment step as needed to increase concentrations to those required for contaminant removal and promotion of sorbent activity.

[28] In another example, the waste water solution from the dewatering step can be simply disposed of by adding to scrubber slurry, if available, or using other disposal methods. This will convert the contaminant to insoluble calcium salts as scrubbers are designed to do.

[29] In one example of the present invention, a regenerated or enhanced sorbent can be improved by use of an additive mixed with the sorbent prior to injecting the regenerated sorbent into a flue gas stream. In one example, the additive can be a calcium-based additive which functions to neutralize acids.

[30] Although the process for regenerating a deactivated sorbent is suitable for various forms of sorbent, a descriptive example of a regeneration process according to the invention (including test results) follows. In this example, an activated carbon sorbent was used. The regeneration of several carbon sorbents was tested, including

the powdered Norit FGD sorbent, an aerogel carbon film sorbent, and a carbon filter consisting of fine carbon particles imbedded on a polymer fiber matrix.

[31] The carbon sorbents were initially tested in a heated bed where a synthetic flue gas stream containing elemental mercury (11 $\mu g/m^3$) was passed through the bed. Concentrations of total and elemental mercury in the effluent gas were determined using a PSI Sir Galahad mercury continuous emission monitor (CEM). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original FGD powdered carbon sorbent with the sorbent after regeneration by washing with 0.1 N HBr, collecting the powder by centrifugation, and drying, revealed that the mercury capture activity was increased from an initial capture efficiency of about 50% of the mercury in the inlet to 100% capture. A comparison of the sorbent after it is regenerated again with HBr after its second service cycle revealed that the mercury capture is again 100% at the start of the test, and stays at higher capture efficiency for a substantially longer period of time. Similar results were obtained with the carbon film and carbon fiber sorbents by regeneration with 0.1 N HCl.

[32] FIG. 1 is a block diagram illustrating one example of the application of the sorbent regeneration technology of the present invention. FIG. 1 should not be considered limiting, but rather depicts an exemplary system for incorporating the technology.

[33] The process illustrated in FIG. 1 is laid out around the sorbent regeneration and treatment process 10 that, as a minimum, contacts the sorbent materials with the

aqueous chemical reagent. This step could also include stronger agitation or grinding balls to expose fresh surfaces. Fresh sorbent and used sorbent are fed from separate storage silos 12 and 14 and metered at rates dependent upon mercury control feedback from the treated flue-gas. A contact reactor receives a mixture of fresh and used sorbent and facilitates the sorbent regeneration and treatment process 10. In one example, the mixture includes about 80 percent used sorbent and 20 percent fresh sorbent. Of course, other ratios can also be used. In one example, used sorbent is regenerated without using fresh sorbent. In the contact reactor, the sorbent mixture is exposed to an aqueous acidic solution to restore mercury sorption effectiveness to the used sorbent, as described above. After the sorbent regeneration and treatment process 10, the resulting slurry is passed through an initial dewatering process 16 (e.g., via a hydroclone, vacuum filter, settling tank, heat exchanger, or other device) to remove sorbent particles from the aqueous acidic solution. The dewatering process 16 is followed by a final drying process 18 that utilizes hot process gas to bring the regenerated sorbent to a point of apparent dryness to allow subsequent handling and injection into the power system for mercury control. The majority of the aqueous solution from the dewatering process 16 is sent back to the regeneration reactor (via the path shown by arrow 20) along with a make up stream 22 comprised of water and fresh chemical reagent. A portion 24 of the aqueous solution is also sent to a system 26 that uses lime addition in a settling tank 28 and ion exchange (via ion exchanger 30) to remove sulfates prior to reuse. For some applications, the economics may favor replacing the sulfate removal step with a simple blow down stream and increased use of fresh aqueous chemical reagent (described below). In another example, as an

alternative to dewatering and drying, the wet sorbent can be injected back into a flue gas stream, where it will almost instantly dry.

[34] FIG. 2 is a block diagram illustrating another example of the application of the sorbent regeneration technology of the present invention. FIG. 2 is similar to the block diagram shown in FIG. 1, with a few differences. First, FIG. 2 shows an ash separation system 32, which separates fly ash from the used sorbent.

[35] Like the block diagram shown in FIG. 1, FIG. 2 shows storage silos 12 and 14 for providing fresh and use sorbent to a contact reactor. The contact reactor receives the mixture of fresh and used sorbent and facilitates the sorbent regeneration and treatment process 10. After the sorbent regeneration and treatment process 10, the resulting slurry is passed through a dewatering process 16 and drying process 18. Some of the aqueous solution from the dewatering process 16 is sent back to the regeneration reactor (via the path shown by arrow 20) along with a make up stream 22, as is described above. A portion 24 of the aqueous solution is also sent to a system 26 that uses lime addition in a settling tank 28 and ion exchange (via ion exchanger 30) to remove sulfates prior to reuse. As mentioned above, for some applications, the economics may favor replacing the sulfate removal step 34 with a simple blow down stream (shown as "Option A" in FIG. 2) and increased use of fresh aqueous chemical reagent.

[36] The present invention may also be used to enhance the effectiveness of a new sorbent. FIG. 3 is a block diagram illustrating a process for enhancing the effectiveness of a sorbent. FIG. 3 is similar to FIG. 2, without a source of used

sorbent. FIG. 3 shows storage silos 12 for providing fresh sorbent to a contact reactor. The contact reactor receives the fresh sorbent and facilitates the sorbent treatment process 10, which will enhance the effectiveness of the sorbent. The remainder of FIG. 3 is the same as FIG. 2.

[37] In the preceding detailed description, the invention is described with reference to specific exemplary embodiments thereof. Various modifications and changes may be made thereto without departing from the broader spirit and scope of the invention as set forth in the claims. The specification and drawings are, accordingly, to be regarded in an illustrative rather than a restrictive sense.

CLAIMS

What is claimed is:

1. A method of regenerating a used sorbent comprising:
creating a sorbent mixture containing used sorbent and unused sorbent;
exposing the sorbent mixture to a solution to remove contaminants collected on the used sorbent to restore mercury sorption effectiveness to the sorbent;
dewatering the sorbent mixture to remove sorbent particles from the solution; and
drying the dewatered sorbent mixture.

2. The method of claim 1, wherein ash is separated from the used sorbent prior to exposure of the sorbent mixture to the solution.

3. The method of claim 1, wherein the solution includes an inorganic acid solution.

4. The method of claim 3, the inorganic acid solution includes at least one of hydrochloric acid (HCl), hydrobromic acid (HBr), and hydroiodic acid (HI).

5. The method of claim 1, wherein the solution is a salt solution.

6. The method of claim 5, the salt solution includes a halide salt, containing an associated cation, such as ammonium, sodium, potassium, iron, aluminum, boron, zinc, manganese, magnesium, calcium.

7. The method of claim 1, wherein the solution includes an organic acid.

8. The method of claim 7, the organic acid solution includes at least one of citric acid, tartaric acid, oxalic acid, malonic acid, maleic acid, formic acid, and acetic acid.

9. The method of claim 1, wherein the solution includes an organic salt solution.

10. The method of claim 9, wherein the organic salt solution includes:
at least one anion from at least one of citric acid, tartaric acid, oxalic acid, malonic acid, maleic acid, formic acid, and acetic acid; and
at least one associated cation, such as ammonium, sodium, potassium, iron, aluminum, boron, zinc, manganese, magnesium, or calcium.

11. The method of claim 1, wherein the solution contains only water.

12. The method of claim 1, wherein the used sorbent contains constituents derived from a flue gas stream.

13. The method of claim 1, wherein the sorbent is activated carbon.

14. The method of claim 1, wherein the contaminant includes sulfuric acid.

15. The method of claim 1, wherein the mercury sorption effictiveness of the sorbent is restored by removing anions collected on the used sorbent.

16. The method of claim 1, wherein the mercury sorption effectiveness of the sorbent is restored by removing sulfuric acid from the sorbent.

17. The method of claim 1, further comprising agitating the sorbent mixture and the solution.

18. The method of claim 1, further comprising mixing an additive with the regenerated sorbent prior to injecting the regenerated sorbent into the flue gas stream.

19. The method of claim 18, wherein the additive neutralizes acids.

20. The method of claim 18, wherein the additive is a calcium-based additive.

21. A method of regenerating a used sorbent comprising:
exposing the used sorbent to a solution to remove contaminants collected on the used sorbent to restore mercury sorption effectiveness to the sorbent;
dewatering the sorbent to remove sorbent particles from the solution; and
drying the dewatered sorbent mixture.

22. The method of claim 21, wherein the solution includes an inorganic acid solution.

23. The method of claim 21, wherein the solution is a salt solution.

24. The method of claim 21, wherein the solution includes an organic acid.

25. The method of claim 21, wherein the solution includes an organic salt solution.

26. The method of claim 21, wherein the sorbent is activated carbon.

27. A method of regenerating a used sorbent comprising:

creating a sorbent mixture containing used sorbent and unused sorbent;
regenerating the used sorbent by exposing the sorbent mixture to a solution to remove contaminants collected on the used sorbent to restore mercury sorption effectiveness to the sorbent; and
exposing the regenerated sorbent to a flue gas stream.

28. The method of claim 27, wherein the regenerated sorbent is exposed to the flue gas stream by injecting the regenerated sorbent into the flue gas stream.

29. The method of claim 27, wherein the regenerated sorbent is exposed to the flue gas stream using a fixed sorbent bed.

30. The method of claim 27, wherein the regenerated sorbent is exposed to the flue gas stream using a traveling sorbent bed.

31. The method of claim 27, wherein the regenerated sorbent is exposed to the flue gas stream using a traveling fiber filter.

32. The method of claim 27, wherein the solution includes an inorganic acid solution.

33. The method of claim 27, wherein the solution is a salt solution.

34. The method of claim 27, wherein the solution includes an organic acid.

35. The method of claim 27, wherein the solution includes an organic salt solution.

36. The method of claim 27, wherein the sorbent is activated carbon.

37. A method of enhancing the effectiveness of a sorbent comprising:
exposing the sorbent to a solution that increases sorbent effectiveness;
dewatering the sorbent to remove sorbent particles from the solution; and
drying the dewatered sorbent.

38. The method of claim 37, wherein the solution includes an inorganic acid solution.

39. The method of claim 37, wherein the solution is a salt solution.

40. The method of claim 37, wherein the solution includes an organic acid.

41. The method of claim 37, wherein the solution includes an organic salt solution.

42. The method of claim 37, wherein the sorbent is activated carbon.

43. A method of enhancing the effectiveness of a sorbent comprising:
enhancing the sorbent by exposing the sorbent to a solution that increases sorbent effectiveness; and
exposing the enhanced sorbent to a flue gas stream.

44. The method of claim 43, wherein the enhanced sorbent is exposed to the flue gas stream by injecting the enhanced sorbent into the flue gas stream.

45. The method of claim 43, wherein the enhanced sorbent is exposed to the flue gas stream using a fixed sorbent bed.

46. The method of claim 43, wherein the enhanced sorbent is exposed to the flue gas stream using a traveling sorbent bed.

47. The method of claim 43, wherein the enhanced sorbent is exposed to the flue gas stream using a traveling fiber filter.

48. The method of claim 43, wherein the solution includes an inorganic acid solution.

49. The method of claim 43, wherein the solution is a salt solution.

50. The method of claim 43, wherein the solution includes an organic acid.

51. The method of claim 43, wherein the solution includes an organic salt solution.

52. The method of claim 43, wherein the solution includes a compound comprised of a halogen combined with a Group V or Group VI element.

53. The method of claim 52, wherein the compound includes one or more of thionyl chloride, sulfuryl chloride, phosphorus trichloride, phosphorus oxychloride, hypochlorous acid, and chlorine.

54. The method of claim 52, wherein the compound is includes one or more of thionyl bromide, sulfuryl bromide, phosphorus tribromide, phosphorus oxybromide, hypobromous acid, and bromine.

55. The method of claim 43, wherein the sorbent is activated carbon.

56. A method of removing mercury or other pollutants in a flue gas stream during the burning of fossil fuels, comprising:
exposing the sorbent to the flue gas stream to remove contaminants from the flue gas stream;
mixing the used sorbent with fresh sorbent and exposing the mixture to a solution to remove contaminants collected on the used sorbent to restore mercury sorption effectiveness to the sorbent;
dewatering the mixture to remove sorbent particles from the solution;
drying the sorbent particles; and
exposing the dried sorbent particles to the flue gas stream to remove additional contaminants from the flue gas stream.

57. The method of claim 56, wherein the sorbent is activated carbon.

58. The method of claim 56, wherein the solution includes an inorganic acid solution.

59. The method of claim 56, wherein the solution is a salt solution.

60. The method of claim 56, wherein the solution includes an organic acid.

61. The method of claim 56, wherein the solution includes an organic salt solution.

62. An apparatus for regenerating a sorbent comprising:
a contact reactor for receiving and containing a mixture of used sorbent and unused sorbent, wherein the mixture in the contact reactor is exposed to an aqueous acidic solution to restore mercury sorption effectiveness to the sorbent;
a dewatering device for removing sorbent particles from the aqueous acidic solution; and
a dryer for drying the sorbent particles.

63. The apparatus of claim 62, wherein the contact reactor further comprises one or more methods for agitating the mixture.

64. The apparatus of claim 62, wherein the dewatering device is comprised of a hydroclone.

65. The apparatus of claim 62, wherein the dewatering device is comprised of a settling tank or thickener.

66. The apparatus of claim 62, wherein the dewatering device is comprised of a filtration device.

67. The apparatus of claim 62, wherein the dryer is comprised of a heat exchanger.

68. The apparatus of claim 62, wherein the dryer is comprised of a fluidization chamber.

69. The apparatus of claim 62, further comprising a sorbent ash separator for separating the used sorbent from ash prior to being received by the contact reactor.

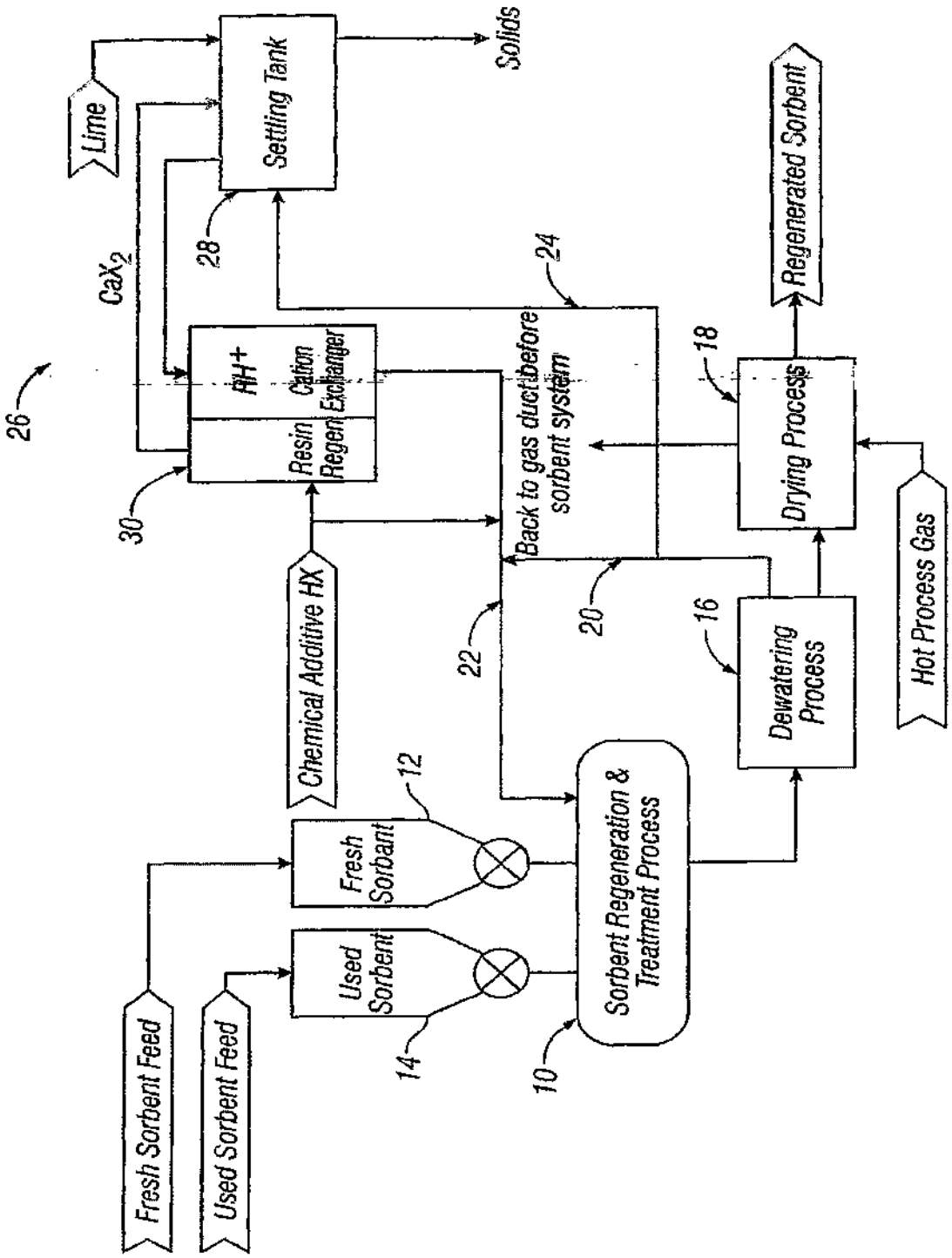

Fresh Sorbent Feed
Used Sorbent Feed
Fresh Sorbant
Used Sorbent
12
14
10
Sorbent Regeneration & Treatment Process
Chemical Additive HX
22
20
Back to gas duct before sorbent system
16
Dewatering Process
18
Drying Process
Regenerated Sorbent
Hot Process Gas
24
28
30
26
AH+
Cation Exchanger
Resin Regen
CaX2
Lime
Settling Tank
Solids

FIG. 1

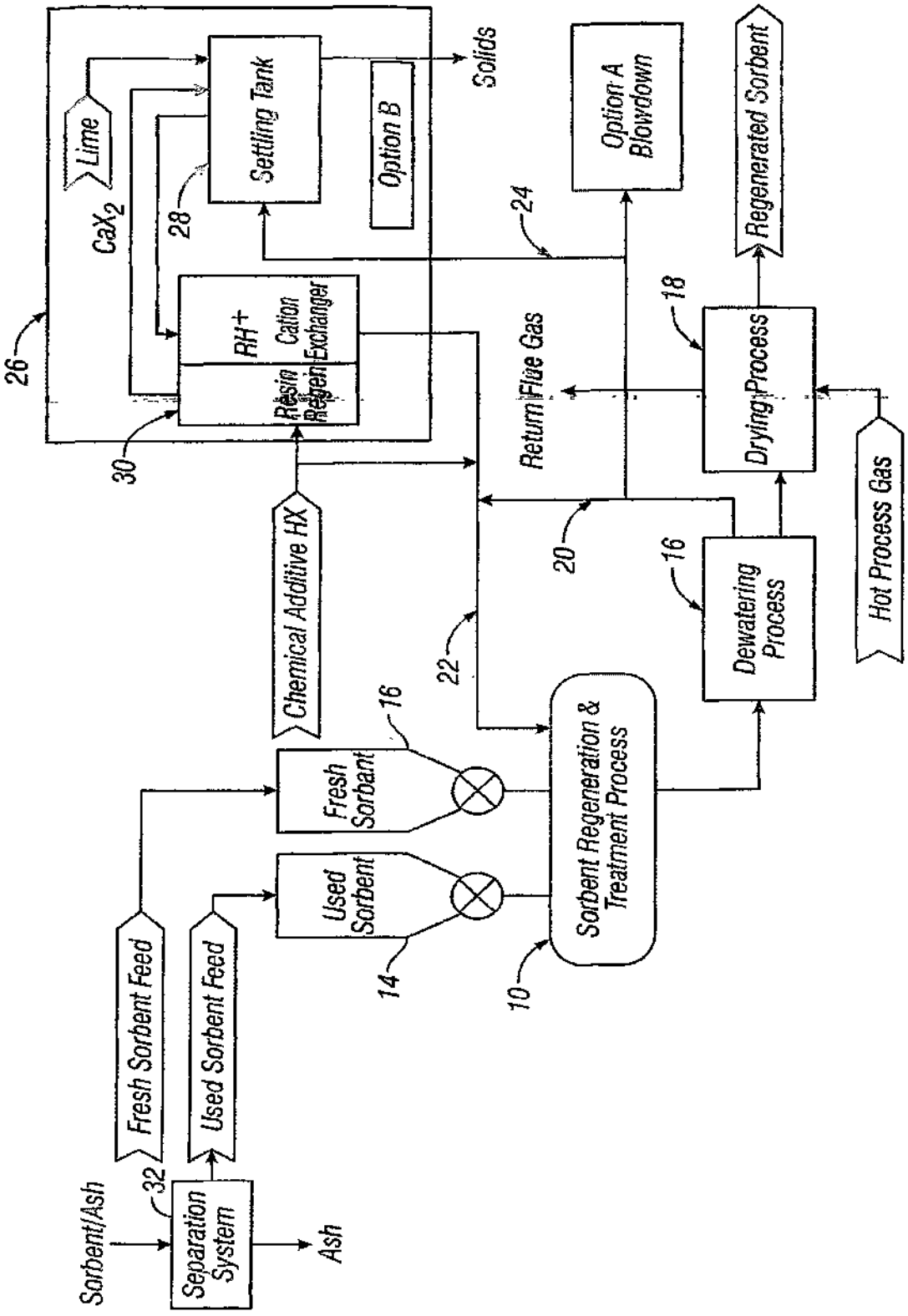

Sorbent/Ash
Separation System
32
Ash
Fresh Sorbent Feed
Used Sorbent Feed
Fresh Sorbant
Used Sorbent
16
14
10
Sorbent Regeneration & Treatment Process
22
Chemical Additive HX
30
26
Lime
CaX_2
28
Settling Tank
Option B
Solids
RH^+ Cation Exchanger
Resin Regen
24
Option A Blowdown
Return Flue Gas
20
16
Dewatering Process
18
Drying Process
Regenerated Sorbent
Hot Process Gas

FIG. 2

3/3

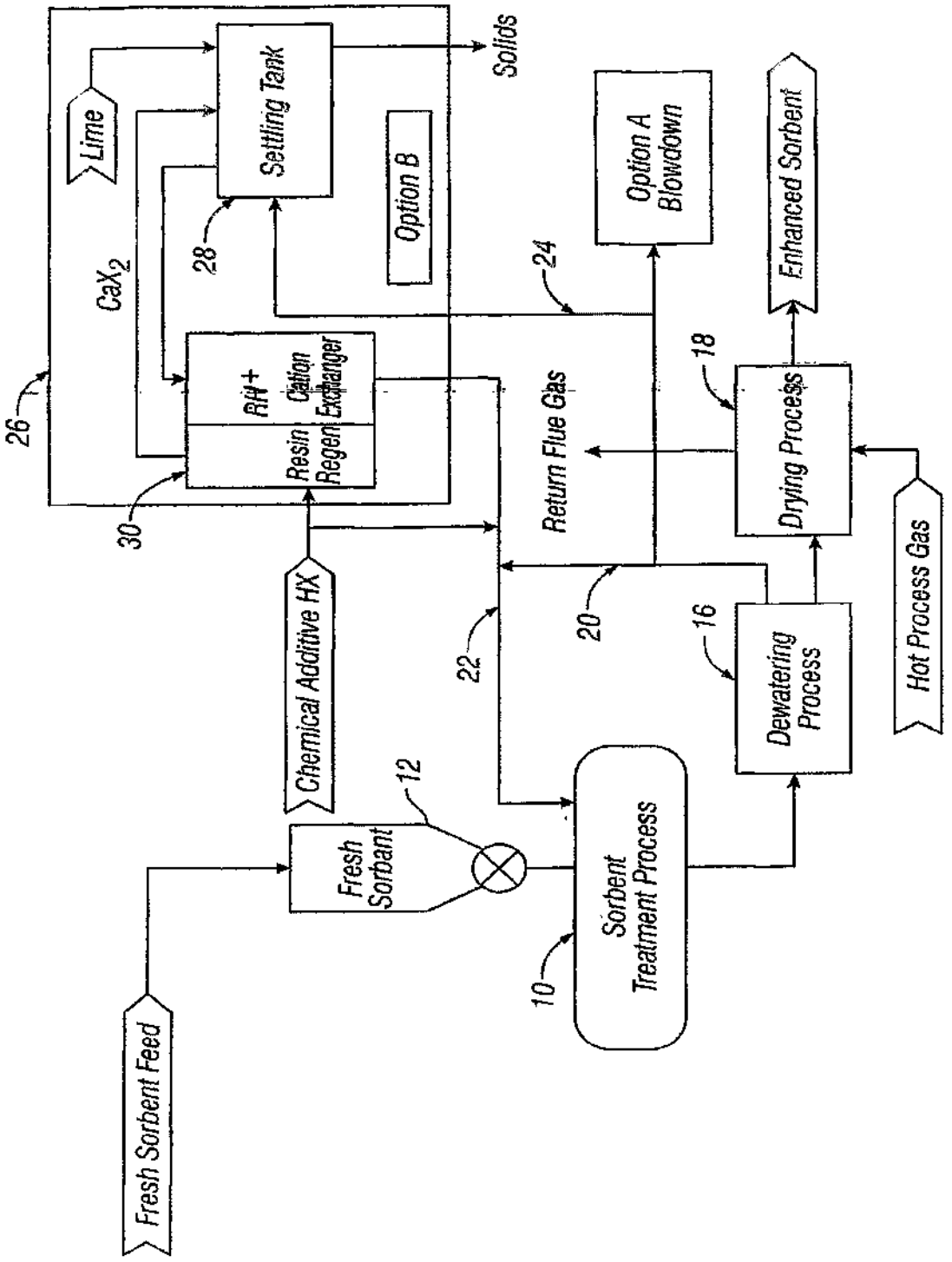

Fresh Sorbent Feed
Chemical Additive HX
Lime
Settling Tank
Solids
Option B
Option A Blowdown
Enhanced Sorbent
Hot Process Gas
Return Flue Gas
Drying Process
Dewatering Process
Sorbent Treatment Process
Fresh Sorbant
Resin Regen
RH+ Cation Exchanger
CaX2
10
12
16
18
20
22
24
26
28
30

FIG. 3

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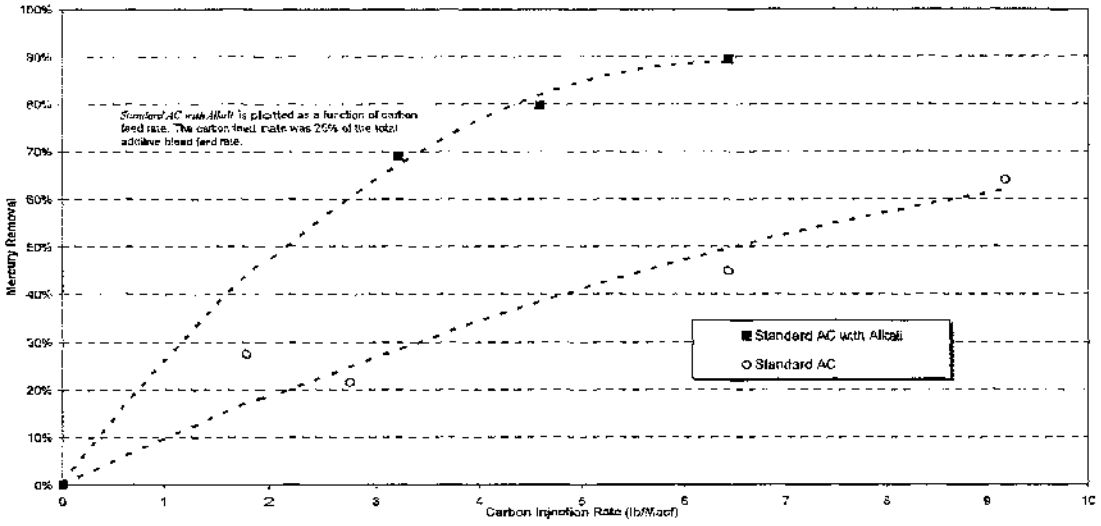
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(54) Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY



(57) Abstract: A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

WO 2006/039007 A2

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with United States Government support under the U.S. Environmental Protection Agency Grant Nos. R 827649-01 and CR 830929-01. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

Technical Field of the Invention

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic

silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens,

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and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have an mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the

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reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury from a flue gas at lower removal rates with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

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In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-

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containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages 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 that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also 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

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

Figure 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

Figure 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

Figure 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

Figure 4 is a diagram illustrating breakthrough curves for 5 wt/wt% brominated NORIT Darco FGD sorbent (37 mg + 113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

Figure 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg + 113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

Figure 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

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Figure 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

Figure 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

Figure 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

Figure 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury *via* mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require *in situ* activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to Figure 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas form a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base

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activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to Figure 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

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In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to Figure 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals

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of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to Figure 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional akali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Optional alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to *both* transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in Figure 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points 116 or 119 are shown in Figure 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device (s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at a location upstream and/or downstream of 140 when parallel, sequential, or combinations

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thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142, and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152, and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

An optional Continuous Emission Monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35, to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25, by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury "clean" flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, 209 can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

Referring still to Figure 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base activated carbon from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base activated carbon prior to injection point 116. This option is one form of what is referred to herein as "in-flight" preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with base activated carbon prior to entering

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transport line 115. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebullated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in Figure 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to Figure 1.

Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131b and 131c.

Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions..

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebullated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

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In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the

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mercury on the sorbent and ash is very short – less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. In Addition to halide ions, this phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, the modified cationic carbon has a high chemical potential for oxidation of the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

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Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection

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system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.
- The inventive process uses existing hardware and operation procedures.
- The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjection with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or

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optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a *carbocation* that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine- containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1 -Preparation and Testing of Halogenated Carbon (& Comparative Example)

Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, TX (USA), although others are suitable, as will be recognized by those skilled in the

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art), was placed in a rotating plastic barrel with side blades (a 5 ft^3 (0.14 m^3) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°–50°C. The vapor pressure of the bromine was such that a dark red gas is generated a passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight to that the excess of nitrogen is released after the bromine is transfer to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2–5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5–17 wt%), but does not require further drying for use. The moisture is driven out at higher temperatures (>150°C), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G.E.; Miller, S.J. Chang, R.; Bergman, P. *Environmental Progress* **1998**, *17*, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (-400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125°C) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O_2 (6%), CO_2 (12%), SO_2 (600 ppm), NO (120 ppm) NO_2 (6 ppm), HCl (1 ppm), Hg^0 (11 $\mu g/m^3$), H_2O (15%), and N_2 (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations

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in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach FL USA), and a $SnCl_2$ cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to Figure 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%–1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30–60 minutes (breakthrough point), depending on the sorbent. Figure 4 illustrates the breakthrough curves for 5 wt/wt% brominated NORIT Darco FGD sorbent (37 mg + 113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a per cent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

Figure 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%–50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2 - Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3 - Liquid Phase (water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110°C for

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several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4 - Addition of the Optional Second Halide Component.

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5 - Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110°C in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6 - Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 μm) sorbent was developed, prepared, and tested.

Treatment - Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°–50°C, and the outlet from this gaseous bromine generator was connected via a 1/4 inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had

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combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the "Particulate Test Combustor" (hereinafter "PTC"), is a 550,000-Btu/hr (about 161 kW) pulverized coal ("PC")-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a "fabric filter") or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O_2, CO, CO_2, SO_2, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO_2 was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

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The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m^3/min) of flue gas at 300°F (about 150°C), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300°F (150°C). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCMM (normal m^3/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in Figure 6. As can be observed in Figure 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter ("FF"). Note that in Figure 6 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or "MACM").

Referring now to Figure 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because >60 μm sorbent particles have been successfully demonstrated, superior mercury control can be obtained with >40 μm particles, which may be preferred in some applications, depending

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on the sorbent particle/ash separation system used. Note that in Figure 7 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet.

Example 7 - Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110°C for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8 - Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100°C in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu g/m^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, FL, USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus

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enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9 - Fluidized/Ebullated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10 - Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu g/m^3$. The ash and injected carbon were collected in the baghouse at 350°F to 375°F (about 175-190°C). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 $\mu g/m^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A - Addition of Optional Alkaline Component – Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with

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inert sand is shown in Figure 8, and the breakthrough curve for the mixture with CaO is shown in Figure 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B - Addition of Optional Alkaline Component – Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as "AC") and an alkali material upstream of a fabric filter. Typical results are illustrated in Figure 10. As shown in Figure 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12- Brominated Carbon Sorbent for Gasification Fuel Gas

Preparation of 5%Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol% solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt% brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by

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vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110°C until a stable weight was obtained The moisture was reduced to 15%.

Preparation of 5%Br2D-AC

A brominated sorbent was prepared from Br_2 addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5%PBr3-AC

A phosphohalogenated sorbent was prepared from PBr_3 using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere - Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/m^3 of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/m^3). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400°C). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no $SnCl_2$ trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5%Br2W-AC and 5%BrD-AC), and the phosphobrominated sorbent

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(5%PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100°C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400°C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400°C.

Table 1

Times for 50% Breakthrough
Maximum Observed Hg Concentrations for Sorbents
(10% Hydrogen Streams)

Sorbent	Temp (°C)	50% breakthrough (min)	Maximum [Hg] ($\mu g/m^3$)	Time (min)
F-400	250	6	20.3	6.5
5%Br2W-AC	250	>150	1.4	150
5%Br2W -AC	300	>180	4.3	180
5%Br2W-AC	350	160	15.1	180
5%Br2W-AC	400	60	13.9	65
5%PBr3-AC	250	>140	0.4	140
5%PBr3-AC	300	>150	0.5	150
5%PBr3-AC	350	>150	1.4	150
5%Br2D-AC	350	>180	2.1	180
5%Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications

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thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

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WE CLAIM:

1. A promoted carbon sorbent comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

2. The promoted carbon sorbent of claim 1 wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than 40 micrometers, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V halides, Group VI halides, hydrohalides, and combinations thereof.

3. The promoted carbon sorbent of claim 2 wherein the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon.

4. The promoted carbon sorbent of claim 3 further comprising an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

5. The promoted carbon sorbent of claim 4 further comprising an optional alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

6. The promoted carbon sorbent of claim 4 wherein the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

7. The promoted carbon sorbent of claim 6 wherein the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof.

8. The promoted carbon sorbent of claim 7 wherein the optional secondary component is selected from the group consisting of I_2, HI, and combinations thereof.

9. The promoted carbon sorbent of claim 8 wherein the promoter is substantially in vapor form when combined with the base activated carbon.

10. The promoted carbon sorbent of claim 8 wherein the promoter is combined with an

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organic solvent prior to reaction with the base activated carbon.

11. The promoted carbon sorbent of claim 8 wherein the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously.

12. The promoted carbon sorbent of claim 8 further comprising a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

13. The promoted carbon sorbent of claim 12 wherein the promoter is selected from the group consisting of Br_2, HBr, and combinations thereof.

14. The promoted carbon sorbent of claim 3 further comprising a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

15. The promoted carbon sorbent of claim 14 further comprising an optional alkaline component comprising an alkaline or alkaline earth element wherein the promoter is selected from the group consisting of Br_2, HBr, and combinations thereof.

16. A method comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream.

17. The method of claim 16 wherein the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon.

18. The method of claim 16 wherein the reaction product has an average particle size distribution greater than about 40 micrometers.

19. The method of claim 16 wherein the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof.

20. The method of claim 19 wherein the promoter is in the gas phase when contacting the activated carbon.

21. The method of claim 19 wherein the promoter is in an organic solvent when contacting the activated carbon.

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22. The method of claim 20 wherein the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

23. The method of claim 18 further comprising providing an optional alkaline component to improve the effectiveness of mercury removal.

24. The method of claim 20 further comprising reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

25. The method of claim 24 further comprising providing an optional alkaline component to improve the effectiveness of mercury removal.

26. The method of claim 24 wherein the promoter and optional secondary component are contacted simultaneously with the activated carbon.

27. The method of claim 24 wherein the optional secondary component comprises I_2 or HI.

28. The method of claim 20 further comprising adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

29. The method of claim 24 further comprising adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

30. A method for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas.

31. The method of claim 30 further comprising co-injecting an optional alkaline component into the mercury containing flue gas stream.

32. The method of claim 30 further comprising monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent.

33. The method of claim 30 wherein the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

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34. The method of claim 33 wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof.

35. The method of claim 34 wherein the promoter is selected from the group consisting of Br_2, HBr, Group V bromides, Group VI bromides, and combinations thereof.

36. The method of claim 35 wherein the promoter is reacted in the gas phase or as a vapor.

37. The method of claim 36 wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

38. The method of claim 37 wherein the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

39. The method of claim 38 wherein the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof.

40. The method of claim 39 further comprising co-injecting an optional alkaline component into the mercury containing flue gas stream.

41. The method of claim 39 wherein the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content.

42. The method of claim 41 wherein the optional secondary component is selected from the group consisting of I_2, HI, and combinations thereof.

43. The method of claim 42 wherein the optional secondary component is added in the gas phase or as a vapor.

44. The method of claim 41 further comprising adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

45. The method of claim 32 further comprising using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent.

46. The method of claim 40 further comprising monitoring the mercury content of the clean

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flue gas and using the monitored mercury content to control the composition of the sorbent and the alkaline-to-sorbent injection ratio.

47. The method of claim 45 wherein the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

48. A method for reducing the mercury content of a gas stream comprising the steps of injecting a powdered activated carbon sorbent having a mass-mean particle size >40μm into a gas stream containing mercury and ash particles, capturing mercury from the gas stream on the sorbent particles, mechanically separating the sorbent particles from the ash particles, and re-injecting the separated sorbent particles into the gas stream.

49. The method of claim 48 further comprising regenerating the sorbent particles to substantially remove contaminants therefrom to recover capacity for capturing mercury.

50. The method of claim 48 further comprising co-injecting into the gas stream an alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

51. The method of claim 48 wherein the powdered activated carbon sorbent further comprises a promoter selected from the group consisting of halides, halogens, and combinations thereof.

52. The method of claim 51 further comprising co-injecting into the gas stream an alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

53. The method of claim 48 wherein the particulate activated carbon sorbent has a mass-mean particle size >60μm.

54. The method of claim 52 wherein the particulate activated carbon sorbent has a mass-mean particle size >60μm.

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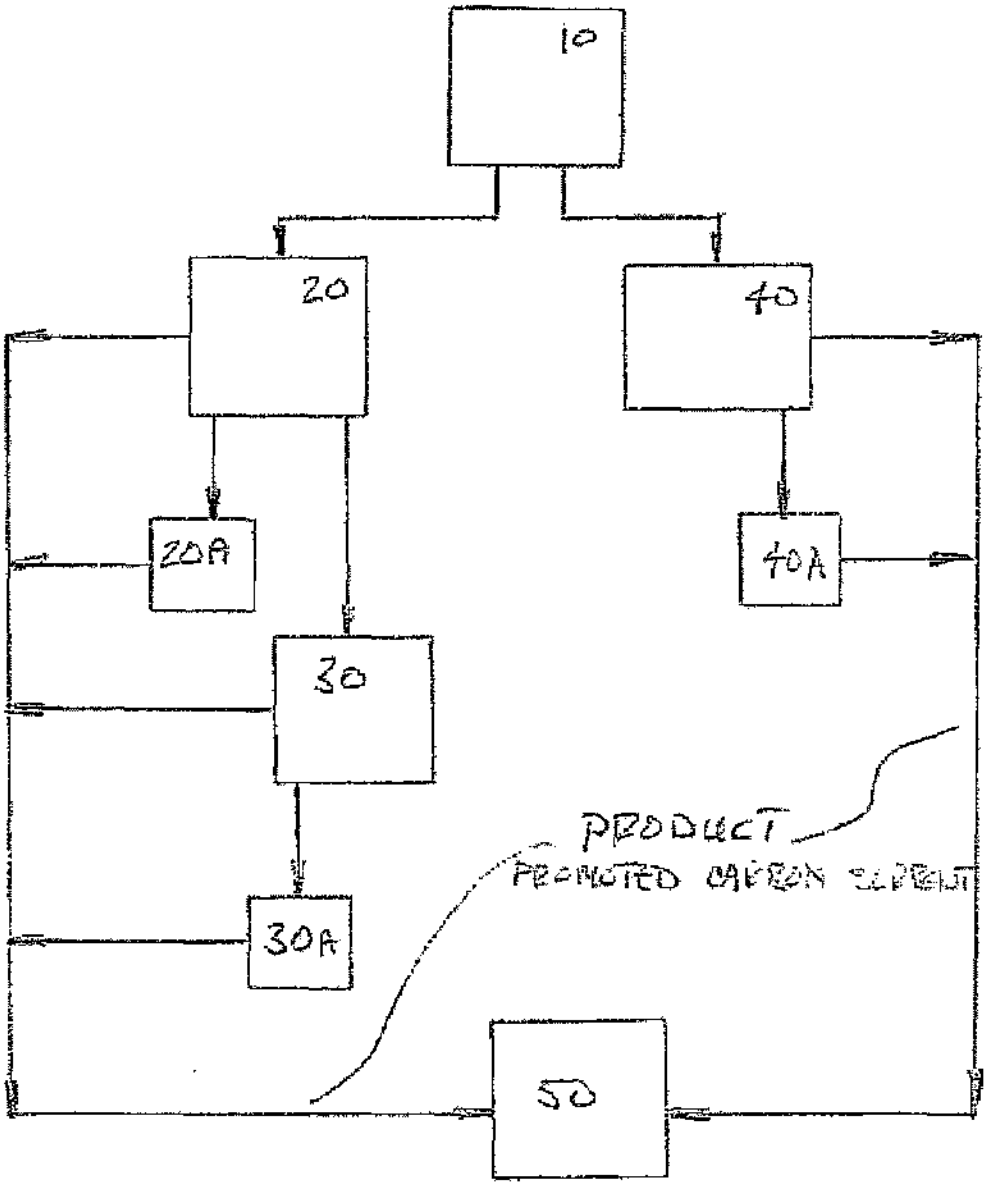


FIG. 1

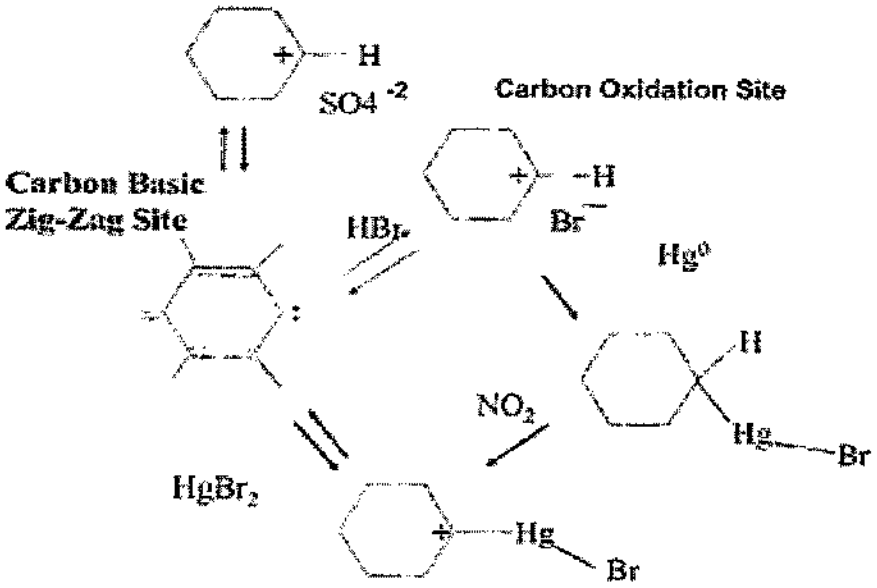

H
SO4 -2
Carbon Oxidation Site
Carbon Basic
Zig-Zag Site
HBr
H
Br
Hg°
H
NO2
Hg
Br
HgBr2
Hg
Br

FIG. 2

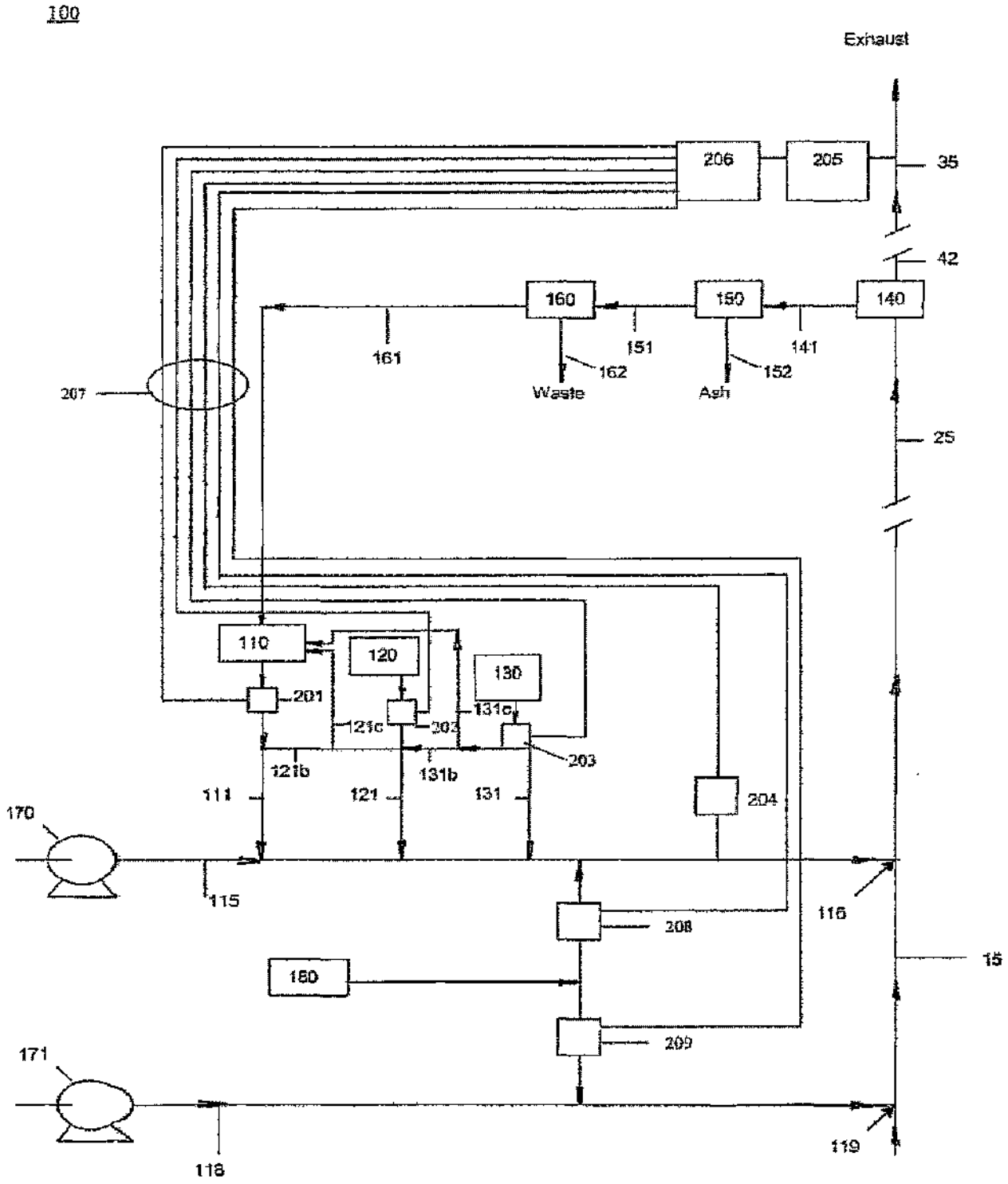

100
Exhaust
206
205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
25
110
120
130
201
131c
121c
203
121b
131b
111
121
131
204
170
115
116
208
15
180
209
171
119
118

FIG. 3

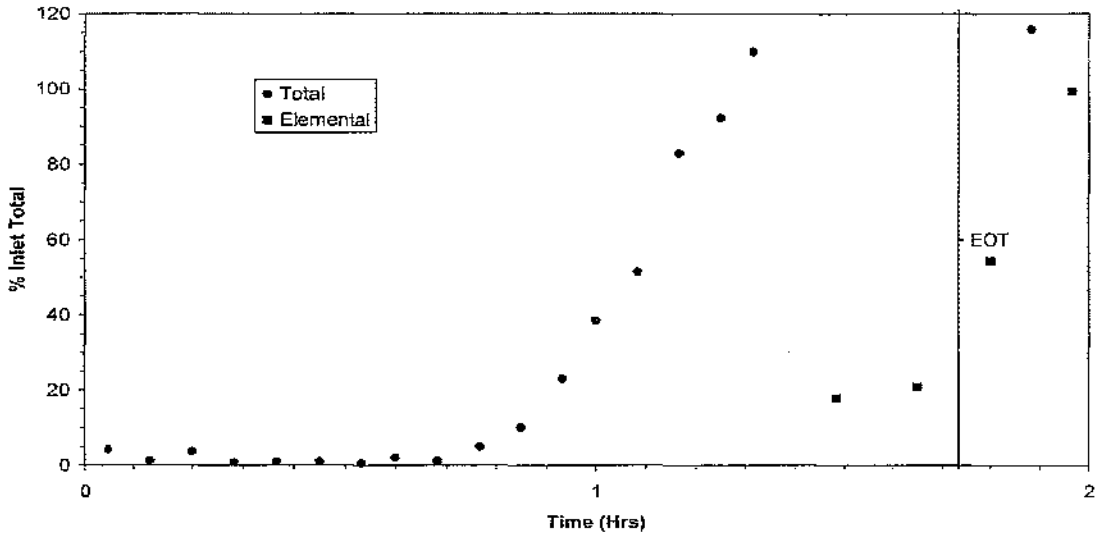

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
2
Time (Hrs)

FIG. 4

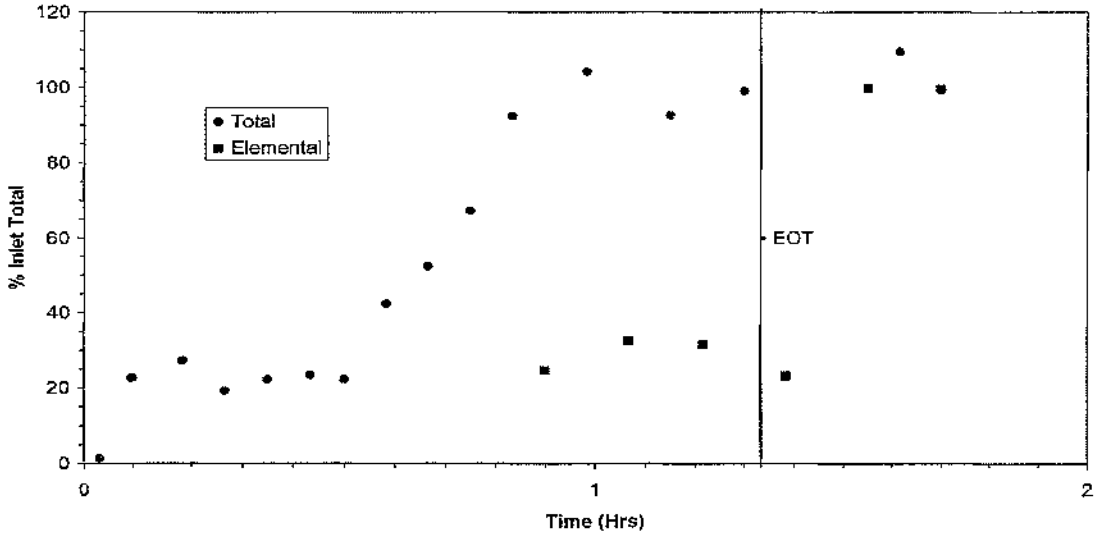

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
2
Time (Hrs)

FIG. 5

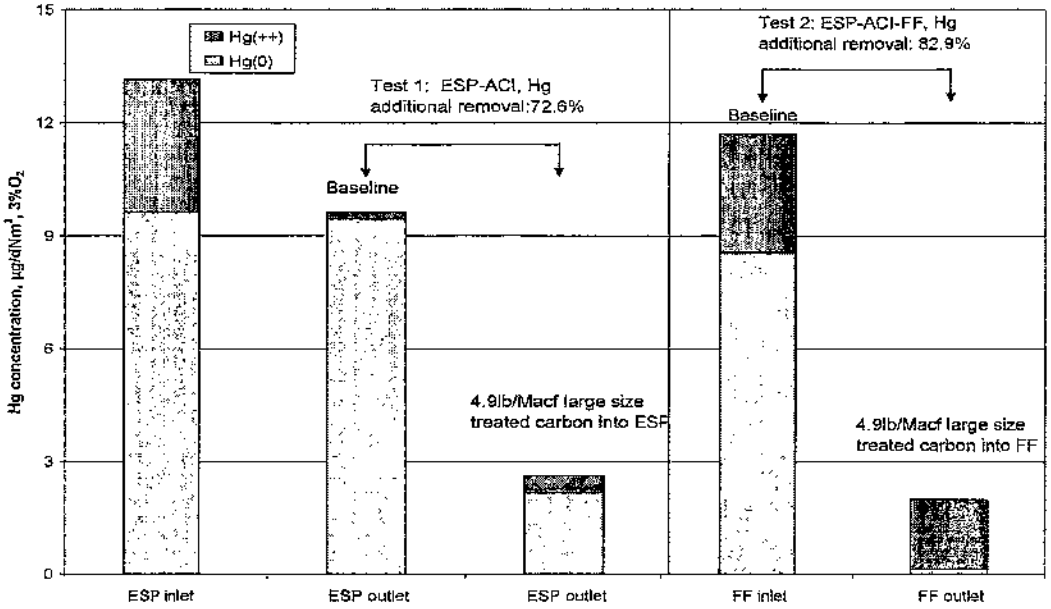

Hg(++)
Hg(0)
Test 1: ESP-ACI, Hg additional removal:72.6%
Test 2: ESP-ACI-FF, Hg additional removal: 82.9%
Baseline
Baseline
4.9lb/Macf large size treated carbon into ESP
4.9lb/Macf large size treated carbon into FF
Hg concentration, µg/dNm³, 3%O₂
ESP inlet
ESP outlet
ESP outlet
FF inlet
FF outlet

FIG. 6

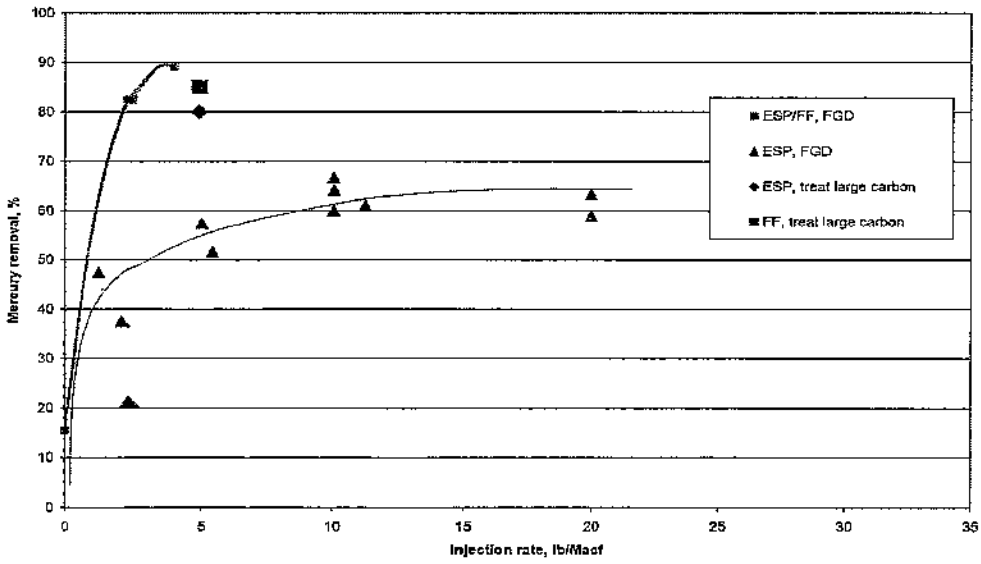

ESP/FF, FGD
ESP, FGD
ESP, treat large carbon
FF, treat large carbon
Mercury removal, %
Injection rate, lb/Macf

FIG. 7

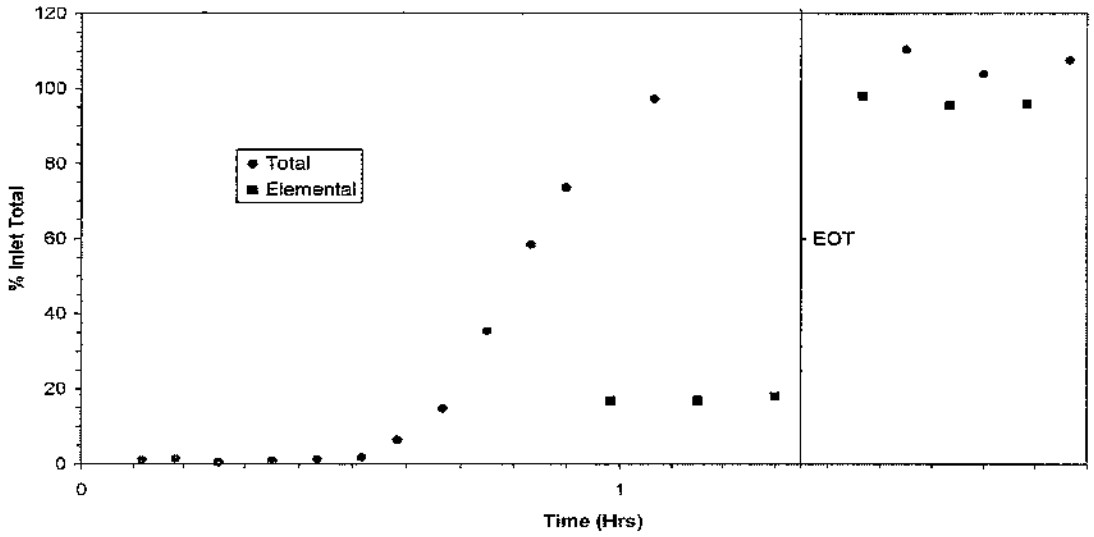

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
Time (Hrs)

FIG. 8

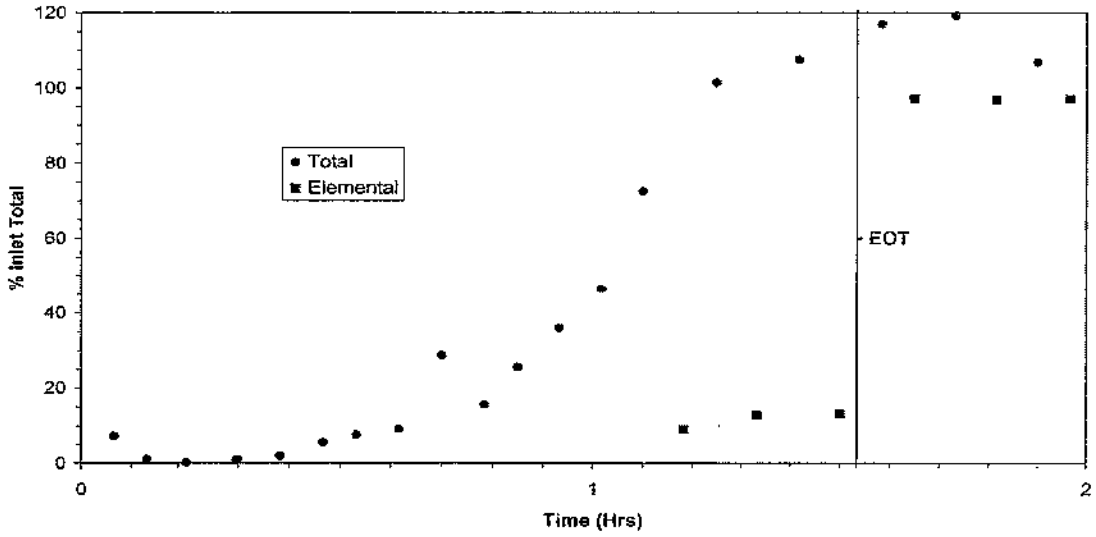

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
2
Time (Hrs)

FIG. 9

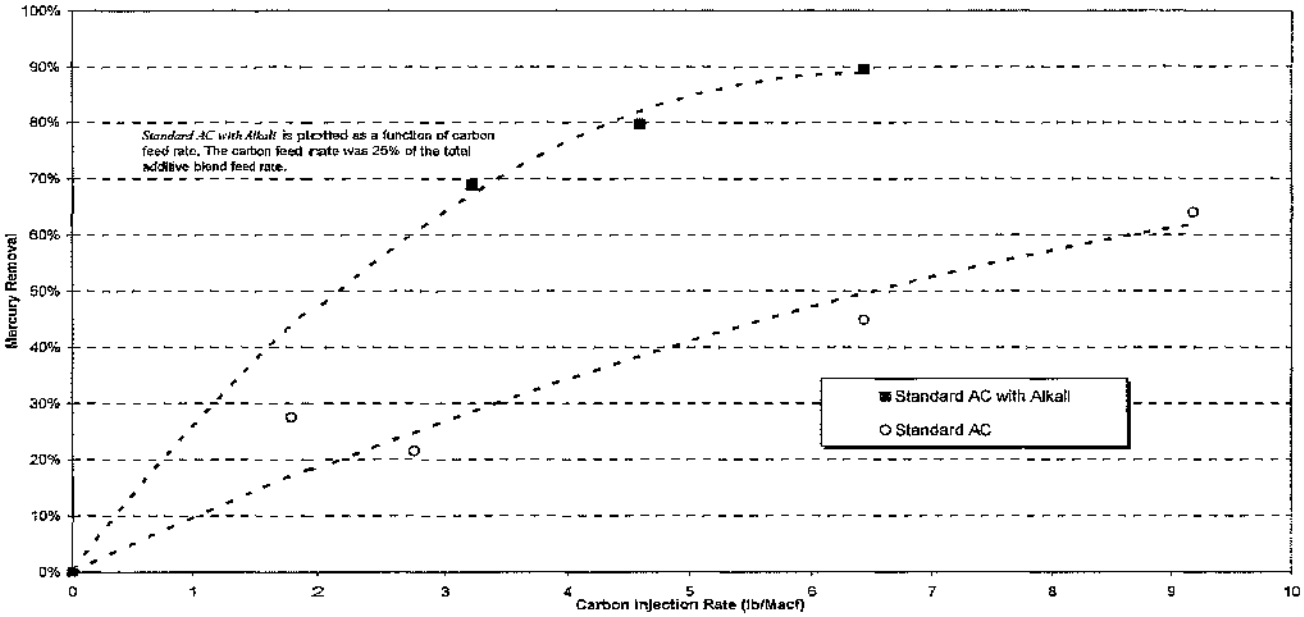

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Mercury Removal
0
1
2
3
4
5
6
7
8
9
10
Carbon Injection Rate (lb/Macf)
Standard AC with Alkali is plotted as a function of carbon feed rate. The carbon feed rate was 25% of the total additive blend feed rate.
Standard AC with Alkali
Standard AC

FIG. 10

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60/759,994	18 January 2006 (18.01.2006)	US
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(54) Title: REDUCING MERCURY EMISSIONS FROM THE BURNING OF COAL

(57) Abstract: Sorbent components containing calcium, alumina, silica, and halogen are used in combination during coal combustion to produce environmental benefits. Sorbents are added to the coal ahead of combustion and/or are added into the flame or downstream of the flame, preferably at minimum temperatures to assure complete formation of the refractory structures that result in various advantages of the methods. When used together, the components • reduce emissions of mercury and sulfur: • reduce emissions of elemental and oxidized mercury; • increase the efficiency of the coal burning process through de-slagging of boiler tubes; • increase the level of Hg, As, Pb, and/or Cl in the coal ash; • decrease the levels of leachable heavy metals (such as Hg) in the ash, preferably to levels below the detectable limits; and • make a highly cementitious ash product.

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REDUCING MERCURY EMISSIONS FROM THE BURNING OF COAL

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S Provisional Application 60/662,911 filed March 17, 2005; of U.S. Provisional Application 60/742,154 filed December 2, 2005; of U.S. Provisional Application 60/759,994 filed January 18, 2006; and of U.S. Provisional Application 60/765,944 filed February 7, 2006.

INTRODUCTION

[0002] The invention provides compositions and methods for reducing the levels of mercury emitted into the atmosphere upon burning of mercury-containing fuels such as coal. In particular, the invention provides for addition of various halogen and other sorbent compositions into the coal burning system during combustion.

[0003] Significant coal resources exist around the world capable of meeting large portions of the world's energy needs into the next two centuries. High sulfur coal is plentiful, but requires remediation steps to prevent excess sulfur from being released into the atmosphere upon combustion. In the United States, low sulfur coal exists in the form of low BTU value coal in the Powder River basin of Wyoming and Montana, in lignite deposits in the North Central region of North and South Dakota, and in lignite deposits in Texas. But even when coals contain low sulfur, they still contain non-negligible levels of elemental and oxidized mercury and/or other heavy metals.

[0004] Unfortunately, mercury is at least partially volatilized upon combustion of coal. As a result, the mercury tends not to stay with the ash, but rather becomes a component of the flue gases. If remediation is not undertaken, the mercury tends to escape from the coal burning facility into the surrounding atmosphere. Some mercury today is captured by utilities, for example in wet scrubber and SCR control systems. However, most mercury is not captured and is therefore released through the exhaust stack.

[0005] Mercury emissions into the atmosphere in the United States are approximately 50 tons per year. A significant fraction of the release comes from emissions from coal burning facilities such as electric utilities. Mercury is a known environmental hazard and leads to health problems for both humans and non-human

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animal species. 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 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.

[0006] In addition to wet scrubber and SCR control systems that tend to remove mercury partially from the flue gases of coal combustion, other methods of control have included the use of activated carbon systems. Use of such systems tends to be associated with high treatment costs and elevated capital costs. Further, the use of activated carbon systems leads to carbon contamination of the fly ash collected in exhaust air treatments such as the bag house and electrostatic precipitators.

[0007] At the same time, demand for cementitious materials such as portland cement is expected to increase as developed countries maintain their infrastructure and developing countries build and maintain roads, dams, and other major constructions for the benefit of their citizens.

[0008] When coal is burned to produce heat energy from combustion of carbonaceous material, the unburned material and particulate combustion products form an ash with pozzolanic and/or cementitious properties. While the chemical composition of coal ash depends on the chemical composition of the coal, the ash normally contains a major amount of silica and alumina, and significant but lesser amount of calcium.

[0009] So-called fly ash produced from burning of pulverized coal in a coal fired furnace or boiler is a powdery particulate matter made of the components of coal that do not volatize upon combustion. The ash is normally carried off in the flue gas and is usually collected from the flue gas using conventional apparatus such as electrostatic precipitators, filtration devices such as bag houses, and/or mechanical devices such as cyclones. The burning of coal entails the production of a large amount of coal ash, which must be dealt with by the coal burning facility. For example, under certain circumstances ash from burning coal has been successfully used in portland cement concrete as a partial replacement for portland cement. Coal ash has further been used a component in the production of flowable fill and as a component as stabilized base and sub-based mixtures. In these applications, the amount of ash used, especially as a

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replacement for portland cement in such applications, is limited by the cementitious nature or lack thereof of the particular ash product.

[0010] Even though reuse of the ash is preferred for economic reasons, in many situations, the ash is not suitable to be used as a component of cementitious mixtures. In many cases the ash must be land filled or otherwise treated as a waste product.

[0011] Methods and compositions for burning coal to produce an ash product having highly cementitious qualities would be a significant advance, because it would both reduce costs of waste disposal from coal burning utilities and reduce the cost of concrete products for needed building projects.

SUMMARY

[0012] Processes and compositions are provided for decreasing emissions of mercury upon combustion of fuels such as coal. Various sorbent compositions are provided that contain components that reduce the level of mercury and/or sulfur emitted into the atmosphere from such combustion. In various embodiments, use of the sorbent compositions leads to a fly ash combustion product from which mercury or other heavy metals do not significantly leach under acidic conditions.

[0013] In various embodiments, the sorbent compositions are added directly to the fuel before combustion; into the furnace or fireball while the fuel is burning; into the flue gas post combustion zone; or in various combinations. The sorbent compositions comprise a source of calcium, alumina, and silica, preferably in the form of alkaline powders. In various embodiments, use of a sorbent containing calcium, silica, and alumina as alkaline powders lowers the amount of sulfur and/or mercury emitted from the facility into the atmosphere. In one aspect, use of the alkaline powders lowers the oxidized mercury, for example in systems where the flame temperature is low, for example down to about 1000°F.

[0014] In a preferred embodiment, the sorbent also includes a source of halogen, and/or a sorbent containing a source of halogen is separately added into the coal-burning system. Among the halogens, iodine and bromine are preferred. In various embodiments, inorganic bromides make up a part of the sorbent compositions. In various embodiments mercury sorbent compositions containing halogen, especially

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bromine and/or iodine, are added to the fuel as a powder or a liquid prior to combustion. Alternatively, the sorbent compositions containing halogen such as bromine and iodine are injected into the flue gas at a point after the combustion chamber where the temperature is higher than about 500°C (932°F), preferably higher than 1500°F (about 800°C), and/or into the furnace during combustion.

[0015] In preferred embodiments, mercury emissions from coal burning facilities are reduced to such an extent that 90% or more of the mercury in the coal is captured before release into the atmosphere. Most of the mercury is captured in the fly ash in non-leaching form; corrosion from sulfur gases is also reduced. In preferred embodiments, significant sulfur reduction is achieved.

[0016] Methods and compositions are provided for burning coal to produce an ash product that is highly cementitious in nature. In various embodiments, the cementitious nature of the ash allows for formulation of portland cement concrete and similar products with up to 50% or more of the portland cement being substituted by the ash product. In various embodiments, the strength activity index of portland type cement products formulated with up to 50% or more ash is greater than 75% and preferably 100% or greater. Accordingly, in some embodiments, the ash product of the invention is used as the main cementitious material in portland cement concretes, in stabilized base, in sub-base mixtures, in flowable fill (also called controlled low strength material or CLSM), and the like.

[0017] The fly ash produced from combusting coal with these sorbent components is generally higher in calcium content than the specifications for class F or class C fly ash, and the combined content of silica, alumina, and iron oxide, while significant, is considerably below the specifications for class F and class C fly ash.

[0018] In various embodiments, the invention provides a variety of cement products such as portland cement concrete, flowable fill, stabilized base, and similar products in which the conventional cement (portland cement) otherwise used in the products is replaced in whole or in part with the cementitious ash product described herein. In particular, in preferred embodiments, the cementitious ash product of the current disclosure is used to replace 40% or more of the portland cement conventionally used in such products.

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[0019] In various embodiments, use of the cementitious ash in building products as total or partial replacement for portland cement results in reduced carbon dioxide emissions that would otherwise result from the manufacture of portland cement. In addition to avoided carbon dioxide emissions from calcining of limestone to make portland cement and the burning of fossil fuels to provide the energy needed to make portland cement, use of the sorbent components tends to increase the efficiency of energy production from burning of coal, further reducing greenhouse emissions from the burning of fossil fuel to produce energy.

DESCRIPTION

[0020] Sorbents, sorbent components and methods for their use are described herein; in U.S. Provisional Application No. 60/662,911 filed March 17, 2005; in U.S. Provisional Application No. 60/742,154 filed December 2, 2005; in U.S. Provisional Application No. 60/759,994 filed January 18, 2005; and in U.S. Provisional Application No. 60/765,944 filed February 7, 2006, the disclosures of which are hereby incorporated by reference. Apparatus and methods of injection of the various sorbent compositions are described herein and in U.S. Provisional Applications No. 60/759,943 filed January 18, 2006 and No. 60/760,424 filed January 19, 2006, the disclosures of which are incorporated by reference.

[0021] In various embodiments, the invention provides compositions and methods for reducing emissions of mercury that arise from the combustion of mercury-containing fuels such as coal. A commercially valuable embodiment is use of the invention to reduce sulfur and/or mercury emissions from coal burning facilities to protect the environment and comply with government regulations and treaty obligations.

[0022] In various embodiments, the methods prevent release of mercury into the atmosphere from point sources, such as coal-burning utilities by capturing the mercury in the ash. Further, the methods prevent release of mercury and other heavy metals into the environment by leaching from solid wastes such as coal ash produced by burning the mercury containing coal. In both these ways, mercury is kept out of bodies of water. Thus, prevention or reduction of mercury emissions from such facilities as coal-burning utilities leads to a variety of environmental benefits, including less air pollution, less water pollution, and less hazardous waste production, with less resulting

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ground contamination. For convenience but without limitation, advantageous features of the invention are illustrated as preventing air, water, and ground pollution by mercury or other heavy metals.

[0023] Various sorbent components are used in combination to treat coal ahead of combustion and/or to be added into the flame or downstream of the flame, preferably at minimum temperatures to assure complete formation of the refractory structures that result in various advantages of the methods. The sorbent components comprise calcium, alumina, silica, and halogen. In various embodiments, together, the components

- reduce emissions of mercury and sulfur;
- reduce emissions of elemental and oxidized mercury;
- increase the efficiency of the coal burning process through de-slagging of boiler tubes;
- increase the level of Hg, As, Pb, and/or Cl in the coal ash;
- decrease the levels of leachable heavy metals (such as Hg) in the ash, preferably to levels below the detectable limits; and
- make a highly cementitious ash product.

[0024] By calcium is meant a compound or composition that has a non-negligible amount of calcium. For example, many alkaline powders contain 20% or more calcium, based on CaO. Examples are limestone, lime, calcium oxide, calcium hydroxide (slaked lime), portland cement and other manufactured products or by-products of industrial processes, and calcium-containing aluminosilicate minerals. Silica and alumina content is based on SiO_2 and Al_2O_3 equivalents, even though it is appreciated that silica and alumina are often present in a more complex chemical or molecular form.

[0025] As used herein, all percentages are on a weight basis, unless indicated as otherwise. It should be noted that the chemical compositions of various materials described herein are expressed in terms of simple oxides calculated from elemental analysis, typically determined by x-ray fluorescence techniques. While the various simple oxides may be, and often are, present in more complex compounds in the material, the oxide analysis is a useful method for expressing the concentration of compounds of interest in the respective compositions.

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[0026] Although much of the following discussion will refer to coal as the fuel, it is to be understood that the description of coal burning is for illustrative purposes only and the invention is not necessarily to be limited thereby. For example, other types of facilities that burn fuels with potentially harmful levels of mercury or other heavy metals include incineration plants, such as those used to incinerate household waste, hazardous waste, or sewage sludge. In addition, many facilities burn fuel mixtures that comprise coal as well as other fuels, such as natural gas, synthetic gas, or waste-derived fuels.

[0027] A variety of waste streams are incinerated in such plants, which often operate in populated areas for logistical reasons. Household waste can contain mercury from a variety of sources, such as discarded batteries and thermometers as well as a wide variety of consumer items with detectable mercury levels. Hazardous waste streams include mercury from a number of commercial or industrial sources. Sewage sludge contains mercury resulting from ingestion and elimination of mercury-containing foods and from other sources. All of the waste streams also contain mercury from a number of natural sources as well. When burned in an incinerator, the wastes can release volatile mercury or mercury compounds into the air, which tend to settle to the ground close to the incineration plant, leading to local contamination of the soil and groundwater, as well as lowered air quality. Accordingly, in various embodiments of the invention, waste streams containing mercury or other heavy metals are incinerated in the presence of various mercury sorbents added into the incineration system as described below. In preferred embodiments, halogen and preferably silica and alumina are added in sufficient amounts to reduce mercury emissions into the atmosphere and to render mercury non-leachable that is captured in the ash.

[0028] Major elements in coal, besides carbon, include silica, alumina, and calcium, along with lesser amounts of iron. In addition, trace heavy metals such as arsenic, antimony, lead, chromium, cadmium, nickel, vanadium, molybdenum, manganese, copper, and barium are normally present. These elements tend to report to the ash upon combustion of coal. Coal also contains significant amounts of sulfur. Upon combustion, the sulfur in coal burns to produce volatile sulfur oxides, which tend to escape from the coal burning utility in gaseous form. It is desired to remediate or reduce the level of sulfur oxides emitted from coal burning plants.

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[0029] Coal also contains mercury. Although present at a low level, mercury tends to volatilize during combustion and escape from the coal burning utility. Even at the low levels produced from the combustion of coal, the release of mercury into the environment is undesirable because the element is toxic and tends to accumulate in body tissues. Because of mercury's damaging effect on health and the environment, its release has recently come under regulatory control in the United States and elsewhere in the world. Whether mercury is subject to regulatory controls or not, it is highly desirable to reduce the amount of mercury emitted from coal burning utilities.

[0030] In a typical coal burning facility, raw coal arrives in railcars and is delivered onto a receiving belt, which leads the coal into a pug mill. After the pug mill, the coal is discharged to a feed belt and deposited in a coal storage area. Under the coal storage area there is typically a grate and bin area; from there a belt transports the coal to an open stockpile area, sometimes called a bunker. Stoker furnaces can be fed with coal from the bunker or from a crusher. For furnaces burning pulverized coal, the coal is delivered by belt or other means to milling equipment such as a crusher and ultimately to a pulverizer. In a storage system, coal is pulverized and conveyed by air or gas to a collector, from which the pulverized coal is transferred to a storage bin, from which the coal is fed to the furnace as needed. In a direct fired system, coal is pulverized and transported directly to the furnace. In a semi-direct system, the coal goes from the pulverizer to a cyclone collector. The coal is fed directly from the cyclone to the furnace.

[0031] During operation coal is fed into the furnace and burned in the presence of oxygen. For high btu fuels, typical flame temperatures in the combustion chamber are on the order of 2700°F (about 1480°C) to about 3000°F (about 1640°C) or even higher, such as 3300°F (about 1815°C) to 3600°F (about 1982°C).

[0032] In various embodiments, sorbent compositions according to the invention are added to the raw coal, in the pug mill, on the receiving belt or feed belt, in the coal storage area, in the collector, in the storage bin, in the cyclone collector, in the pulverizer before or during pulverization, and/or while being transported from the pulverizer to the furnace for combustion. Conveniently, in various embodiments the sorbents are added to the coal during processes that mix the coal such as the in the pug

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mill or in the pulverizer. In a preferred embodiment, the sorbents are added onto the coal in the pulverizers.

[0033] Alternatively or in addition, sorbent components are added into the coal burning system by injecting them into the furnace during combustion of the fuel. In a preferred embodiment, they are injected into the fireball or close to the fireball, for example where the temperature is above 2000°F, above 2300°F, or above 2700°F. According to the design of the burners and the operating parameters of the furnace, effective sorbent addition takes place along with the fuel, with the primary combustion air, above the flame, with or above the overfire air, and so on. Also depending on the furnace design and operation, sorbents are injected from one or more faces of the furnace and/or from one or more corners of the furnace. Addition of sorbent compositions and sorbent components tends to be most effective when the temperature at injection is sufficiently high and/or the aerodynamics of the burners and furnace set up lead to adequate mixing of the powder sorbents with the fuel and/or combustion products. Alternatively or in addition, sorbent addition is made to the convective pathway downstream of the flame and furnace. In various embodiments, optimum injection or application points for sorbents are found by modeling the furnace and choosing parameters (rate of injection, place of injection, distance above the flame, distance from the wall, mode of powder spraying, and the like) that give the best mixing of sorbent, coal, and combustion products for the desired results.

[0034] In coal burning systems, hot combustion gases and air move by convection away from the flame through the convective pathway in a downstream direction (i.e., downstream in relation to the fireball). The convective pathway of the facility contains a number of zones characterized by the temperature of the gases and combustion products in each zone. Generally, the temperature of the combustion gas falls as it moves in a direction downstream from the fireball. From the furnace, where the coal in one example is burning at a temperature of approximately 2700°F – 3600°F (about 1480°C – 1650°C), the fly ash and combustion gases move downstream in the convective pathway to zones of ever decreasing temperature. To illustrate, downstream of the fireball is a zone with temperature less that 2700°F. Further downstream, a point is reached where the temperature has cooled to about 1500°F. Between the two points is a zone having a temperature from about 1500°F to about 2700°F. Further downstream, a

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zone of less than 1500°F is reached, and so on. Further along in the convective pathway, the gases and fly ash pass through lower temperature zones until the baghouse or electrostatic precipitator is reached, which typically has a temperature of about 300°F before the gases are emitted up the stack.

[0035] The combustion gases contain carbon dioxide as well as various undesirable gases containing sulfur and mercury. The convective pathways are also filled with a variety of ash which is swept along with the high temperature gases. To remove the ash before emission into the atmosphere, particulate removal systems are used. A variety of such removal systems, such as electrostatic precipitators and a bag house, are generally disposed in the convective pathway. In addition, chemical scrubbers can be positioned in the convective pathway. Additionally, there may be provided various instruments to monitor components of the gas such as sulfur and mercury.

[0036] Thus, in various embodiments, the process of the present invention calls for the application of sorbents

directly into the furnace during combustion (addition "co-combustion")

directly to a fuel such as coal before combustion (addition "pre-combustion");

directly into the gaseous stream after combustion preferably in a temperature zone of greater than 500°C and preferably greater than 800°C (addition "post-combustion); or

in a combination of pre-combustion, co-combustion, and post-combustion additions.

[0037] Application of the sorbents is made "into the coal burning system" in any of pre-combustion, co-combustion, or post-combustion modes, or in any combination. When the sorbents are added into the coal burning system, the coal or other fuel is said to be combusted "in the presence" the various sorbents, sorbent compositions, or sorbent components

[0038] In a preferred embodiment downstream addition is carried out where the temperature is about 1500°F (815.5°C) to about 2700°F (1482.2°C). In some aspects, and depending upon the specifics of furnace design and the layout of the convective pathways, the cutoff point or distinction between "into the furnace", "into the

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fireball", and "into the convective pathways" can be rather arbitrary. At some point, the combustion gases leave what is clearly a burning chamber or furnace and enter a separate structure that is clearly a flue or convective pathway for gases downstream of the furnace. However, many furnaces are quite large and so permit addition of sorbents "into the furnace" at a considerable distance from where the fuel and air are being fed to form the fireball. For example, some furnaces have overfire air injection ports and the like specifically designed to provide additional oxygen at a location above the fireball to achieve more complete combustion and/or control of emissions such as nitrogen oxides. The overfire air ports can be 20 feet or higher above the fuel injection. In various embodiments, sorbent components or compositions are injected directly into the fireball along with coal being fed, at a location above the coal feed above or below the overfire air ports, or at a higher location within the burning chamber, such as at or just under the nose of the furnace. Each of these locations is characterized by a temperature and by conditions of turbulent flow that contribute to mixing of the sorbents with the fuel and/or the combustion products (such as the fly ash). In embodiments involving applying sorbent compositions into the furnace or downstream of the furnace, application is preferably made where the temperature is above 1500°F, preferably above 2000°F, more preferably where the temperature is above 2300°F, and most preferably where the temperature is above 2700°F.

[0039] In various embodiments, sorbents are added as coal is burned along with other fuels in co-generation plants. Such plants are flexible in the fuels they burn. In addition to bituminous and sub-bituminous coal, such facilities can also burn waste-derived fuels such without limitation as municipal waste, sewage sludge, pet coke, animal waste, plant waste (such as without limitation wood, rice hulls, wood chips, agricultural waste, and/or sawdust), scrap plastics, shredded tires, and the like. To the extent that the fuels contain mercury and sulfur, use of sorbents as described herein tends to mitigate or lower emissions of sulfur and/or mercury that would otherwise be released into the atmosphere upon combustion. Depending on the fuel value, the flame temperature in such co-generation plants varies upward from about 1000°F - 1200°F (for low value fuels or fuels containing high proportions of low value biomass or other low-value components) to 2700°F to 3600°F or higher (for high BTU coal). In various embodiments, use of sorbents of the invention mitigates mercury emissions from systems

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burning at relatively lower temperatures. It is believed the sorbents are especially effective at removing oxidized mercury from the flue gases, and that oxidized mercury in the species predominantly formed by combustion at the lower temperatures.

[0040] Thus, in various embodiments, co-generation plants burning a combination of coal and a wide variety of other fuels (see above) are treated with sorbent compositions to achieve significant reductions in emissions of mercury and/or sulfur.

[0041] In various embodiments described herein, sorbent compositions that tend to reduce or remediate the release of mercury and/or sulfur from coal burning utilities also have the beneficial effect of rendering the ash produced by combustion of the fuel highly cementitious. As a result, the ash is usable in commerce as a partial or complete replacement for portland cement in various cement and concrete products.

[0042] Burning the coal with the sorbent compositions described herein results in an ash that has, in various embodiments, increased levels of the heavy metals compared to coal burned without the sorbent, but which nevertheless contains lower levels of leachable heavy metals than the ash produced without the sorbents. As a result, the ash is safe to handle and to sell into commerce, for example as a cementitious material.

[0043] To make the ash products, a carbonaceous fuel is burned to produce heat energy from combustion of the carbonaceous material. Unburned material and particulate combustion products form ash, some of which collects at the bottom of the furnace, but the majority of which is collected as fly ash from the flue by precipitators or filters, for example a bag house on a coal burning facility. The content of the bottom ash and the fly ash depends on the chemical composition of the coal and on the amount and composition of sorbent components added into the coal burning facility during combustion.

[0044] In various embodiments, mercury emissions from the coal burning facility are monitored. Emissions are monitored as elemental mercury, oxidized mercury, or both. Elemental mercury means mercury in the ground or zero oxidation state, while oxidized mercury means mercury in the +1 or +2 oxidation state. Depending on the level of mercury in the flue gas prior to emission from the plant, the amount of sorbent composition added pre-, co-, and/or post-combustion is raised, lowered, or is maintained unchanged. In general, it is desirable to remove as high a level of mercury as

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is possible. In typical embodiments, mercury removal of 90% and greater is achieved, based on the total amount of mercury in the coal. This number refers to the mercury removed from the flue gases so that mercury is not released through the stack into the atmosphere. Normally, removal of mercury from the flue gases leads to increased levels of mercury in the ash. To minimize the amount of sorbent added into the coal burning process so as to reduce the overall amount of ash produced in the furnace, it is desirable in many embodiments to use the measurements of mercury emissions to adjust the sorbent composition rate of addition to one which will achieve the desired mercury reduction without adding excess material into the system.

[0045] In various embodiments of burning coal or other fuels with the added sorbent components, mercury and other heavy metals in the coal such as arsenic, antimony, lead, and others report to the bag house or electrostatic precipitator and become part of the overall ash content of the coal burning plant; alternatively or in addition, the mercury and heavy metals are found in the bottom ash. As such, mercury and other heavy metals are not emitted from the facility. In general, mercury and other heavy metals in the ash are resistant to leaching under acidic conditions, even though they tend to be present in the ash at elevated levels relative to ash produced by burning coal without the sorbent components described herein. Advantageously, heavy metals in the ash do not leach beyond regulatory levels; in fact, a decreased level of leachable heavy metal is observed in the ash on a ppm basis, even though the ash normally contains a higher absolute level of heavy metals by virtue of being produced by burning with the sorbents. Because in addition the cementitious nature of the ash is enhanced, the ash from the combustion (coal ash) is valuable for sale in commerce and use, for example, as a cementitious material to make portland cements as well as concrete products and ready mixes.

[0046] In preferred embodiments, leaching of heavy metals is monitored or analyzed periodically or continuously during combustion. The TCLP procedure of the United States Environmental Protection Agency is a commonly used method. The amount of sorbent, particularly of sorbent components with Si (SiO_2 or equivalents) and/or Al (Al_2O_3 or equivalents), is adjusted based on the analytical result to maintain the leaching in a desired range.

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[0047] In one embodiment, a method is provided for burning coal to reduce the amount of mercury released into the atmosphere. The method involves applying a sorbent composition comprising a halogen compound into the system in which the coal is being combusted. The halogen compound is preferably a bromine compound; in a preferred embodiment, the sorbent is free of alkali metal compounds so as to avoid corrosion on boiler tubes or other furnace components. The coal is combusted in the furnace to produce ash and combustion gases. The combustion gases contain mercury, sulfur and other components. To accomplish a desired reduction of mercury in the combustion gases in order to limit release into the atmosphere, the mercury level in the combustion gases is preferably monitored, for example by measuring the level analytically. In preferred embodiments, the amount of the sorbent composition applied is adjusted (i.e., by increasing it, decreasing it, or in some cases deciding to leave it unchanged) depending on the value of the mercury level measured in the combustion gases. In a preferred embodiment, the sorbent is added into the system by applying it to the coal pre-combustion, then delivering the coal containing the sorbent into the furnace for combustion.

[0048] In another embodiment, sorbent components comprising a halogen (preferably bromine or iodine, and most preferably bromine) compound and at least one aluminosilicate material are applied into the coal burning system. The components are added separately or as a single sorbent composition, and are optionally added onto the coal pre-combustion, into the furnace during combustion, or into the flue gases downstream of the furnace at suitable temperatures. In a preferred embodiment, the components are added to the coal pre-combustion, and the coal containing the sorbent is then delivered into the furnace for combustion. As before, preferably mercury is monitored in the flue gases and the sorbent application rate is adjusted depending on the value of the measured mercury level. The halogen contributes to lowering the level of mercury emissions, while the aluminosilicate contributes to making mercury captured in the ash non-leaching.

[0049] In a related embodiment, a method for reducing leaching of mercury and/or of other heavy metals from ash produced from the combustion of coal or other fuel in a coal burning system or in an incinerator involves introducing sorbents containing silica and alumina into the incinerator or coal burning system during

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combustion, measuring leaching of mercury and/or other heavy metals from the resulting ash, and adjusting the level of silica and alumina added according to the measured leaching of heavy metals. If leaching is higher than desired, the rate of application of the sorbent can be increased to bring the leaching back down into the desired range. In a preferred embodiment, the sorbent further contains a halogen (e.g. bromine) compound to enhance capture of mercury in the ash.

[0050] In one embodiment, the invention provides a method for reducing the amount of oxidized mercury in flue gases that are generated by combustion of mercury-containing carbonaceous fuel such as coal while at the same time producing a cementitious ash product. The method comprises burning the fuel in the presence of an alkaline powder sorbent wherein the powder sorbent comprises calcium, silica, and alumina. The alkaline powder is added to the coal pre-combustion, injected into the furnace during combustion, applied into the flue gases downstream of the furnace (preferably where the temperature is 1500°F or greater), or in any combination. The powders are alkaline, characterized by a pH above 7 when combined with water, preferably above 8 and preferably above 9. Preferably, the sorbent contains about 0.01 to about 5% by weight of alkalis such as those based on Na_2O and K_2O. In various embodiments, the sorbent further contains iron and magnesium. In various embodiments, the aluminum content of the sorbent is higher than the alumina content of portland cement, preferably above about 5% or above about 7% alumina.

[0051] While the fuel is burning, a level of mercury (oxidized, elemental, or both) is measured in the flue gases downstream from the furnace. The measured mercury level is compared to a target level and, if the measured level is above the targeted level, the amount of powder sorbent added relative to the amount of fuel being burned is increased. Alternatively, if the measured level is at or below the target level, the rate of sorbent addition can be decreased or maintained unchanged.

[0052] In another embodiment, the powder composition is an alkaline sorbent composition that contains an alkaline calcium component as well as significant levels of silica and alumina. In a non-limiting embodiment, the powder composition comprises 2 to 50% of an aluminosilicate material and 50 to 98% by weight of an alkaline powder comprising calcium. In a preferred embodiment, the alkaline powder comprises one or more of lime, calcium oxide, portland cement, cement kiln dust, lime kiln dust, and sugar

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beet lime, while the aluminosilicate material contains one or more selected from the group consisting of calcium montmorillonite, sodium montmorillonite, and kaolin. The powder composition is added to the coal at a rate of about 0.1 to about 10% by weight, based on the amount of coal being treated with the sorbents for a batch process, or on the rate of coal being consumed by combustion for a continuous process. In a preferred embodiment, the rate is from 1 to 8% by weight, 2 to 8% by weight, 4 to 8% by weight, 4 to 6% by weight, or about 6% by weight. In preferred embodiments, the powder composition is injected to the fireball or furnace during combustion and/or is applied to the coal under ambient conditions, prior to its combustion. The temperature at the injection point is preferably at least about 1000°F or higher. For some low value fuels, this corresponds to injection into or close to the fireball.

[0053] In another embodiment, the invention provides novel sorbent compositions comprising about 50 to 98% by weight of at least one of portland cement, cement kiln dust, lime kiln dust, sugar beet lime, and 2 to 50% by weight of an aluminosilicate material. In a various embodiments, the compositions further comprise a bromine compound, for example a bromide such as calcium bromide. Use of the sorbents during the coal burning process as described herein tends to lessen the amount of harmful sulfur and mercury products emitted from the facility, while at the same time producing an ash that is environmentally acceptable (e.g. leaching of heavy metals is below regulatory levels and is lower than in ash produced by burning the coal without the sorbent components) and highly cementitious in nature so that the ash serves as a complete or partial (greater than 40%, preferably greater than 50%) replacement for portland cement in cementitious mixtures and processes for their use.

[0054] In yet another embodiment, a method is provided for burning a fuel containing mercury and optionally sulfur so that the level of harmful compounds emitted in the combustion gases and released into the environment is reduced. In a preferred embodiment, the method involves applying a sorbent onto the fuel and burning the fuel containing the sorbent to produce gases and fly ash. The sorbent contains bromine, calcium, silica, and alumina.

[0055] In a further embodiment, a method for reducing mercury and/or sulfur emitted into the environment during combustion of coal in a coal burning system comprises adding sorbent components comprising bromine, calcium, silica, and alumina

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into the coal burning system and combusting the coal in the presence of the sorbent components to produce combustion gases and fly ash. The amount of mercury in the combustion gases is measured and level of components containing bromine added into the system is adjusted depending on the measured value of mercury in the combustion gases.

[0056] In various embodiments, the four components (calcium, silica, alumina, and bromine) are added together or separately to the coal pre-combustion, to the furnace, and/or to the flue gases at suitable temperature as described herein. Preferably, bromine is present at a level effective to a capture, in the ash, at least 90% of the mercury in the coal, and silica and alumina are present at levels effective to produce fly ash with a leaching value of less than 0.2 ppm (200 ppb) with respect to mercury, preferably less than 100 ppb Hg, less than 50 ppb, and most preferably less than 2 ppb with respect to mercury. A level of 2 ppb represents the current lower detectable limit of the TCLP test for mercury leaching.

[0057] In a particular embodiment, a dual sorbent system is used wherein calcium, silica, and alumina are added in a powder sorbent, while bromine or other halogen(s) is added in a liquid sorbent. The liquid and powder sorbents are added into the coal burning system onto the coal pre-combustion, into the furnace, into the flue gases (at suitable temperatures as described herein), or in any combination. In a preferred embodiment, liquid sorbent is added to the coal pre-combustion and powder sorbent is added either to the coal pre-combustion or to the furnace during combustion. Treatment levels of the liquid and powder sorbents, as well as preferred compositions, are described herein.

[0058] In preferred embodiments, the methods provide coal ash and/or fly ash containing mercury at a level corresponding to capture in the ash of at least 90% of the mercury originally in the coal before combustion. In some embodiments, the mercury level is higher than in known fly ashes due to capture of mercury in the ash rather than release of mercury into the atmosphere. Fly ash produced by the process contains up to 200 ppm mercury or higher; in some embodiments the mercury content of the fly ash is above 250 ppm. Since the volume of ash is normally increased by use of the sorbents (in typical embodiments, the volume of ash about doubles), the increased measured levels of mercury represent significant capture in the ash of mercury that without the sorbents

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would have been released into the environment. The content in the fly ash of mercury and other heavy metals such as lead, chromium, arsenic, and cadmium is generally higher than in fly ash produced from burning coal without the added sorbents or sorbent components.

[0059] In various embodiments, an ash product is produced by burning coal in the presence of sorbent components comprising calcium, silica, alumina, and preferably a halogen such as bromine. The components are added as parts of one or more sorbent compositions into the coal-burning system. In a non-limiting example, sorbent components calcium, silica, and alumina are added together in an alkaline powder sorbent composition that comprises about 2 to 15% by weight Al_2O_3, about 30 to 75% by weight CaO, about 5 to 20% by weight SiO_2, about 1 to 10% Fe_2O_3, and about 0.1 to 5% by weight total alkali, such as sodium oxide and potassium oxide. In a preferred embodiment, the sorbents comprise about 2 to 10% by weight Al_2O_3, about 40 to 70% by weight CaO, and about 5 to 15% by weight SiO_2 in addition to the total alkalis. In a preferred embodiment, powder sorbent compositions described herein contain one or more alkaline powders containing calcium, along with lesser levels of one or more aluminosilicate materials. The halogen component, if desired, is added as a further component of the alkaline powder or is added separately as part of a liquid or powder composition. Advantageously, use of the sorbents leads to a reduction in the levels of sulfur, mercury, other heavy metals such as lead and arsenic, and/or chlorine from the coal burning system.

[0060] In another embodiment, the method of the invention provides coal ash containing mercury at a level corresponding to capture in the ash of at least 90% of the mercury originally in the coal before combustion. A process for making the coal ash involves burning coal in the presence of added calcium, silica, and alumina, and preferably in the further presence of a halogen such as bromine. In a preferred embodiment, ash is prepared by burning coal in the presence of sorbents or sorbent components described herein. Preferably, the mercury in the coal ash is non-leaching in that it exhibits a concentration of mercury in the extract of less than 0.2 ppm when tested using the Toxicity Characteristic Leaching Procedure (TCLP), test Method 1311 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW – 846 – Third Edition, as incorporated by reference in 40 CFR §260.11. It is normally

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observed that fly ash from burning coal with the sorbents described herein has less leachable mercury than ash produced from burning coal without the sorbent, even though the total mercury content in ash produced from the sorbent treated coal is higher by as much as a factor of 2 or more over the level in ash produced by burning without the sorbents. To illustrate, typical ash from burning of PRB coal contains about 100-125 ppm mercury; in various embodiments, ash produced by burning PRB coal with about 6% by weight of the sorbents described herein has about 200-250 ppm mercury or more.

[0061] In another embodiment, the invention provides a hydraulic cement product containing portland cement and from 0.1% to about 99% by weight, based on the total weight of the cement product, of a coal ash or fly ash described above.

[0062] In a further embodiment, the invention provides a pozzolanic product comprising a pozzolan and from 0.01% to about 99% by weight, based on the total weight of the pozzolanic product of the ash described above.

[0063] The invention also provides a cementitious mixture containing the hydraulic cement product.

[0064] The invention further provides a concrete ready mix product containing aggregate and the hydraulic cement product.

[0065] In another embodiment, a cementitious mixture contains coal ash described herein as the sole cementitious component; in these embodiments, the ash is a total replacement for conventional cements such as portland cement. The cementitious mixtures contain cement and optionally aggregate, fillers, and/or other admixtures. The cementitious mixtures are normally combined with water and used as concrete, mortars, grout, flowable fill, stabilized base, and other applications.

[0066] The methods thus encompass burning coal with the added sorbents to produce coal ash and energy for heat or electricity generation. The ash is then recovered and used to formulate cementitious mixtures including cements, mortars, and grouts.

[0067] Sorbent compositions used in various embodiments of the invention described above and herein contain components that contribute calcium, silica, and/or alumina, preferably in the form of alkaline powders. In various embodiments, the compositions also contain iron oxide, as well as basic powders based on sodium oxide (Na_2O) and potassium oxide (K_2O). In a non-limiting example, the powder sorbent contains about 2-10% by weight Al_2O_3, about 40-70% CaO, about 5-15% SiO_2, about 2-

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9% Fe_2O_3, and about 0.1-5% total alkalis such as sodium oxide and potassium oxide. The components comprising calcium, silica, and alumina - and other elements if present - are combined together in a single composition or are added separately or in any combination as components to the fuel burning system. In preferred embodiments, use of the sorbents leads to reductions in the amount of sulfur and/or mercury released into the atmosphere. In various embodiments, use of the sorbent compositions leads to the removal of mercury, especially oxidized mercury. In addition, the compositions reduce the amount of sulfur given off from combustion by a virtue of their calcium content.

[0068] Advantageously, the sorbent compositions contain suitable high levels of alumina and silica. It is believed that the presence of alumina and/or silica leads to several advantages seen from use of the sorbent. To illustrate, it is believed that the presence of alumina and/or silica and/or the balance of the silica/alumina with calcium, iron, and other ingredients contributes to the low acid leaching of mercury and/or other heavy metals that is observed in ash produced by combustion of coal or other fuels containing mercury in the presence of the sorbents.

[0069] In various embodiments, it is observed that use of the sorbent compositions during combustion of coal or other fuel leads to the formation of a refractory lining on the walls of the furnace and on the boiler tubes. It is believed that such a refractory lining reflects heat in the furnace and leads to higher water temperature in the boilers. In various embodiments, it is also observed that use of the sorbent results in reduced scale formation or slagging around the boiler tubes. In this way, use of the sorbents leads to cleaner furnaces, but more importantly improves the heat exchange between the burning coal and the water in the boiler tubes. As a result, in various embodiments use of the sorbents leads to higher water temperature in the boiler, based on burning the same amount of fuel. Alternatively, it has been observed that use of the sorbent allows the feed rate of, for example, coal to be reduced while maintaining the same power output or boiler water temperature. In an illustrative embodiment, use of a sorbent at a 6% rate results in combustion of a coal/sorbent composition that produces as much power as a composition of the same weight that is all coal. It is seen in such embodiments that use of the sorbent, which is normally captured in the fly ash and recycled, actually increases the efficiency of the coal burning process, leading to less consumption of fuel. Advantageously in such a process, the fly ash, which is normally

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increased in volume by virtue of the use of the sorbent, is recycled for use in portland cement manufacture and the like, it having an improved cementitious nature and low heavy metal leaching.

[0070] As noted, the components that contribute calcium, silica, and/or alumina are preferably provided as alkaline powders. Without being limited by theory, it is believed that the alkaline nature of the sorbent components leads at least in part to the desirable properties described above. For example, it is believed the alkaline nature of the powders leads to a reduction in sulfur pitting. After neutralization, it is believed a geopolymeric ash is formed in the presence of the sorbents, coupling with silica and alumina present in the sorbent to form a ceramic like matrix that reports as a stabilized ash. The stabilized ash is characterized by very lowing leaching of mercury and other heavy metals. In some embodiments, the leaching of mercury is below detectable limits.

[0071] Sources of calcium for the sorbent compositions of the invention include, without limitation, calcium powders such as calcium carbonate, limestone, dolomite, calcium oxide, calcium hydroxide, calcium phosphate, and other calcium salts. Industrial products such as limestone, lime, slaked lime, and the like contribute major proportions of such calcium salts. As such, they are suitable components for the sorbent compositions of the invention.

[0072] Other sources of calcium include various manufactured products. Such products are commercially available, and some are sold as waste products or by-products of other industrial processes. In preferred embodiments, the products further contribute either silica, alumina, or both to the compositions of the invention. Non-limiting examples of industrial products that contain silica and/or alumina in addition to calcium include portland cement, cement kiln dust, lime kiln dust, sugar beet lime, slags (such as steel slag, stainless steel slag, and blast furnace slag), paper de-inking sludge ash, cupola arrester filter cake, and cupola furnace dust.

[0073] These and optionally other materials are combined to provide alkaline powders or mixtures of alkaline powders that contain calcium, and preferably also contain silica and alumina. Other alkaline powders containing calcium, silica, and alumina include pozzolanic materials, wood ash, rice hull ash, class C fly ash, and class F fly ash. In various embodiments, these and similar materials are suitable components of sorbent compositions, especially if the resulting composition containing them as

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components falls within the preferred range of 2 to 15% by weight Al_2O_3, about 30 to 75% by weight CaO, about 5 to 20% by weight SiO_2, about 1 to 10% Fe_2O_3, and about 0.1 to 5% by weight total alkali. Mixtures of materials are also used. Non-limiting examples include mixtures of portland cement and lime, and mixtures containing cement kiln dust, such as cement kiln dust and lime kiln dust.

[0074] Sugar beet lime is a solid waste material resulting from the manufacture of sugar from sugar beets. It is high in calcium content, and also contains various impurities that precipitate in the liming procedure carried out on sugar beets. It is an item of commerce, and is normally sold to landscapers, farmers, and the like as a soil amendment.

[0075] Cement kiln dust (CKD) generally refers to a byproduct generated within a cement kiln or related processing equipment during portland cement manufacturing.

[0076] Generally, CKD comprises a combination of different particles generated in different areas of the kiln, pre-treatment equipment, and/or material handling systems, including for example, clinker dust, partially to fully calcined material dust, and raw material (hydrated and dehydrated) dust. The composition of the CKD varies based upon the raw materials and fuels used, the manufacturing and processing conditions, and the location of collection points for CKD within the cement manufacturing process. CKD can include dust or particulate matter collected from kiln effluent (*i.e.,* exhaust) streams, clinker cooler effluent, pre-calciner effluent, air pollution control devices, and the like.

[0077] While CKD compositions will vary for different kilns, CKD usually has at least some cementitious and/or pozzolanic properties, due to the presence of the dust of clinker and calcined materials. Typical CKD compositions comprise silicon-containing compounds, such as silicates including tricalcium silicate, dicalcium silicate; aluminum-containing compounds, such as aluminates including tricalcium aluminate; and iron-containing compounds, such as ferrites including tetracalcium aluminoferrite. CKD generally comprises calcium oxide (CaO). Exemplary CKD compositions comprise about 10 to about 60% calcium oxide, optionally about 25 to about 50%, and optionally about 30 to about 45% by weight. In some embodiments, CKD comprises a concentration of free lime (available for a hydration reaction with water) of about 1 to

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about 10 %, optionally of about 1 to about 5%, and in some embodiments about 3 to about 5%. Further, in certain embodiments, CKD comprises compounds containing alkali metals, alkaline earth metals, and sulfur, *inter alia*.

[0078] Other exemplary sources for the alkaline powders comprising calcium, and preferably further comprising silica and alumina, include various cement-related byproducts (in addition to portland cement and CKD described above). Blended-cement products are one suitable example of such a source. These blended cement products typically contain mixes of portland cement and/or its clinker combined with slag(s) and/or pozzolan(s) (*e.g.*, fly ash, silica fume, burned shale). Pozzolans are usually silicaceous materials that are not in themselves cementitious, but which develop hydraulic cement properties when reacted with free lime (free CaO) and water. Other sources are masonry cement and/or hydraulic lime, which include mixtures of portland cement and/or its clinker with lime or limestone. Other suitable sources are aluminous cements, which are hydraulic cements manufactured by burning a mix of limestone and bauxite (a naturally occurring, heterogeneous material comprising one or more aluminum hydroxide minerals, plus various mixtures of silica, iron oxide, titania, aluminum silicates, and other impurities in minor or trace amounts). Yet another example is a pozzolan cement, which is a blended cement containing a substantial concentration of pozzolans. Usually the pozzolan cement comprises calcium oxide, but is substantially free of portland cement. Common examples of widely-employed pozzolans include natural pozzolans (such as certain volcanic ashes or tuffs, certain diatomaceous earth, burned clays and shales) and synthetic pozzolans (such as silica fume and fly ash).

[0079] Lime kiln dust (LKD) is a byproduct from the manufacturing of lime. LKD is dust or particulate matter collected from a lime kiln or associated processing equipment. Manufactured lime can be categorized as high-calcium lime or dolomitic lime, and LKD varies based upon the processes that form it. Lime is often produced by a calcination reaction conducted by heating calcitic raw material, such as calcium carbonate ($CaCO_3$), to form free lime CaO and carbon dioxide (CO_2). High-calcium lime has a high concentration of calcium oxide and typically some impurities, including aluminum-containing and iron-containing compounds. High-calcium lime is typically formed from high purity calcium carbonate (about 95% purity or greater). Typical calcium oxide content in an LKD product derived from high-calcium lime processing is

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greater than or equal to about 75% by weight, optionally greater than or equal to about 85% by weight, and in some cases greater than or equal to about 90% by weight. In some lime manufacturing, dolomite ($CaCO_3 \cdot MgCO_3$) is decomposed by heating to primarily generate calcium oxide (CaO) and magnesium oxide (MgO), thus forming what is known as dolomitic lime. In LKD generated by dolomitic lime processing, calcium oxide can be present at greater than or equal to about 45% by weight, optionally greater than about 50% by weight, and in certain embodiments, greater than about 55% by weight. While LKD varies based upon the type of lime processing employed, it generally has a relatively high concentration of free lime. Typical amounts of free lime in LKD are about 10 to about 50%, optionally about 20 to about 40%, depending upon the relative concentration of calcium oxide present in the lime product generated.

[0080] Slags are generally byproduct compounds generated by metal manufacturing and processing. The term "slag" encompasses a wide variety of byproduct compounds, typically comprising a large portion of the non-metallic byproducts of ferrous metal and/or steel manufacturing and processing. Generally, slags are considered to be a mixture of various metal oxides, however they often contain metal sulfides and metal atoms in an elemental form.

[0081] Various examples of slag byproducts useful for certain embodiments of the invention include ferrous slags, such as those generated in blast furnaces (also known as cupola furnaces), including, by way of example, air-cooled blast furnace slag (ACBFS), expanded or foamed blast furnace slag, pelletized blast furnace slag, granulated blast furnace slag (GBFS), and the like. Steel slags can be produced from basic oxygen steelmaking furnaces (BOS/BOF) or electric arc furnaces (EAF). Many slags are recognized for having cementitious and/or pozzolanic properties, however the extent to which slags have these properties depends upon their respective composition and the process from which they are derived, as recognized by the skilled artisan. Exemplary slags comprise calcium-containing compounds, silicon-containing compounds, aluminum-containing compounds, magnesium-containing compounds, iron-containing compounds, manganese-containing compounds and/or sulfur-containing compounds. In certain embodiments, the slag comprises calcium oxide at about 25 to about 60%, optionally about 30 to about 50%, and optionally about 30 to about 45% by

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weight. One example of a suitable slag generally having cementitious properties is ground granulated blast furnace slag (GGBFS).

[0082] As described above, other suitable examples include blast (cupola) furnace dust collected from air pollution control devices attached to blast furnaces, such as cupola arrester filter cake. Another suitable industrial byproduct source is paper de-inking sludge ash. As recognized by those of skill in the art, there are many different manufactured/industrial process byproducts that are feasible as a source of calcium for the alkaline powders that form the sorbent compositions of the invention. Many of these well known byproducts comprise alumina and/or silica, as well. Some, such as lime kiln dust, contain major amounts of CaO and relatively small amounts of silica and alumina. Combinations of any of the exemplary manufactured products and/or industrial byproducts are also contemplated for use as the alkaline powders of certain embodiments of the invention.

[0083] In various embodiments, desired treat levels of silica and/or alumina are above those provided by adding materials such as portland cement, cement kiln dust, lime kiln dust, and/or sugar beet lime. Accordingly, it is possible to supplement such materials with aluminosilicate materials, such as without limitation clays (e.g. montmorillonite, kaolins, and the like) where needed to provide preferred silica and alumina levels. In various embodiments, supplemental aluminosilicate materials make up at least about 2%, and preferably at least about 5% by weight of the various sorbent components added into the coal burning system. In general, there is no upper limit from a technical point of view as long as adequate levels of calcium are maintained. However, from a cost standpoint, it is normally desirable to limit the proportion of more expensive aluminosilicate materials. Thus, the sorbent components preferably comprise from about 2 to 50%, preferably 2 to 20%, and more preferably, about 2 to 10% by weight aluminosilicate material such as the exemplary clays. A non-limiting example of a sorbent is about 93% by weight of a blend of CKD and LKD (for example, a 50:50 blend or mixture) and about 7% by weight of an aluminosilicate clay.

[0084] In various embodiments, an alkaline powder sorbent composition contains one or more calcium-containing powders such as portland cement, cement kiln dust, lime kiln dust, various slags, and sugar beet lime, along with an aluminosilicate clay such as, without limitation, montmorillonite or kaolin. The sorbent composition

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preferably contains sufficient SiO_2 and Al_2O_3 to form a refractory-like mixture with calcium sulfate produced by combustion of the sulfur-containing coal in the presence of the CaO sorbent component such that the calcium sulfate is handled by the particle control system; and to form a refractory mixture with mercury and other heavy metals so that the mercury and other heavy metals are not leached from the ash under acidic conditions. In preferred embodiments, the calcium containing powder sorbent contains by weight a minimum of 2% silica and 2% alumina, preferably a minimum of 5% silica and 5% alumina. Preferably, the alumina level is higher than that found in portland cement, that is to say higher than about 5% by weight, preferably higher than about 6% by weight, based on Al_2O_3.

[0085] In various embodiments, the sorbent components of the alkaline powder sorbent composition work together with optional added halogen (such as bromine) compound or compounds to capture chloride as well as mercury, lead, arsenic, and other heavy metals in the ash, render the heavy metals non-leaching under acidic conditions, and improve the cementitious nature of the ash produced. As a result, emissions of harmful elements are mitigated, reduced, or eliminated, and a valuable cementitious material is produced as a by-product of coal burning.

[0086] Suitable aluminosilicate materials include a wide variety of inorganic minerals and materials. For example, a number of minerals, natural materials, and synthetic materials contain silicon and aluminum associated with an oxy environment along with optional other cations such as, without limitation, Na, K, Be, Mg, Ca, Zr, V, Zn, Fe, Mn, and/or other anions, such as hydroxide, sulfate, chloride, carbonate, along with optional waters of hydration. Such natural and synthetic materials are referred to herein as aluminosilicate materials and are exemplified in a non-limiting way by the clays noted above.

[0087] In aluminosilicate materials, the silicon tends to be present as tetrahedra, while the aluminum is present as tetrahedra, octahedra, or a combination of both. Chains or networks of aluminosilicate are built up in such materials by the sharing of 1, 2, or 3 oxygen atoms between silicon and aluminum tetrahedra or octahedra. Such minerals go by a variety of names, such as silica, alumina, aluminosilicates, geopolymer, silicates, and aluminates. However presented, compounds containing aluminum and/or

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silicon tend to produce silica and alumina upon exposure to high temperatures of combustion in the presence of oxygen

[0088] In one embodiment, aluminosilicate materials include polymorphs of $SiO_2 \cdot Al_2O_3$. For example, silliminate contains silica octahedra and alumina evenly divided between tetrahedra and octahedra. Kyanite is based on silica tetrahedra and alumina octahedra. Andalusite is another polymorph of $SiO_2 \cdot Al_2O_3$.

[0089] In other embodiments, chain silicates contribute silicon (as silica) and/or aluminum (as alumina) to the compositions of the invention. Chain silicates include without limitation pyroxene and pyroxenoid silicates made of infinite chains of SiO_4 tetrahedra linked by sharing oxygen atoms.

[0090] Other suitable aluminosilicate materials include sheet materials such as, without limitation, micas, clays, chrysotiles (such as asbestos), talc, soapstone, pyrophillite, and kaolinite. Such materials are characterized by having layer structures wherein silica and alumina octahedra and tetrahedra share two oxygen atoms. Layered aluminosilicates include clays such as chlorites, glauconite, illite, polygorskite, pyrophillite, sauconite, vermiculite, kaolinite, calcium montmorillonite, sodium montmorillonite, and bentonite. Other examples include micas and talc.

[0091] Suitable aluminosilicate materials also include synthetic and natural zeolites, such as without limitation the analcime, sodalite, chabazite, natrolite, phillipsite, and mordenite groups. Other zeolite minerals include heulandite, brewsterite, epistilbite, stilbite, yagawaralite, laumontite, ferrierite, paulingite, and clinoptilolite. The zeolites are minerals or synthetic materials characterized by an aluminosilicate tetrahedral framework, ion exchangeable "large cations" (such as Na, K, Ca, Ba, and Sr) and loosely held water molecules.

[0092] In other embodiments, framework or 3D silicates, aluminates, and aluminosilicates are used. Framework aluminosilicates are characterized by a structure where SiO_4 tetrahedra, AlO_4 tetrahedra, and/or AlO_6 octahedra are linked in three dimensions. Non-limiting examples of framework silicates containing both silica and alumina include feldspars such as albite, anorthite, andesine, bytownite, labradorite, microcline, sanidine, and orthoclase.

[0093] In one aspect, the sorbent powder compositions are characterized in that they contain a major amount of calcium, preferably greater than 20% by weight

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based on calcium oxide, and that furthermore they contain levels of silica, and/or alumina higher than that found in commercial products such as portland cement. In preferred embodiments, the sorbent compositions comprise greater than 5% by weight alumina, preferably greater than 6% by weight alumina, preferably greater than 7% by weight alumina, and preferably greater than about 8% by weight alumina.

[0094] Coal or other fuel is treated with sorbent components at rates effective to control the amount of sulfur and/or mercury released into the atmosphere upon combustion. In various embodiments, total treatment levels of the sorbent components ranges from about 0.1% to about 20% by weight, based on the weight of the coal being treated or on the rate of the coal being consumed by combustion, when the sorbent is a powder sorbent containing calcium, silica, and alumina. When the sorbent components are combined into a single composition, the component treat levels correspond to sorbent treat levels. In this way a single sorbent composition can be provided and metered or otherwise measured for addition into the coal burning system. In general, it is desirable to use a minimum amount of sorbent so as not to overload the system with excess ash, while still providing enough to have a desired effect on sulfur and/or mercury emissions. Accordingly, in preferred embodiments, the treatment level of sorbent ranges from about 1% to about 10% by weight, and preferably from about 1 or 2% by weight to about 10% by weight. For many coals, an addition rate of 6% by weight of powder sorbent has been found to be acceptable.

[0095] The powder sorbents containing calcium, silica, and alumina as described herein are generally effective to reduce the amount of sulfur in gases emitted from the coal burning facility. For reduction of sulfur emissions, it is preferred to provide calcium in the sorbent components at a molar ratio of at least 1:1, and preferably above 1:1, measured against the moles of sulfur in the fuel (such as coal) being burned. If it is desired to avoid production of excess ash, the amount of calcium delivered by way of the sorbent can be limited to, say, a maximum molar ratio of 3:1, again measured against sulfur in the coal.

[0096] In some embodiments, the amount of mercury released is also mitigated, lowered, or eliminated by use of such sorbents even without additional halogen. It is believed that the sorbents are effective at removing oxidized mercury in systems where the flame temperature is as low as 1000°F. However, in many

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embodiments, including some in which the flame temperature is considerably higher than 1000°F, it is preferable to treat the coal with sorbent compositions that contain a halogen compound. The use of the halogen compound along with the alkaline powder sorbent tends to reduce the amount of unoxidized mercury in the gases of combustion.

[0097] Sorbent compositions comprising a halogen compound contain one or more organic or inorganic compounds that contain a halogen. Halogens include chlorine, bromine, and iodine. Preferred halogens are bromine and iodine. The halogen compounds are sources of the halogens, especially of bromine and iodine. For bromine, sources of the halogen include various inorganic salts of bromine including bromides, bromates, and hypobromites. In various embodiments, organic bromine compounds are less preferred because of their cost or availability. However, organic sources of bromine containing a suitably high level of bromine are considered within the scope of the invention. Non-limiting examples of organic bromine compounds include methylene bromide, ethyl bromide, bromoform, and carbon tetrabromide. Non-limiting inorganic sources of iodine include hypoiodites, iodates, and iodides, with iodides being preferred. Organic iodine compounds can also be used.

[0098] When the halogen compound is an inorganic substituent, it is preferably a bromine or iodine containing salt of an alkaline earth element. Exemplary alkaline earth elements include beryllium, magnesium, and calcium. Of halogen compounds, particularly preferred are bromides and iodides of alkaline earth metals such as calcium. Alkali metal bromine and iodine compounds such as bromides and iodides are effective in reducing mercury emissions. But in some embodiments, they are less preferred as they tend to cause corrosion on the boiler tubes and other steel surfaces and/or contribute to tube degradation and/or firebrick degradation. In various embodiments, it has been found desirable to avoid potassium salts of the halogens, in order to avoid problems in the furnace.

[0099] In various embodiments, it has been found that the use of alkaline earth salts such as calcium tends to avoid such problems with sodium and/or potassium. Thus in various embodiments, the sorbents added into the coal burning system contain essentially no alkali metal-containing bromine or iodine compounds, or more specifically essentially no sodium-containing or potassium-containing bromine or iodine compounds.

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[0100] In various embodiments, sorbent compositions containing halogen are provided in the form of a liquid or of a solid composition. In various embodiments, the halogen-containing composition is applied to the coal before combustion, is added to the furnace during combustion, and/or is applied into flue gases downstream of the furnace. When the halogen composition is a solid, it can further contain the calcium, silica, and alumina components described herein as the powder sorbent. Alternatively, a solid halogen composition is applied onto the coal and/or elsewhere into the combustion system separately from the sorbent components comprising calcium, silica, and alumina. When it is a liquid composition it is generally applied separately.

[0101] In various embodiments, liquid mercury sorbent comprises a solution containing 5 to 60% by weight of a soluble bromine or iodine containing salt. Non-limiting examples of preferred bromine and iodine salts include calcium bromide and calcium iodide. In various embodiments, liquid sorbents contain 5-60% by weight of calcium bromide and/or calcium iodide. For efficiency of addition to the coal prior to combustion, in various embodiments it is preferred to add mercury sorbents having as high level of bromine or iodine compound as is feasible. In a non-limiting embodiment, the liquid sorbent contains 50% or more by weight of the halogen compound, such as calcium bromide or calcium iodide.

[0102] In various embodiments, the sorbent compositions containing a halogen compound further contain a nitrate compound, a nitrite compound, or a combination of nitrate and nitrite compounds. Preferred nitrate and nitrite compounds include those of magnesium and calcium, preferably calcium.

[0103] To further illustrate, one embodiment of the present invention involves the addition of liquid mercury sorbent directly to raw or crushed coal prior to combustion. For example, mercury sorbent is added to the coal in the coal feeders. Addition of liquid mercury sorbent ranges from 0.01 to 5%. In various embodiments, treatment is at less than 5%, less than 4%, less than 3%, or less than 2%, where all percentages are based on the amount of coal being treated or on the rate of coal consumption by combustion. Higher treatment levels are possible, but tend to waste material, as no further benefit is achieved. Preferred treatment levels are from 0.025 to 2.5% by weight on a wet basis. The amount of solid bromide or iodide salt added by way of the liquid sorbent is of course reduced by its weight fraction in the sorbent. In an

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illustrative embodiment, addition of bromide or iodide compound is at a low level such as from 0.01 % to 1% by weight based on the solid. When a 50% by weight solution is used, the sorbent is then added at a rate of 0.02% to 2% to achieve the low levels of addition. For example, in a preferred embodiment, the coal is treated by a liquid sorbent at a rate of 0.02 to 1%, preferably 0.02 to 0.5 % calculated assuming the calcium bromide is about 50% by weight of the sorbent. In a typical embodiment, approximately 1%, 0.5%, or 0.25% of liquid sorbent containing 50% calcium bromide is added onto the coal prior to combustion, the percentage being based on the weight of the coal. In a preferred embodiment, initial treatment is started at low levels (such as 0.01% to 0.1%) and is incrementally increased until a desired (low) level of mercury emissions is achieved, based on monitoring of emissions. Similar treatment levels of halogen are used when the halogen is added as a solid or in multi-component compositions with other components such as calcium, silica, alumina, iron oxide, and so on.

[0104] When used, liquid sorbent is sprayed, dripped, or otherwise delivered onto the coal or elsewhere into the coal burning system. In various embodiments, addition is made to the coal or other fuel at ambient conditions prior to entry of the fuel/sorbent composition into the furnace. For example, sorbent is added onto powdered coal prior to its injection into the furnace. Alternatively or in addition, liquid sorbent is added into the furnace during combustion and/or into the flue gases downstream of the furnace. Addition of the halogen containing mercury sorbent composition is often accompanied by a drop in the mercury levels measured in the flue gases within a minute or a few minutes; in various embodiments, the reduction of mercury is in addition to a reduction achieved by use of an alkaline powder sorbent based on calcium, silica, and alumina.

[0105] In another embodiment, the invention involves the addition of a halogen component (illustratively a calcium bromide solution) directly to the furnace during combustion. In another embodiment, the invention provides for an addition of a calcium bromide solution such as discussed above, into the gaseous stream downstream of the furnace in a zone characterized by a temperature in the range of 2700°F to 1500°F, preferably 2200°F to 1500°F. In various embodiments, treat levels of bromine compounds, such as calcium bromide are divided between co-, pre- and post-combustion addition in any proportion.

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[0106] In one embodiment, various sorbent components are added onto coal prior to its combustion. The coal is preferably particulate coal, and is optionally pulverized or powdered according to conventional procedures. In a non-limiting example, the coal is pulverized so that 75% by weight of the particles passes through a 200 mesh screen (a 200 mesh screen has hole diameters of 75 μm). In various embodiments, the sorbent components are added onto the coal as a solid or as a combination of a liquid and a solid. Generally, solid sorbent compositions are in the form of a powder. If a sorbent is added as a liquid (illustratively as a solution of one or more bromine or iodine salts in water), in one embodiment the coal remains wet when fed into the burner. In various embodiments, a sorbent composition is added onto the coal continuously at the coal burning facility by spraying or mixing onto the coal while it is on a conveyor, screw extruder, or other feeding apparatus. In addition or alternatively, a sorbent composition is separately mixed with the coal at the coal burning facility or at the coal producer. In a preferred embodiment, the sorbent composition is added as a liquid or a powder to the coal as it is being fed into the burner. For example, in a preferred commercial embodiment, the sorbent is applied into the pulverizers that pulverize the coal prior to injection. If desired, the rate of addition of the sorbent composition is varied to achieve a desired level of mercury emissions. In one embodiment, the level of mercury in the flue gases is monitored and the level of sorbent addition adjusted up or down as required to maintain the desired mercury level.

[0107] In various embodiments, levels of mercury and/or sulfur emitted from the facility are monitored with conventional analytical equipment using industry standard detection and determination methods. In one embodiment, monitoring is conducted periodically, either manually or automatically. In a non-limiting example, mercury emissions are monitored once an hour to ensure compliance with government regulations. To illustrate, the Ontario Hydro method is used. In this known method, gases are collected for a pre-determined time, for example one hour. Mercury is precipitated from the collected gases, and the level of elemental and/or oxidized mercury is quantitated using a suitable method such as atomic absorption. Monitoring can also take more or less frequently than once an hour, depending on technical and commercial feasibility. Commercial continuous mercury monitors can be set to measure mercury and produce a number at a suitable frequency, for example once every 3 to 7 minutes. In

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various embodiments, the output of the mercury monitors is used to control the rate of addition of mercury sorbent. Depending on the results of monitoring, the rate of addition of the mercury sorbent is adjusted by either increasing the level of addition; decreasing it; or leaving it unchanged. To illustrate, if monitoring indicates mercury levels are higher than desired, the rate of addition of sorbent is increased until mercury levels return to a desired level. If mercury levels are at desired levels, the rate of sorbent addition can remain unchanged. Alternatively, the rate of sorbent addition can be lowered until monitoring indicates it should be increased to avoid high mercury levels. In this way, mercury emission reduction is achieved and excessive use of sorbent (with concomitant increase of ash) is avoided.

[0108] Mercury is monitored in the convective pathway at suitable locations. In various embodiments, mercury released into the atmosphere is monitored and measured on the clean side of the particulate control system. Mercury can also be monitored at a point in the convective pathway upstream of the particulate control system. Experiments show that as much as 20 to 30% of the mercury in coal is captured in the ash and not released into the atmosphere when no mercury sorbent is added. In preferred embodiments, addition of mercury sorbents described herein raises the amount of mercury capture to 90% or more. Mercury emissions into the atmosphere are correspondingly reduced.

[0109] In various embodiments, sorbent components or a sorbent composition is added more or less continuously to the coal before combustion, to the furnace during combustion, and/or to the convective pathway in the 1500°F to 2700°F zone as described above. In various embodiments, automatic feedback loops are provided between the mercury monitoring apparatus and the sorbent feed apparatus. This allows for a constant monitoring of emitted mercury and adjustment of sorbent addition rates to control the process.

[0110] In preferred embodiments, mercury and sulfur are monitored using industry standard methods such as those published by the American Society for Testing and Materials (ASTM) or international standards published by the International Standards Organization (ISO). An apparatus comprising an analytical instrument is preferably disposed in the convective pathway downstream of the addition points of the mercury and sulfur sorbents. In a preferred embodiment, a mercury monitor is disposed

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on the clean side of the particulate control system. Alternatively or in addition, the flue gases are sampled at appropriate locations in the convective pathway without the need to install an instrument or monitoring device. In various embodiments, a measured level of mercury or sulfur is used to provide feedback signals to pumps, solenoids, sprayers, and other devices that are actuated or controlled to adjust the rate of addition of a sorbent composition into the coal burning system. Alternatively or in addition, the rate of sorbent addition can be adjusted by a human operator based on the observed levels of mercury and/or sulfur.

[0111] In various embodiments, the ash produced by burning coal in the presence of the sorbents described herein is cementitious in that it sets and develops strength when combined with water. The ash tends to be self-setting due its relatively high level of calcium. The ash serves alone or in combination with portland cement as a hydraulic cement suitable for formulation into a variety of cementitious mixtures such as mortars, concretes, and grouts.

[0112] The cementitious nature of ash produced as described herein is demonstrated for example by consideration of the strength activity index of the ash, or more exactly, of a cementitious mixture containing the ash. As described in ASTM C311-05, measurement of the strength activity index is made by comparing the cure behavior and property development of a 100% portland cement concrete and a test concrete wherein 20% of the portland cement is replaced with an equal weight of a test cement. In the standard test, strength is compared at 7 days and at 28 days. A "pass" is considered to be when the strength of the test concrete is 75% of the strength of the portland cement concrete or greater. In various embodiments, ashes of the invention exhibit of strength activity of 100% to 150% in the ASTM test, indicating a strong "pass". Similar high values are observed when tests are run on test mixtures with other than an 80:20 blend of portland cement to ash. In various embodiments, a strength activity index of 100% to 150% is achieved with blends of 85:15 to 50:50, where the first number of the ratio is portland cement and the second number of the ratio is ash prepared according to the invention. In particular embodiments, the strength development of an all-ash test cementitious mixture (i.e., one where ash represents 100% of the cement in the test mixture) is greater than 50% that of the all-portland cement control, and is preferably greater than 75%, and more preferably 100% or more, for example 100 –

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150%. Such results demonstrate the highly cementitious nature of ash produced by burning coal or other fuel in the presence of the sorbent components described herein.

[0113] Because the ash resulting from combustion of coal according to the invention contains mercury in a non-leaching form, it is available to be sold into commerce. Non-limiting uses of spent or waste fly ash or bottom ash include as a component in a cement product such as portland cement. In various embodiments, cement products contain from about 0.1% up to about 99% by weight of the coal ash produced by burning compositions according to the invention. In one aspect, the non-leaching property of the mercury and other heavy metals in the coal ash makes it suitable for all known industrial uses of coal ash.

[0114] Coal ash according to the invention, especially the fly ash collected by the particle control systems (bag house, electrostatic precipitators, etc.) is used in portland cement concrete (PCC) as a partial or complete replacement for portland cement. In various embodiments, the ash is used as a mineral admixture or as a component of blended cement. As an admixture, the ash can be total or partial replacement for portland cement and can be added directly into ready mix concrete at the batch plant. Alternatively, or in addition, the ash is inter-ground with cement clinker or blended with portland cement to produce blended cements.

[0115] Class F and Class C fly ashes are defined for example in U.S. Standard ASTM C 618. The ASTM Standard serves as a specification for fly ash when it is used in partial substitution for portland cement. It is to be noted that coal ash produced by the methods described herein tends to be higher in calcium and lower in silica and alumina than called for in the specifications for Class F and Class C fly ash in ASTM C 618. Typical values for the fly ash of the invention is >50% by weight CaO, and <25% $SiO_2/Al_2O_3/Fe_2O_3$. In various embodiments, the ash is from 51 to 80 % by weight CaO and from about 2 to about 25% of total silica, alumina, and iron oxide. It is observed that fly ash according to the invention is highly cementitious, allowing for substitutions or cutting of the portland cement used in such cementitious materials and cementitious materials by 50% or more. In various applications, the coal ash resulting from burning coal with sorbents described herein is sufficiently cementitious to be a complete (100%) replacement for portland cement in such compositions.

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[0116] To further illustrate, the American Concrete Institute (ACI) recommends that Class F fly ash replace from 15 to 25% of portland cement and Class C fly ash replace from 20 to 35%. It has been found that coal ash produced according to the methods described herein is sufficiently cementitious to replace up to 50% of the portland cement, while maintaining 28 day strength development equivalent to that developed in a product using 100% portland cement. That is, although in various embodiments the ash does not qualify by chemical composition as Class C or Class F ash according to ASTM C 618, it nevertheless is useful for formulating high strength concrete products.

[0117] Coal ash made according to the invention can also be used as a component in the production of flowable fill, which is also called controlled low strength material or CLSM. CLSM is used as a self leveling, self compacting back fill material in place of compacted earth or other fill. The ash described herein is used in various embodiments as a 100% replacement for portland cement in such CLSM materials. Such compositions are formulated with water, cement, and aggregate to provide a desired flowability and development of ultimate strength. For example, the ultimate strength of flowable fill should not exceed 1035 kPa (150 pounds per square inch) if removability of the set material is required. If formulated to achieve higher ultimate strength, jack hammers may be required for removal. However, when it is desired to formulate flowable fill mixes to be used in higher load bearing applications, mixtures containing a greater range of compressive strength upon cure can be designed.

[0118] Coal ash produced according to the methods described herein is also usable as a component of stabilized base and sub base mixtures. Since the 1950's numerous variations of the basic lime/fly ash/aggregate formulations have been used as stabilized base mixtures. An example of the use of stabilized base is used as a stabilized road base. To illustrate, gravel roads can be recycled in place of using ash according to the composition. An existing road surface is pulverized and re-deposited in its original location. Ash such as produced by the methods described herein is spread over the pulverized road material and mixed in. Following compaction, a seal coat surface is placed on the roadway. Ash according to the invention is useful in such applications because it contains no heavy metals that leach above regulatory requirements. Rather, the ash produced by methods of the invention contains less leachable mercury and less

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leachable other heavy metals (such as arsenic and lead) than does coal ash produced by burning coal without the sorbents described herein.

[0119] Thus, the invention provides various methods of eliminating the need to landfill coal ash or fly ash resulting from combustion of coal that contains high levels of mercury. Instead of a costly disposal, the material can be sold or otherwise used as a raw material.

[0120] In a preferred embodiment, use of the sorbents results in a cementitious ash that can replace portland cement in whole or in part in a variety of applications. Because of the re-use of the cementitious product, at least some portland cement manufacture is avoided, saving the energy required to make the cement, and avoiding the release of significant amounts of carbon dioxide which would have arisen from the cement manufacture. Other savings in carbon dioxide emissions result from the reduced need for lime or calcium carbonate in desulfurization scrubbers. The invention thus provides, in various embodiments, methods for saving energy and reducing green house emissions such as carbon dioxide. Further detail of various embodiments of this aspect of the invention are given below.

[0121] Portland cement is manufactured in a wet or a dry process kiln. While the wet and dry processes differ, both processes heat the raw material in stages. Cement manufacturing raw materials comprise sources of calcium, silica, iron, and alumina, and usually include limestone, as well as a variety of other materials, such as clay, sand, and/or shale, for example. The first stage is a pre-heating stage that drives off any moisture from the raw materials, removes water of hydration, and raises the material temperature up to approximately 1500°F. The second stage is the calcination stage which generally occurs between about 1500°F and 2000°F, where the limestone ($CaCO_3$) is converted to lime (CaO) by driving off carbon dioxide (CO_2) in a calcination reaction. The raw materials are then heated to a maximum temperature of between about 2500°F to 3000°F in the burning zone, where they substantially melt and flux, thus forming inorganic compounds, such as tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. A typical analysis of portland cement products shows that they contain approximately 65-70% CaO, 20% SiO_2, 5% Al_2O_3, 4% Fe_2O_3, with lesser amounts of other compounds, such as oxides of magnesium, sulfur, potassium, sodium, and the like. The molten raw material is cooled to solidify into an

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intermediate product in small lumps, known as "clinker" that is subsequently removed from the kiln. Clinker is then finely ground and mixed with other additives (such as a set-retardant, gypsum) to form portland cement. Portland cement can then be mixed with aggregates and water to form concrete.

[0122] Cement production is an energy sensitive process in which a combination of raw materials is chemically altered through intense heat to form a compound of binding properties. Cement manufacturing is the largest non-energy industrial source of carbon dioxide emissions. The emissions result from heating limestone, which constitutes approximately 80% of the feed to cement kilns. During cement production, high temperatures are used to transform the limestone into lime, releasing carbon dioxide into the atmosphere. In this process, one molecule of calcium carbonate is decomposed into one molecule of carbon dioxide gas and one molecule of calcium oxide.

[0123] The cement manufacturer utilizes nearly 100% of the calcium oxide obtained from calcinated calcium carbonate. Thus, the amount of calcium oxide in the cement clinker is a good measure of the carbon dioxide produced during production. In an example, to estimate carbon dioxide emission from cement production, an emission factor is derived by multiplying the fraction of lime in the cement clinker by a constant that reflects the mass of carbon released per unit of lime. In one example, assuming an average lime content of 64.6% based on recommendations of the International Panel for Climate Control, an emissions factor of 0.138 tons of carbon per ton of clinker produced is obtained. Additional carbon dioxide may be released as a result of adding extra lime to make masonry cement, a more plastic cement that typically is used in mortar.

[0124] In cement making, carbon dioxide emissions result from energy use and from decomposition of calcium carbonate during clinker production. Depending on the fuel source that provides the energy, carbon dioxide emissions may vary. For example, the use of a cleaner burning fuel, such as natural gas, produces less carbon dioxide emissions than the use of a fuel such as coal. In various embodiments, the invention described above may be used in the production of cement. In such embodiments, the use of the invention in the production of cement will reduce carbon dioxide emissions.

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[0125] In various embodiments, the invention described herein, may be used in the production of cement to produce carbon dioxide emission credits by lowering carbon dioxide emission in the production of cement. In preferred embodiments, a point source for air emissions, such as a cement plant or a coal-fired power plant, is brought into compliance with the Kyoto protocol.

[0126] Although the invention is not to be limited by theory, it is believed that the sorbent compositions described above provide additional or supplemental sources of silica and alumina into the coal burning process. Combustion of the coal with the added silica and alumina forms a geopolymeric matrix such as is known in cold ceramics. Although coal naturally contains small amounts of silica and/or alumina, it is believed that the amount of the materials naturally occurring in coal is normally not sufficient to provide the geopolymeric matrix upon combustion. Further, the silica and alumina naturally occurring in coal is not necessarily balanced with the natural occurring calcium in order to provide optimum sulfur and/or mercury capture and/or cementitious ash product upon combustion.

[0127] In various embodiments, the invention provides methods for improving the leaching quality of heavy metals such as mercury from coal. The methods involve adding sufficient silica and/or alumina to the coal to cause a geopolymer to form upon combustion. Preferably, the silica and alumina are added along with sufficient alkali powders to reduce sulfur pitting. The alkali powders tend to neutralize the silica and alumina, with formation of geopolymeric ash along with coupling silica and/or alumina to form a ceramic like matrix that reports as a stabilized ash. It may also be that the alumina and silica burning with the coal forms a refractory like mixture compound with mercury, lead, arsenic, cadmium, antimony, cobalt, copper, manganese, zinc, and/or other heavy metals. As a result, the resulting coal ash or fly ash containing heavy metals is resistant to leaching under standard conditions. As noted above, the non-leaching quality of the coal ash leads to commercial advantages because the product would no longer be considered as a hazardous material.

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EXAMPLES

[0128] In Examples 1 - 6, coals of varying BTU value, sulfur, and mercury content are burned in the CTF furnace at the Energy Environmental Research Center (EERC) at the University of North Dakota. Percent mercury is reported based on the total amount of the element in the coal prior to combustion. Percentage sulfur removal is a percentage reduction above baseline, the baseline determined by measuring sulfur emissions from burning without sorbent.

Example 1

[0129] This example illustrates the mercury sorption ability of a calcium bromide/water solution when applied to a Powder River basin sub-bituminous coal. The as-fired coal has a moisture content of 2.408%, ash content of 4.83%, sulfur content of 0.29%, a heating value of 8,999 BTU and a mercury content of 0.122 μg/g. Combustion without sorbent results in a mercury concentration of 13.9 $\mu g/m^3$ in the exhaust gas. The fuel is ground to 70% passing 200 mesh and blended with 6% of a sorbent powder and 0.5% of a sorbent liquid, based on the weight of the coal. The powder contains by weight 40-45% portland cement, 40-45% calcium oxide, and the remainder calcium- or sodium montmorillonite. The liquid is a 50% by weight solution of calcium bromide in water.

[0130] The sorbents are mixed directly with the fuel for three minutes and then stored for combustion. The treated coal is fed to the furnace. Combustion results in a 90% mercury (total) removal at the bag house outlet and a 80% removal of sulfur as measured at the bag house outlet.

Example 2

[0131] This example illustrates the use of powder and liquid sorbents applied to three bituminous coals of varying mercury content. All coals are prepared as in example #1, with the same addition levels of sorbents.

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Parameter		Coal	% of Mercury Removal	% Sulfur Removal
% Moisture % Sulfur Mercury BTU value	8.48 2.28 16.2 μg /m^3 13,324	Pittsburgh, Seam, Bailey Coal	97.97	40.0
% Moisture % Sulfur Mercury BTU value	10.46 4.24 8.53 μg /m^3 11,824	Freeman Crown III	97.9	36.0
% Moisture % Sulfur Mercury BTU value	1.0 1.25 5.26 μg /m^3 12,937	Kentucky Blend	90.1	52.0

Example 3

[0132] This example illustrates addition of a mercury sorbent post-combustion. Pittsburgh Seam-Bailey Coal is ground to 70% passing 200 mesh. No sorbent was added to the fuel pre-combustion. Liquid sorbent containing 50% calcium bromide in water is duct injected into the gaseous stream of the furnace in the 2200°F – 1500°F zone. The liquid sorbent is injected at the rate of approximately 1.5% by weight of the coal.

Coal Type	Sorbent Composition	% S reduction	# Hg Reduction
Pittsburgh Seam-Bailey Coal	50% $CaBr_2$ 50% H20	28.13	96.0

Example 4

[0133] This example illustrates addition of a liquid and a powder sorbent post-combustion. No sorbent was added directly to the fuel. Both fuels are bituminous and noted as Freeman Crown III and Pittsburgh Seam – Bailey Coal. In both cases the coal was ground to 70% minus 200 mesh prior to combustion. The powder and liquid sorbents are as used in Example 1. Rates of liquid and powder addition (percentages

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based on the weight of the coal being burned), as well as mercury and sulfur reduction levels, are presented in the table.

Coal Type	Liquid sorbent injection rate	Powder sorbent injection rate	S Reduction	Hg Reduction
Freeman Crown III	1.0	4.0	36.27	97.89
Pittsburgh Seam – Bailey Coal	1.5	6.10	33.90	96.00

Example 5

[0134] Pittsburgh Seam Bailey Coal is prepared as in Example 1. The powder sorbent of Example 1 is added to the coal pre-combustion at 9.5% by weight. The liquid sorbent of Example 1 (50% calcium bromide in water) is injected post-combustion in the 1500°F – 2200°F zone at a rate of 0.77%, based on the burn rate of the coal. Sulfur reduction is 56.89% and mercury reduction is 93.67%.

Example 6

[0135] Kentucky Blend Coal is prepared as in Example 1. The powder sorbent of Example 1 is added to the coal pre-combustion at 6% by weight. The liquid sorbent of Example 1 (50% calcium bromide in water) is injected post-combustion in the 1500°F – 2200°F zone at a rate of 2.63%, based on the burn rate of the coal. Sulfur reduction is 54.91% and mercury reduction is 93.0%.

[0136] In Examples 7 - 10, coals of varying BTU value, sulfur, and mercury content are burned in a variety of boilers at electrical utilities. Percent mercury reduction is reported based on the total amount of the element in the coal prior to combustion. Percentage sulfur removal is a percentage reduction above baseline, the baseline determined by measuring sulfur emissions from burning without sorbent.

Example 7

[0137] A fuel containing bituminous and sub-bituminous coals, pet coke, wood chips, and rubber tire scraps is burned in a stoker furnace to produce 60 megawatts of power. The furnace is operating in a balanced draft manner. Baseline emissions of mercury from burning the fuel with no added sorbent indicate the mercury is mostly in

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the oxidized form. After establishing a baseline, a powder sorbent composition is added at a treat rate of 5.5 - 6% by weight to the furnace about two feet above the grate through the fly ash recycle/reinjection tubes of the furnace. After steady state is reached, the mercury capture is 96%. The powder sorbent composition is 93% by weight of a 50:50 mixture of cement kiln dust and lime kiln dust; and 7% by weight calcium montmorillonite. While maintaining addition of the powder sorbent composition, a liquid sorbent containing 50% by weight calcium bromide in water is added onto the fuel prior to combustion at a rate of 0.5%, based on the weight of the fuel being consumed. On addition of the liquid sorbent, the mercury capture increases to 99.5%.

Example 8

[0138] PRB coal (pulverized to 75% passing 200 Mesh) is burned in a tangentially fired boiler operating in a balanced draft manner to produce 160 megawatts of electric power. After establishing baseline S and Hg emissions from burning of the coal without added sorbent, a powder sorbent composition as in Example 7 is added at a treat level of 5.5 - 6% into the furnace. Addition is made through a lance positioned 4 feet from the inside wall of the furnace and 20 feet above the fireball. The temperature of the flue gases at the point of injection is about 2400°F to 2600°F, measured by a temperature sensor. Sulfur capture is increased by 65 % over baseline. Mercury capture is 3 %, based on the total amount of mercury in the PRB coal. Then, while continuing addition of the powder sorbent, a 50% calcium bromide in water solution is added to the pulverized coal in the coal feeders by drip feed at a treat rate of 0.5 %, based on the rate of coal consumption. Mercury capture increases to 90 %.

Example 9

[0139] PRB coal pulverized to about 200 mesh is burned in a tangentially fired furnace operating in a positive draft manner to produce about 164 megawatts of electric power. After establishing baseline sulfur and mercury emissions from burning the coal without added sorbent (the mercury is predominantly in elemental form in the flue gas emissions), a powder sorbent composition as in Example 7 is added at a treatment rate of 5.5 – 6.0% by weight of fuel into the furnace just below the neck of the furnace, about 20 feet above the fireball. The temperature at the injection point is about 3000°F to 3300°F. Addition is made through a series of 3 lances along one side of the

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furnace. Each lance conveys approximately the same amount of powder and protrudes approximately 3 feet into the furnace from the inside wall. Sulfur capture is increased by 50% over baseline. Mercury capture is approximately 1 - 3% over baseline. While continuing addition of the powder sorbent composition into the furnace, a 50% by weight solution of calcium bromide in water is added directly to the fuel in the fuel feeder at a rate of approximately 0.2% by weight, based on the weight of coal being consumed by combustion. Mercury capture increases to 90%.

Example 10

[0140] The same process as Example 9 is also followed except the powder sorbent is added directly to the coal feeders (upstream of the furnace) rather than directly into the furnace. The same sulfur and mercury reductions are observed as with Example 9.

Example 11

[0141] PRB coal is burned in a positive draft tangentially fired boiler to generate electricity for consumer use. Powdered coal (75% passing 200 mesh) is fed to the boiler. Before introduction of the powdered coal into the boiler, a powder sorbent is added to the coal at a rate of 6% by weight, based on the rate of coal being consumed by combustion. The powder sorbent contains 93% by weight of a 50/50 mixture of cement kiln dust and lime kiln dust, and 7% by weight of calcium montmorillonite. At the same time, a 50% by weight solution of calcium bromide in water is dripped onto the coal at a rate of 0.1 to 2% by weight based on the rate of consumption of coal by combustion. Fly ash samples are collected before addition of sorbents (baseline), and after addition of the powder and liquid sorbents. The levels of chlorine and heavy metals are determined according to standard methods. Results are in the table (Table 1).

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Table 1

Fly Ash Composition with and without sorbents

Element	Test – After sorbent addition (ppm except for chlorine)	Baseline – Prior to sorbent addition (ppm except for chlorine)
As	59.3	26.5
Ba	1.3	1.4
Cd	2.3	1.1
Co	44.8	38.5
Cr	52.0	34.3
Cu	61.0	48.8
Mn	455.7	395.5
Mo	26.0	31.5
Ni	208.5	325.5
Pb	45.8	31.3
Sb	23.0	7.3
V	473.0	874.5
Zn	3954.0	974.7
Mercury	0.246	0.128
Chlorine	0.940%	0.56%

[0142] It is seen that use of the sorbents increases the level of several heavy metals found in the fly ash. For example, arsenic, cadmium, chromium, lead, mercury, and chlorine are present at higher levels in the test ash than in the baseline. This is believed to represent increased capture of the elements in the ash. The increased level of zinc in the test ash is unexplained. However, it could be due to the fact that a great deal of de-slagging is observed from the boiler tubes upon use of sorbents of the invention. It could be that the increased levels of zinc are attributable to material removed from the boiler tubes during combustion with the sorbents.

Example 12

Next the ash samples are tested according to the TCLP procedure of the U.S. Environmental Protection Agency (EPA) to determine the acid leaching thresholds of key elements. Results are in Table 2.

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Table 2

Fly Ash TCLP Test Results

Element	EPA Threshold Limit (ppm)	Baseline – prior to sorbent addition (ppm)	Test – with sorbent addition (ppm)
Arsenic	5.0	<0.04	<0.04
Barium	100.0	0.814	0.313
Cadmium	1.0	<0.04	<0.04
Chromium	5.0	0.030	<0.007
Lead	5.0	0.513	0.096
Mercury	0.20	0.095	0.078
Selenium	1.0	<0.07	<0.07
Silver	5.0	3.835	3.291

[0143] Table 2 shows that, while the ash is higher in absolute levels of elements such as arsenic, lead, and mercury, nevertheless the amount of leachable arsenic, lead, and mercury is actually lower in the test ash than in the baseline.

Example 13

[0144] PRB coal (75% passing 200 mesh) is burned in a balanced draft tangentially fired furnace to produce 160 MWatts of power. The coal is burned for a time period to produce 8 box cars of fly ash. A powder sorbent is added at a rate of 4-6% by weight into the system during the time period. For the first third of the time period, addition of sorbent is solely into the furnace at a location just below the nose of the furnace through a lance inserted through the furnace wall; for the next third, addition of sorbent is half into the furnace and half onto the powdered coal pre-combustion; for the final third, addition of powder sorbent is 100% onto the coal pre-combustion. Throughout the time period, a liquid sorbent (50% by weight calcium bromide in water) is added onto the powdered coal pre-combustion at a rate of 0.15% by weight, based on the rate of coal consumption. A consolidated sample representative of the eight box cars of ash is collected and measured for leaching using the US EPA TCLP procedure. The leaching result for barium is 26 ppm, well below the regulatory level of 100 ppm. TCLP values for As, Cd, Cr, Pb, Hg, Se, and Ag are below the detection limits of the test. In particular, mercury leaching is <0.0020 ppm, which is less than 2 ppb.

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CLAIMS

I claim:

1. A process for burning coal in a coal burning system to reduce the amount of mercury released into the atmosphere comprising

applying a sorbent composition comprising a halogen into the coal burning system, wherein the sorbent composition is free of alkali metal compounds;

combusting the coal to produce ash and combustion gases;

measuring a mercury level in the combustion gases; and

adjusting the amount of sorbent composition applied based on the value of the mercury level.

2. A process according to claim 1, comprising applying the sorbent composition onto the coal, delivering the coal containing the sorbent into the furnace for combustion, and adjusting the amount of sorbent applied to the coal based on the value of the mercury level.

3. A process according to claim 1, wherein the sorbent composition comprises a bromine compound or an iodine compound.

4. A method according to claim 1, wherein the sorbent composition comprises a bromide.

5. A method according to claim 1, wherein the sorbent composition comprises calcium bromide.

6. A method according to claim 1, comprising applying a solution containing a bromine compound onto the coal.

7. A method according to claim 1, comprising applying a solution containing a iodine compound onto the coal.

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8. A method according to claim 1, comprising contacting the coal with an aqueous solution comprising calcium bromide.

9. A method according to claim 8, wherein the solution comprises 20% to 60% by weight calcium bromide.

10. A method according to claim 8, wherein the solution comprises greater than 50% by weight calcium bromide.

11. A method for reducing mercury in the flue gases resulting from combustion of coal in a coal burning system, comprising

applying sorbent components into the coal burning system, wherein the components comprise a halogen compound and at least one aluminosilicate mineral;

combusting the coal to produce ash and combustion gases;

measuring a mercury level in the combustion gases; and

adjusting the amount of halogen compound applied based on the value of the mercury level.

12. A method according to claim 1, comprising applying the components to the coal before combustion and delivering the coal containing the components to the furnace for combustion.

13. A method according to claim 11, wherein the sorbent comprises a bromide.

14. A method according to claim 11, wherein the sorbent comprises calcium bromide.

15. A method according to claim 11, wherein the aluminosilicate mineral is a layered structure comprising at least one mineral selected from the group consisting of

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clay, kaolinite, sodium montmorillonite, calcium montmorillonite, vermiculite, mica, talc, chrysotile, and pyrophillite.

16. A method according to claim 11, wherein the aluminosilicate mineral comprises at least one layered structure selected from the group consisting of kaolinite, calcium montmorillonite, and sodium montmorillonite.

17. A method for reducing the amount of oxidized mercury in flue gases generated by combustion of mercury-containing carbonaceous fuels, the method comprising

burning the fuel in the presence of an alkaline powder sorbent;
measuring the level of mercury in the flue gases;
comparing the measured mercury level to a target level; and
if the measured value is above the targeted level, increasing the amount of powder sorbent added relative to the fuel,

wherein the powder sorbent comprises calcium, silica, and alumina.

18. A method according to claim 17, wherein the powder sorbent further comprises iron and magnesium.

19. A method according to claim 17, wherein the alumina content of the sorbent is higher than the alumina content of portland cement.

20. A method according to claim 17, wherein the alumina content of the powder sorbent is greater than 7% by weight.

21. A method according to claim 17, comprising injecting the powder sorbent into the furnace during the burning.

22. A method according to claim 17, wherein the fuel comprises coal and one or more components selected from the group consisting of biomass, polymer scrap, and rubber tires.

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23. A method according to claim 17, wherein the powder sorbent comprises one or more materials selected from the group consisting of portland cement, calcium oxide, lime, limestone, sugar beet lime, cement kiln dust, and lime kiln dust, and further comprises an aluminosilicate material.

24. A method according to claim 23, wherein the powder sorbent comprises two or more of the materials.

25. A method of reducing sulfur and/or mercury in the flue gases produced by the combustion of coal in the furnace of a coal burning facility, comprising applying a powder composition onto the coal before combustion and/or into the furnace during combustion, wherein the powder composition comprises 50 to 98% by weight of an alkaline powder comprising calcium, and 2 to 50% by weight of an aluminosilicate material.

26. A method according to claim 25, comprising combusting the fuel at a temperature of about 1000°F.

27. A method according to claim 25, wherein the powder composition comprises 5 to 25% by weight of the aluminosilicate material.

28. A method according to claim 25, wherein the powder sorbent comprises 5 to 10% by weight of the aluminosilicate material.

29. A method according to claim 25, wherein the alkaline powder comprises one or more materials selected from the group consisting of portland cement, cement kiln dust, lime kiln dust, and sugar beet lime.

30. A method according to claim 25, wherein the alkaline powder comprises cement kiln dust and lime kiln dust.

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31. A method according to claim 25, wherein the aluminosilicate material comprises at least one material selected from the group consisting of calcium montmorillonite, sodium montmorillonite, and kaolin.

32. A method according to claim 25, comprising applying the powder composition at 0.1 to 10% by weight based on the weight of the coal being combusted.

33. A method according to claim 25, comprising injecting the powder composition into the furnace.

34. A method according to claim 33, wherein the temperature at the point of injection is greater than 2000°F.

35. A sorbent composition comprising 50 to 98% by weight of an alkaline powder and 2 to 50% of an aluminosilicate mineral, wherein the alkaline powder comprises one or more of portland cement, cement kiln dust, lime kiln dust, and sugar beet lime.

36. A composition according to claim 35, further comprising a bromine compound.

37. A composition according to claim 35, wherein the alkaline powder comprises cement kiln dust and lime kiln dust.

38. A method according to claim 35, comprising 2 to 20% by weight of the aluminosilicate material.

39. A method according to claim 38, wherein the aluminosilicate material is one or more selected from the group consisting of calcium montmorillonite, sodium montmorillonite, and kaolin.

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40. A process for burning coal to reduce the amount of mercury released into the atmosphere comprising

applying a liquid sorbent composition comprising a bromine compound onto the coal;

delivering the coal containing the sorbent into a coal burning furnace;

injecting a powder composition into the furnace during combustion, the powder composition comprising sources of calcium, silica, and alumina;

combusting the coal together with the liquid and powder composition in the coal burning furnace to produce ash and combustion gases.

41. A process according to claim 40, further comprising

measuring leaching of mercury from the ash; and

adjusting the amount of silica and alumina added by way of the sorbent composition applied to the coal based on the value of the measured leaching.

42. A method according to claim 40, wherein the liquid sorbent composition comprises a bromide.

43. A method according to claim 42, wherein the liquid sorbent composition contains essentially no alkali metal compound.

44. A method according to claim 40, wherein the powder composition comprises an aluminosilicate mineral.

45. A method according to claim 40, wherein the powder composition comprises one or more of portland cement, cement kiln dust, and lime kiln dust.

46. A method according to claim 40, wherein the sorbent comprises cement kiln dust, lime kiln dust, and an aluminosilicate mineral.

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47. A method according to claim 40, comprising injecting the powder where the temperature is above 2000°F.

48. A method according to claim 40, comprising injecting the powder where the temperature is above 2300°F.

49. A method according to claim 40, comprising injecting the powder where the temperature is above 2700°F.

50. A method for burning mercury-containing coal in a combustion system comprising a furnace and convective pathway for flue gases downstream of the furnace, the method comprising:

adding a liquid composition into the system;

adding a powder composition comprising calcium, silica, and alumina into the system during combustion; and

combusting coal to produce flue gases and fly ash;

wherein the liquid composition comprises a bromine compound and the powder composition comprises at least 2% by weight silica and at least 2% by weight alumina.

51. A method according to claim 50, comprising adding the liquid composition to the coal before combustion.

52. A method according to claim 50, comprising adding the powder composition to the coal before combustion.

53. A method according to claim 50, wherein the liquid composition comprises calcium bromide.

54. A method according to claim 50, wherein the powder composition comprises an aluminosilicate mineral and further comprises one or more of portland cement, cement kiln dust, sugar beet lime, and lime kiln dust.

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55. A method according to claim 50, comprising adding the powder sorbent at a 1 to 10% by weight based on the weight of the coal being combusted.

56. A method according to claim 50, comprising adding the bromine compound at 0.05 to 1% by weight based on the weight of the coal being consumed by combustion.

57. A method for burning coal with reduced levels of undesirable elements escaping into the environment comprising

adding a sorbent composition comprising calcium, silica, alumina, and a halogen selected from the group consisting of bromine and iodine onto the coal;

burning the coal to produce ash and combustion gases.

58. A method according to claim 57, further comprising measuring a level of mercury in the combustion gases and adjusting the level of bromine added to the coal based on the level of mercury.

59. A method according to claim 57, comprising adding a sufficient amount of bromine onto the coal to reduce the mercury emissions into the environment by 90% or more compared to the emissions produced by burning coal without adding the bromine.

60. A method according to claim 57, wherein the sorbent composition comprises calcium bromide.

61. A method according to claim 57, comprising applying a liquid composition comprising a bromine compound onto the coal.

62. A method according to claim 61, wherein the liquid composition comprises calcium bromide.

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63. A method for reducing mercury in the flue gases resulting from combustion of coal in the furnace of a coal burning system, comprising

applying sorbent components comprising a halogen, calcium, silica, and alumina into the coal burning system; and

combusting the coal to produce ash and combustion gases.

64. A method according to 63, further comprising

measuring a mercury level in the combustion gases; and

adjusting the amount of halogen applied into the system based on the value of the mercury level.

65. A method according to claim 63, wherein the halogen comprises bromine.

66. A method according to claim 63, comprising adding at least one of the components onto the coal prior to combustion.

67. A method according to claim 63, comprising adding at least one of the components directly into the furnace.

68. A method according to claim 63, comprising injecting at least one of the components into a convective pathway of the system downstream of the furnace.

69. A method according to claim 63, comprising adding a liquid sorbent comprising bromine and a powder sorbent comprising calcium, silica, and alumina.

70. A method according to claim 69, wherein the powder sorbent comprises one or more of portland cement, cement kiln dust, lime kiln dust, and aluminosilicate clay.

71. A method according to claim 69, comprising adding 1 to 10% by weight of the powder sorbent, based on the weight of coal being combusted.

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72. A coal ash made by a process comprising burning coal in the presence of added bromine, silica, and alumina.

73. A cement product comprising portland cement and from 0.01% to about 99% by weight, based on the total weight of the cement product, of a coal ash according to claim 72.

74. A pozzolanic product comprising a pozzolan, and from about 0.01% by about 90% by weight, based on the total weight of the pozzolanic product, of a coal ash according to claim 72.

75. A concrete ready mix product comprising aggregate and a cement product, wherein the cement product comprises a coal ash according to claim 72.

76. A composition prepared by adding water to a ready mix product according to claim 75.

77. A set concrete construction prepared by hydrating a ready mix product according to claim 75.

78. A process comprising

burning coal in the presence of 1-10% by weight of an added sorbent, the sorbent comprising about 30-75% by weight CaO, about 2 -15% by alumina, about 5-20% by weight silica, about 1-10% by weight Fe_2O_3, and 0.1-5% by weight of alkali selected from Na_2O and K_2O;

producing an ash by burning the coal;

recovering the ash; and

formulating a cementitious mixture comprising the ash.

79. A process according to claim 78, comprising burning the coal in the further presence of a bromine compound.

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80. A process according to claim 78, wherein the added sorbent comprises an aluminosilicate mineral.

81. A process according to claim 78, wherein the added sorbent comprises cement kiln dust.

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INTERNATIONAL SEARCH REPORT

WO 2006/099611

International application No.
PCT/US2006/010000

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/26(2006.01)i, B01D 53/64(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)

IPC8 B01D

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

Korean patents and applications for inventions since 1975

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

Delphion and keywords: mercury, coal, halogan, emission, aluminosilicate, calcium, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/0086439 A1 (BAYER AKTIENGESELLSCHAFT) May 6, 2004 abstract, section 7, 9, 10, 15, 17, 23	1-16, 40-77
X	US 6808692 B2 (KLAUS H. OEHR) October 26, 2004 abstract, column 3 line 66-column 4 line 54	1-16, 40-77
X	US 6258334 B1 (CORNING INCORPORATED) July 10, 2001 abstract, column 2 line 7-17, column 2 line 51-63, column 5 line 11-25, column 7 line 1-16	11, 13-37, 40-81
X	US 2003/0103882 A1 (JOSEPH JAN BIERMANN) June 5, 2003 abstract, section 7-10, 15	17-34, 40-71, 78-81
X	US 6528030 B2 (McDERMOTT TECHNOLOGY, INC) March 4, 2003 abstract, column 2 line 25-50, column 3 line 44-57, claim 10, 11	17-37, 40-81

☐ 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 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
27 JULY 2006 (27.07.2006)	**31 JULY 2006 (31.07.2006)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	LEE, HYUN SONG Telephone No. 82-42-481-8296

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2006/010000

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.: 38, 39
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:

Claims 38, 39 direct to a method according to claim 35 which discloses a sorbent composition. A method claimed by 38, 39 are not clear whether they are directed to manufacturing method for the sorbent or method of combustion using the sorbent.

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:

See separate sheets

1. ☐ As all required addtional 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 an additional fee, this Authority did not invite payment of any additional fee.

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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Box No. III

Unity of Invention

The International Searching Authority considers that there are 10 inventions covered by the claims indicated as follows:

I: Claims 1-10, 12 directed to a process for burning coal in a coal burning system to reduce the amount of mercury released into the atmosphere comprising applying a sorbent composition comprising a halogen into the coal burning system, wherein the sorbent composition is free of alkali metal compounds

II: Claims 11, 13-16 directed to a method for reducing mercury in the flue gases resulting from combustion of coal in a coal burning system, comprising applying sorbent components into the coal burning system, wherein the components comprise a halogen compound and at least one aluminosilicate mineral.

III: Claims 17-24 directed to a method for reducing the amount of oxidized mercury in flue gases generated by combustion of mercury-containing carbonaceous fuels, the method comprising burning the fuel in the presence of an alkaline powder sorbent, wherein the powder sorbent comprises calcium, silica, and alumina.

IV: Claims 25-34 directed to a method for reducing sulphur and/or mercury in flue gases produced by combustion of coal in the furnace of a coal burning facility, comprising applying a powder composition onto the coal before combustion and/or into the furnace during combustion, wherein the power composition comprises 50 to 98% by weight of an alkaline powder comprising calcium, and 2 to 50% by weight of an aluminosilicate material.

V: Claims 35-37 directed to a sorbent composition comprising 50 to 98% by weight of an alkaline powder and 2 to 50% of an aluminosilicate, wherein the alkaline powder comprises one or more of Portland cement, cement kiln dust, lime kiln dust, and sugar beet lime.

VI: Claims 40-56 directed to a process for burning coal to reduce the amount of mercury released into the atmosphere comprising applying a liquid sorbent composition comprising a bromine compound onto the coal; delivering the coal containing the sorbent into a coal burning furnace; injecting a powder composition into the furnace during combustion, the powder composition comprising sources of calcium, silica, and alumina; combusting the coal together with the liquid and powder composition in the coal burning furnace to produce ash and combustion gases.

VII: Claims 57-62 directed to a method for burning coal with reduced levels of undesirable elements escaping into the environment comprising adding a sorbent composition comprising calcium, silica, alumina, and a halogen selected from the group consisting of bromine and iodine onto the coal.

VIII: Claims 63-71 directed to a method for reducing mercury in the flue gases resulting from combustion of coal in the furnace of a coal burning system, comprising applying sorbent components comprising a halogen, calcium, silica, and alumina into the coal burning system.

IX: Claims 72-77 directed to a coal ash, a cement, a pozzolanic product, a concrete ready mix product, a composition, a set concrete construction.

X: Claims 78-81 directed to a process for formulating a cementitious mixture.

(Continued)

Continuation of Box No. III

The reasons for which the present application has been deemed to contain 10 inventions which are not linked such that they form a single general inventive concept, as required by Rules 13.1, 13.2 and 13.3, PCT are as follows:

The prior art has been identified as: D1(US2004/0086439A1) and D3(US6258334B1)

Invention I:
From a comparison of the disclosure of this prior art D1 and the technical features of claims 1-10, 12, the features which are known from D1 (abstract, section 7-10) are the following: Removing mercury from the flue gases generated by combustion of coal by various bromine compound. The following technical features of claim(s) 1-10, 12 can be seen to make a contribution over this prior art (Rule 13.2 PCT): Using halogens compound, which is free of alkali metal compounds.

Invention II:
From a comparison of the disclosure of this prior art D1 and the technical features of claims 11, 13-16 the following features can be seen to make a contribution over this prior art (Rule 13.2 PCT): Using additional aluminosilicate mineral.

Invention III:
From a comparison of the disclosure of this prior art D3 and the technical features of claims 17-24, the features which are known from D3 (abstract, column 5) are the following: Removing mercury from the flue gases generated by combustion of coal by alumina, silica, aluminosilicate having porosity. The disclosure of this prior art D2 and the technical features of claims 17-24 are overlapped (Rule 13.2 PCT).

Invention IV:
From a comparison of the disclosure of this prior art D3 and the technical features of claims 25-34 the following features can be seen to make a contribution over this prior art (Rule 13.2 PCT): Reducing sulphur and/or mercury in the flue gases with additional alkaline powder.

Invention V:
Claims 35-37 does not linked to other claims because in claims a sorbent composition only (Rule 13.1 PCT).

Invention VI:
From a comparison of the disclosure of this prior art D3 and the technical features of claims 40-56 the following features can be seen to make a contribution over this prior art (Rule 13.2 PCT): Reducing mercury in the flue gases with additional liquid bromine sorbent.

Invention VII:
From a comparison of the disclosure of this prior art D3 and the technical features of claims 57-62 the following features can be seen to make a contribution over this prior art (Rule 13.2 PCT): Reducing undesirable elements with additional bromine.

Invention VIII:
From a comparison of the disclosure of this prior art D3 and the technical features of claims 63-71 the following features can be seen to make a contribution over this prior art (Rule 13.2 PCT): Reducing mercury in the flue gases with additional bromine.

(Contined)

Continuation of Box No. III

Invention IX:
Claims 72-77 does not linked to other claims because in claims a coal ash (Rule 13.1 PCT).

Invention X:
Claims 78-81 does not linked to other claims because in claims a process formulating a cementitious mixture (Rule 13.1 PCT).

The above analysis shows that the special technical features of invention I to invention X does not share any technical relationship among those inventions. Therefore, the groups of claims are not linked by common or corresponding special technical features and define 10 different inventions not linked by a single general inventive concept.

The application, hence does not meet the requirements of Unity of Invention as defined in Rules 13.1 & 13.2 PCT.

The Applicant should be aware that for the above mentioned 10 inventions a full search has been carried out, without additional searching fee: this does not however imply that each of said I to X inventions, fulfil(s) the requirement of unity of invention stipulated in Rule 13.1 & 13.2 PCT.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2006/010000

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		CA2291304AA	2000-06-07

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

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(10) International Publication Number
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(51) International Patent Classification:
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B01D 53/00 (2006.01) *E21B 21/00* (2006.01)

(21) International Application Number:
PCT/US2008/071986

(22) International Filing Date: 1 August 2008 (01.08.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/953,290 1 August 2007 (01.08.2007) US

(71) Applicant *(for all designated States except US)*: **ENERGY & ENVIRONMENTAL RESEARCH CENTER** [US/US]; 15 North 23rd Street, Grand Forks, North Dakota 58202-9018 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **SCHMIDT, Darren, D.** [US/US]; 1444 9th Avenue NE, Thompson, North Dakota 58278 (US).

(74) Agents: **WESTBY, Timothy, S.** et al.; CONLEY ROSE, P.C., P.O. Box 3267, Houston, Texas 77253-3267 (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, BR, BW, BY, BZ, CA, CH, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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19 March 2009

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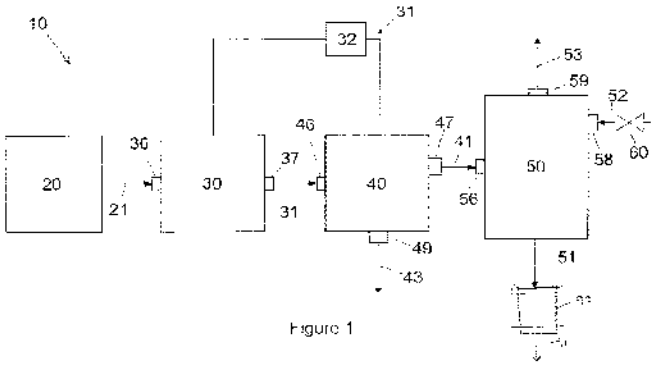


Figure 1

(57) Abstract: A system for controlling the emission of associated gas produced from a reservoir. In an embodiment, the system comprises a gas compressor including a gas inlet in fluid communication with an associated gas source and a gas outlet. The gas compressor adjusts the pressure of the associated gas to produce a pressure-regulated associated gas. In addition, the system comprises a gas cleaner including a gas inlet in fluid communication with the outlet of the gas compressor, a fuel gas outlet, and a waste product outlet. The gas cleaner separates at least a portion of the sulfur and the water from the associated gas to produce a fuel gas. Further, the system comprises a gas turbine including a fuel gas inlet in fluid communication with the fuel gas outlet of the gas cleaner and an air inlet. Still further, the system comprises a choke in fluid communication with the air inlet.

WO 2009/018539 A3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/071986

A. CLASSIFICATION OF SUBJECT MATTER

F17C 5/00(2006.01)i, B01D 53/00(2006.01)i, F02C 6/14(2006.01)i, E21B 21/00(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)
IPC: F17C, F02C, C10G

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 since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKIPASS (KIPO internal) & keywords: "gas compressor", "gas turbine" , "sulfur", "water" and "separate"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 09-256812 A (TOSHIBA CORP.) 30 September 1997 See the abstract and Claim 1.	1, 10
A	US 4,342,192 (KLAUS HEYN et al.) 3 August 1982 See the abstract and Fig. 1.	1, 10
A	US 7,017,330 B2 (JAMES C. BELLOWS) 28 March 2006 See the abstract and Fig. 1.	1, 10
A	KR 10-2002-0052209 A (JGC CORPORATION) 2 July 2002 See page 2, line 31 - page 6, line 1 and Fig. 3.	1, 10

☐ 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 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 2009 (30.01.2009)	**30 JANUARY 2009 (30.01.2009)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
HAN, JAE SEOB
Telephone No. 82-42-481-5439

Form PCT/ISA/210 (second sheet) (July 2008)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2008/071986

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International Bureau

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B01D 53/64 (2006.01)

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2 February 2010 (02.02.2010)

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(54) **Title**: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

(57) **Abstract**: A promoted carbon and/or non-carbon base sorbent are described that are highly effective for the removal of mercury from flue gas streams. The promoted sorbent comprises a carbon and/or non-carbon base sorbent that has reacted with and contains forms of halogen and halides. Optional components may be added to increase and/or preserve reactivity and mercury capacity. These may be added directly with the base sorbent, or in-flight within a gas stream (air, flue gas, etc.), to enhance base sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The promoted sorbent can be regenerated and reused. Base sorbent treatment and preparation methods are also described. New methods for in flight preparation, introduction, and control of the active base sorbent into the mercury contaminated gas stream are described.

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is being filed on 02 February 2010, as a PCT International Patent application in the name of Energy & Environmental Research Center Foundation, a U.S. national corporation, applicant for the designation of all countries except the U.S., and Edwin S. Olson, a citizen of the U.S., Michael J. Holmes, a citizen of the U.S., and John H. Pavlish, a citizen of the U.S., applicants for the designation of the U.S. only, and claims priority to U.S. Continuation-in-Part Patent Application Serial No. 12/429,058 filed on 23 April 2009.

BACKGROUND OF THE INVENTION

Technical Field of the Invention

[0002] The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

[0003] The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, a day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

[0004] Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a particulate control device such as a baghouse or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when an ESP is used to collect the carbon because the contact time of the carbon with the gas is very short.

[0005] A major problem with existing carbon injection systems is that the sorbent is relatively unreactive toward mercury. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

[0006] One solution has been to add an oxidative sorbent comprising an aluminosilicate material impregnated with a very heavy dosage of one or more oxidative metal halides plus activated carbon. For example, refer to Varma et al. (20070140940). However, the amounts of metal salts required for Hg oxidation are generally relatively large and expensive. Also, several of the salts that can be used in such a process are highly toxic. Although the metal salts are present for oxidation in this process, activated carbon is essential for getting adsorption of the Hg. As such, there is no synergistic role for the aluminosilicates as they appear to be only a support for the oxidizing salts.

[0007] Another approach has been the injection of aluminosilicate particulate such as bentonite, which contains neither oxidizing salts nor halogen complexes with a Lewis base site, and thus lacks the more powerful oxidizing capability of the said complexes as described in this application. For example, see U.S. Patent No. 7,413,719. Additionally, the injection of an aluminosilicate (kaolin or metakaolin) containing

calcium hypochlorite which thermally decomposes to form halogen is also known. For example, see U.S. Patent Application No. 20030103882. Thus these and similar impregnated aluminosilicate technologies require time in flight at appropriate high temperatures to heat the impregnated salt(s) to generate an oxidation site. This clearly represents a kinetic barrier to activation in contrast to the extremely fast complexing reaction of the Lewis acid on the surface of the appropriate Lewis base sorbent described in the present patent. The kinetic barrier is only for heating up the calcium hypochlorite to decompose it to Cl atoms or molecules. Halogen (bimolecular or atomic) would complex with carbon or noncarbon at any lower temperature to form reactive oxidation sites. Also, halide would require a very high temp or strong acid to form reactive halogen or halogen complex.

[0008] Yet another approach is the injection of bentonite plus a metal sulfide and a metal salt, none of which is oxidizing to elemental mercury and would require a slow thermal activation step. For example, see U.S. Patent Application No. 20070119300.

[0009] The injection of halogen or halogen precursors in a hot zone, followed by contact with an alkaline material in a wet or dry scrubber is another approach known in the art. With such an approach, elemental mercury is claimed to be oxidized by the halogen to Hg(II) which is collected by the alkaline material in the scrubber. For example, see U.S. Patent No 6,808,692 (Oehr), U.S. Patent No. 3,849,267 (Hilgen), U.S. Patent No. 5,435,980 (Felsvang), U.S. Patent No. 6,375,909 (Dangtran), U.S. Patent Application No. 20020114749 (Cole), U.S. Patent No. 6,638,485 (Iida), U.S. Patent Application No. 20030185718 (Sellakumar), U.S. Patent Application No. 20030147793 (Breen), and U.S. Patent No. 6,878,358 (Vosteen). However, even though it is known to inject halogen forms at some stage of the combustion process, such a process does not utilize a complexing method on a sorbent surface for conducting the oxidation and capture. Further, the alkaline material is rapidly surface-coated by the large concentrations of acid gases, lowering its capacity for adsorption of Hg(II). It is also recognized that the halogen forms initially introduced or generated are far more reactive to the large concentrations of SO_2 and moisture in the flue gas, and so gas-phase reactions of the halogens with Hg are hindered. In contrast, the present invention takes advantage of the Lewis acid complexes that rapidly form on the sorbent surface to effect the Hg oxidation, rather than rely on gas phase reactions for oxidation. Thus HCl, HBr, SO_2Br, and other gas-phase products all festoon the surface and promote the activity of the sorbent by forming complexes with the sorbent to form a promoted sorbent.

[0010] Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants, including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY

[0011] The various embodiments of the present invention overcome the various aspects of the deficiencies of the prior art and provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

[0012] A halogen/halide-promoted sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises any activated carbon and/or non-carbon compound, such as porous or vesicular felsic or basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the promoted sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. Methods for in-flight preparation, introduction, and control of the sorbent, promoter and promoted sorbent into the mercury contaminated gas stream are described.

[0013] When a promoted or a non-promoted base sorbent reacts with elemental or oxidized mercury, a mercury/sorbent chemical composition is formed and, in the case of elemental mercury reacting with the promoted base sorbent, the mercury is oxidized. As discussed in further detail in other portions of the specification, the base sorbent may be either a carbon or a non-carbon material or a combination thereof. Additionally, the mercury/sorbent chemical composition may be comprised of covalent bonds, ionic bonds and/or chemical complexes between the promoted or non-promoted base sorbent and the oxidized mercury. The Lewis basic groups on the non-promoted base sorbent, or the non-promoted portions of a promoted base sorbent, are available for reaction with the Lewis acid groups of already existing oxidized mercury in the mercury containing gas. Thus, mercury may be removed from the mercury containing gas stream through the formation of multiple and various mercury/sorbent chemical compositions even within the same process. For example, multiple sites on a sorbent particulate can form

multiple and various mercury/sorbent chemical compositions in the case where only a portion of the sites on the base sorbent particulate are promoted.

[0014] In some embodiments, a carbon and/or non-carbon promoted sorbent and/or a combination thereof is provided comprising a sorbent structure that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream. The carbon sorbent comprises reactive Lewis acid groups/sites; the non-carbon sorbent comprises reactive Lewis basic groups/sites.

[0015] In an embodiment, a promoted carbon and/or non-carbon sorbent is provided wherein the base sorbent is selected from the group consisting of carbon, activated carbon, porous or vesicular felsic and basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, and/or bicarbonate compounds, or a combination thereof, with an average particle size similar to that of fly ash produced from a thermal process (combustion or gasification) or greater than that of fly ash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the promoted sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter greater than about 40 micrometers.

[0016] In another embodiment, the promoted sorbent comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced.

[0017] In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt% of the concentration of the promoter on the finished sorbent.

[0018] In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the base sorbent.

[0019] In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor

form when combined with the base sorbent. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base sorbent. In another embodiment, the promoter and optional secondary component are combined with the base sorbentsubstantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

[0020] In an embodiment, a method is provided comprising providing a granular base sorbent and reacting the base sorbent with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams of promoter per 100 grams of base sorbent. In another embodiment the reaction product has an average particle-size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment, the reaction product has a mass mean particle diameter greater than about 40 micrometers.

[0021] In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the promoter is in the gas phase when contacting the base sorbent (carbon, non-carbon, or their combination). In another embodiment, the promoter is in an organic solvent when contacting the base sorbent (carbon, non-carbon, or their combination).

[0022] In another embodiment, the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

[0023] In another embodiment, the method further comprises reacting the granular non-carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the promoted sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the non-carbon base sorbent. In another embodiment, the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity,

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mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

[0024] In an embodiment, the promoted sorbent is introduced by direct injection into the flue gas stream. In another embodiment, the base sorbent is promoted within the flue gas stream

[0025] In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a base sorbent, either by injection or in situ creation, into a mercury-containing flue gas stream, collecting greater than 70 wt% of the mercury in the flue gas on the promoted sorbent to produce a cleaned flue gas, and substantially recovering the promoted sorbent from the cleaned flue gas. In embodiments where less than 70 wt% mercury removal is desired, the required removal is attained using less base sorbent as would be required with standard base sorbent. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered promoted sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of base sorbent and promoter. In another embodiment the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

[0026] In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination).

[0027] In another embodiment, the injected promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination), a promoter, and an optional secondary component to enhance the reactivity and capacity of the promoted sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

[0028] In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt% of the promoter content. In another embodiment, the method further comprises adding to the promoted sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2,

CS_2, P_2S_5, and combinations thereof.

[0029] In an embodiment, the method further comprises coinjecting an optional alkaline material, including without limitation alkaline and alkaline-earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce promoted sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

[0030] In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the promoted sorbent. In another embodiment, the promoted sorbent is prepared in-flight by reacting a base sorbent (carbon, non-carbon, or their combination) and a promoter within the flue gas stream or in a transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of the base sorbent (carbon, non-carbon, or their combination), wherein the rate at which the promoter is added and the rate of promoted sorbent injection are determined by a digital computer based, at least in part, on the monitored mercury content of the cleaned flue gas.

[0031] In an embodiment, a method for reducing the mercury content of a mercury and ash-containing gas stream is provided wherein particulate carbon and/or non-carbon promoted sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the promoted sorbent particles, the promoted sorbent particles are separated from the ash particles on the basis of size, and the promoted sorbent particles are reinjected to the gas stream. In another embodiment, the mercury-containing promoted sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is coinjected into the gas stream. In another embodiment, the promoted sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

[0032] In an embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is disclosed. The method comprises reacting a carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted carbon sorbent; allowing said promoted carbon sorbent to interact with a mercury-containing gas to capture mercury

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in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0033] In a further emobodiment, the method comprises reacting a non-carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted non-carbon sorbent; allowing said promoted non-carbon sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the non-carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the non-carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the non-carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0034] In a further embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is presented. The method comprises reacting a base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted sorbent, wherein said base sorbent is selected from the group consisting of a non-carbon material, a carbon material, and combination thereof; allowing said promoted sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas.

[0035] In some embodiments, the base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some

embodiments, the base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In some embodiments, introducing the base sorbent and the promoter comprises injecting the base sorbent and the promoter into the mercury-containing gas. In some embodiments, the promoter is introduced into the mercury-containing gas upstream of the introduction of the base sorbent. In some embodiments, the promoter is introduced upstream of a boiler or a combustion chamber. In an embodiment, the rate at which the base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

[0036] In an embodiment, the base sorbent for the promoted sorbent is selected from the group consisting of carbon, activated carbon, porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof. In embodiments, the non-carbon material comprises Lewis basic groups and the carbon material comprises Lewis acid groups. In some cases, the non-carbon material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals. The alkaline-earth metals comprise Group I and Group II alkaline-earth metals. In some other cases, the non-carbon material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

[0037] In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and inorganic species on the non-carbon base sorbent. In some embodiments, the inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof. In an embodiment, the promoted sorbent comprises metastable complexes formed between the promoter of this disclosure and metal-oxygen-metal structures on the non-carbon base sorbent. In some embodiments, the promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof. In an embodiment, the promoted sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof. In some embodiments, the interaction between promoted sorbent and said mercury-containing

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gas stream comprises mercury diffusing from the gas phase onto said promoted sorbent surface; and reacting with the activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on the promoted sorbent surface.

[0038] In an embodiment, the method for reducing mercury in a mercury-containing gas to a desired level further comprises pretreating the base sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof. In some cases, the pretreating methods comprise chemical treatment, thermal treatment, vacuum treatment, and combinations thereof. In some embodiments, chemical treatment comprises acid treatment and alkaline treatment. In an embodiment, [[,]] the method for reducing mercury in a mercury-containing gas to a desired level further comprises introducing an alkali component into the mercury-containing gas.

[0039] As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from combustion and gasification systems.

[0040] The foregoing has outlined rather broadly the features and technical advantages 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 that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also 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

[0041] For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

[0042] Figure 1 schematically illustrates methods for preparation of promoted carbon and/or non-carbon sorbents in accordance with the present invention.

[0043] Figure 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

[0044] Figure 3 schematically illustrates preparation of promoted carbon and/or non-carbon sorbents and processes for flue gas mercury reduction in flue gases and/or

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product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon and/or non-carbon sorbent.

[0045] Figure 4 illustrates a mechanism for promotion of metal oxide base sorbent via formation of a reactive halogen complex sorbent and subsequent capture of elemental mercury on the promoted sorbent.

[0046] Figure 5A schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

[0047] Figure 5B schematically illustrates an exemplary process flow diagram for in-flight preparation of a promoted carbon and/or non-carbon sorbent.

DETAILED DESCRIPTION

[0048] Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

[0049] The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide-promoted sorbents using a bromide (or other halogen/halide) treatment of the promoted sorbent, that capture mercury via mercury–sorbent surface reactions, at very short contact times of seconds or less. The reactivity of the promoted sorbent toward the pollutants (i.e., mercury) is greatly enhanced, and the sorption capacity can be regenerated; i.e., the promoted sorbent may be regenerated, recycled and/or reused.

[0050] The treated base sorbents (carbon, non-carbon, or their combination), treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

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[0051] Hereinafter the disclosure may at times discuss the use of carbon base sorbents in further details; however the use of non-carbon base sorbents and a combination of carbon and non-carbon base sorbents is also contemplated to at least the same degree as carbon base sorbents.

[0052] Referring now to Figure 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture in a mercury containing gas, such as a flue gas and/or product gas from gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base sorbent while block 20 illustrates adding a halogen or halide promoter that reacts with the base sorbent to produce a product-promoted sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A to produce a product-promoted sorbent suitable for injection.

[0053] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base sorbent as shown by block 10, adding a halogen or halide promoter that reacts with the base sorbent, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product-promoted sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A to produce a product-promoted sorbent suitable for injection.

[0054] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base sorbent as illustrated at block 10 and adding a halogen or halide promoter and a secondary component to the base sorbent together, with which they react to produce a product-promoted sorbent as illustrated by block 40. As above, in embodiments where vapor additions are made to the base sorbent, no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A to produce a product-promoted sorbent suitable for injection.

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[0055] Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-50 in combination with path 20-50. In this embodiment, a base sorbent as illustrated by block 10 is introduced to the mercury containing gas as illustrated by block 50 while a halogen or halide promoter as illustrated by block 20 is introduced to the mercury containing gas stream. Thus the base sorbent and promoter react at block 50 to produce a product-promoted sorbent. In a similar manner, a secondary component as illustrated by block 30 may be added to the halogen or halide promoter as illustrated by block 20 and introduced into the mercury containing gas as illustrated by block 50. In embodiments where both the halogen or halide promoter and secondary component are added, for example, by vapor, no further steps may be taken. In embodiments where the halogen or halide and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A and/or block 30A.

[0056] Referring still to Figure 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a mercury containing gas stream is treated with product-promoted carbon sorbent prepared as described above.

[0057] In some preferred embodiments, the carbon base sorbent provided may preferably be any of several types, as understood by those skilled in the art. For example, the carbon base sorbent may include powdered activated carbon, granular activated carbon, carbon black, unburned carbon, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product-promoted carbon sorbent, or other types as known in the art.

[0058] In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle size greater than the fly ash in a mercury containing gas, such as a flue gas stream, to be treated.

[0059] In some preferred embodiments, the carbon base sorbent provided may preferably have a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle-size distribution greater than that of the fly ash or entrained ash in a flue gas stream, or other mercury containing gas, to be treated, such that the activated carbon and ash can be separated by physical means.

[0060] In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the carbon base sorbent may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

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[0061] Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

[0062] Referring now to Figure 4, a theory is illustrated developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure 4, a molecular bromine molecule forms a complex with the surface of the base sorbent comprising a high surface area form of a metal oxide. Complexing with bromine can occur at surface and defect sites on the surface of the glassy amorphous tectosilicates by association with the Lewis basic oxygen lining the interstitial cavities and the alkali actions on the surface. Molecular hydrogen bromide or an electrophilic or Lewis acid bromine compound react to form a similar structure. The precedence for this promotion of a metal oxide surface complex with an acidic species is described in a paper by Stark and Klabunde (Klabunde, K.J. Chem. Mater. 1996, 8, 1913-1918) who showed addition of acids, HCl, SO_3, and NO, to a MgO surface to form a surface complex. In US Patent 6,517,423 to Koper et al. the described surface complexes were active for destroying biological agents and toxins. As shown in Figure 4, addition of halogens to a metal oxide surface (A) can form a complex that could be described as a bromide-oxybromide species (B), in which electrophilic reactivity is maintained, owing to the formation of positive charges on the surface. The electrophilic complex formed on the metal oxide base sorbent comprises an active site for oxidation of elemental mercury. Addition of mercury to the complex results in formation of a mercury oxygen bond and, simultaneously, a mercury bromine bond as shown in complex C in Figure 4. Thus the final structure is a stable oxidized Hg form (D) described as a metaloxymercuric bromide.

[0063] In summary, it has now been found that the formation of the new bromide complex with the metal oxide surface increases the surface reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus as the mercury electrons are drawn toward the positive surface oxygen, the halide anion electrons are pushing in from the other side, stabilizing the

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positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus adding HBr or Br_2 to the appropriate metal oxide forms a similar surface bromide complex, in which the positive oxygen oxidizes the mercury with the assistance of the bromide ion.

[0064] In embodiments, a non-carbon base sorbent with Lewis basic sites/groups comprising metal-oxygen-metal structures is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the metal-oxygen-metal structures of the non-carbon base sorbent form metastable complexes, which are responsible for mercury capture via chemisorption. For example, metastable complexes may form between a halogen promoter and inorganic species on a non-carbon base sorbent, wherein inorganic species include sodium (Na), calcium (Ca), magnesium (Mg), aluminum (Al), iron (Fe) compounds, and combinations thereof. In some embodiments, the metastable complexes comprise a dihalogen group, such as Br-Cl, Br-Br, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a halogen atom, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a hydrohalogen group, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metastable complexes comprise a Group V or Group VI halide, complexed with metal-oxygen-metal structures of the base sorbent. In some embodiments, the metal-oxygen-metal structures of the base sorbent are complexed with combinations of the functional groups disclosed herein. Without wishing to be limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these metastable complexes.

[0065] In embodiments, a carbon base sorbent with Lewis acid sites/groups comprising graphene sheets is activated by a promoter of this disclosure, forming a promoted sorbent. The promoter and the grapheme sheets of the carbon base sorbent form stable compounds, which are responsible for mercury capture via chemisorption. Without being limited by a theory, it is believed that mercury capture via chemisorption takes place through the action of mercury oxidation provided by these stable compounds. As one skilled in the art would appreciate, the versatility of chemistry associated with the base sorbent (carbon, non-carbon, or combination thereof) and the promoter of this disclosure enables versatile applications of the promoted sorbent system for mercury

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capture. This is especially advantageous because mercury content in flue gases varies from facility to facility, from operation to operation, and from day to day.

[0066] Examples of non-carbon base sorbents are amorphous forms of tectosilicates that comprise nanoscale cavities lined with Lewis basic oxygen associated with Group I alkali metals and Group II alkaline-earth metals. Such tectosilicates can be found in naturally occurring minerals, including, but not limited to, perlite and pumacite. Examples of non-carbon base sorbents also include amorphous forms of phyllosilicates. It is appreciated that other minerals may be used and also treated chemically and thermally to increase the activity of the base sorbent materials, such as phyllosilicates in the amorphous forms.

[0067] In some embodiments, bentonites are used as non-carbon base sorbents, including sodium bentonite and calcium bentonite. The use of other types of bentonites is contemplated as is known to one skilled in the art. The application of bentonite base sorbents is by introducing them into the flue gas at a location of the mercury capture system wherein the temperature of that location is below 800°C.

[0068] In some embodiments, the base sorbents are treated chemically and/or thermally to increase their activity. For example, perlite as a base sorbent may go through vacuum treatment and then thermal treatment so as to reduce the moisture contained therein, increase its activity, and potentially alter its morphology. Other treatment processes include chemical treatment, such acid treatment and alkaline treatment. These treatment methods may be combined to achieve desired effects as known to one skilled in the art. One of the desired effects is to increase the number of available Lewis acid sites/groups in the carbon base sorbent and/or the number of available Lewis basic sites/groups in the non-carbon base sorbent for subsequent activation via reaction with a promoter disclosed herein.

[0069] Referring now to Figure 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted base sorbents and flue gas mercury reduction in accordance with preferred embodiments of the present invention. In the exemplary embodiment shown, there is provided a base sorbent reservoir 110, a halogen/halide promoter reservoir 120, a secondary component reservoir 130, and an alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the alkali component reservoir 180, flow control devices 208 and 209 can be used independently, together, or not at all. Further, reservoirs 110, 120, 130 and 180 are optional and can be used in any combination, or not at all, whereby the otherwise stored components can be

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introduced into the system by other means either together or independently. Further, the alkali and secondary components may not be used at all within the system, if so desired.

[0070] As shown, reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in Figure 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

[0071] For clarity, single injection points 116 or 119 are shown in Figure 3, although one skilled in the art will understand that multiple injection points and/or locations are within the scope of the present invention. In the embodiment shown, transport line 15 comprises multiple lines allowing for multiple injections and separate and/or combined injections of base sorbent 110 and promoter 120 and/or 130. One mode of operation, by example, comprises providing base sorbent 110 in a common line which is promoted inline "in-flight" using promoter 120 and/or 130 and injected at point 116. Another mode of operation, by example, comprises transport and injection of a base sorbent 110 in a separate line to a point downstream of the injection of promoter 120 and/or 130 in a line at point 116 which is upstream of injection of base sorbent 110, resulting in in-flight preparation at a promoted sorbent within stream 15.

[0072] In the exemplary embodiment shown, an optional optical density measuring device(s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

[0073] Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more ESPs, or other particulate removal devices as are

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known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at multiple locations upstream and/or downstream of 140 when parallel, sequential, or combinations thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142 and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152 and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

[0074] An optional continuous emission monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35 to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

[0075] In operation, as example, promoted sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25 by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury clean flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, and 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, and 209 can also be adjusted manually or by some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

[0076] Referring still to Figure 3, several embodiments are illustrated for preparation and injection of promoted sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base sorbent from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206.

The halogen/halide may be combined and react with the base sorbent according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base sorbent prior to injection point 116 or downstream at point 116. This results in in-flight preparation of a promoted sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with the base sorbent prior to entering transport line 115. Still further, the halogen/halide may be contacted and react with the base sorbent by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebulliated or flueidized bed of base sorbent, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base sorbent in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in Figure 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to Figure 1.

[0077] Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131b and 131c.

[0078] Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with the base sorbent, promoted sorbent, or optional secondary components. Being able to vary on-site the amount of the optional alkali component relative to base sorbent, promoted sorbent, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

[0079] In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base sorbent. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

[0080] In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebulliated or flueidized

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bed of granular or fibrous base sorbent, with the promoted sorbent so produced removed from the top of the bed via gas entrainment for injection.

[0081] In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted sorbent may comprise from about 1 to about 30 g of halogen/halide per 100 g of base sorbent. In some preferred embodiments, the promoted sorbent may comprise a secondary component in concentration of from about 1 to about 15 wt% of the concentration of the halogen/halide component.

[0082] In still other embodiments, the product-promoted sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

[0083] In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

[0084] Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with hot flue gas components leaves little to react with elemental mercury. The atomic elemental halogen form, which includes the flueorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury, but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

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[0085] The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view, therefore, a halide salt-treated sorbent will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen-Promoted Sorbent Characteristics

[0086] The promoted sorbent described here has a very high initial reactivity for oxidizing mercury and therefore, can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the promoted sorbents produced using the inventive technology. The time interval required for the mercury and the promoted sorbents of the present invention to successfully interact in a flue gas duct, with subsequent collection of the mercury on the promoted sorbent and ash, is very short – less than seconds. Clearly, such collection times require the promoted sorbent to have both high capacity and high reactivity toward mercury. The promoted sorbent can be utilized in a very finely powdered form to minimize mass-transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the promoted sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a promoted sorbent containing a halide component formed on and/or within the base sorbent structure that provides a sorbent that is highly active on initial contact with the mercury-contaminated gas stream, which allows for very effective capture of the mercury.

[0087] The inventive sorbents chemically combine bromine species with Lewis acid/basic sites on the base sorbent. For example, x-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus the promoted sorbent produced from halogen and base sorbent does not represent a molecular halogen form, but rather a new chemically modified structure. This phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of

mercury. Thus an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury shown in Figure 2. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

[0088] It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the promoted sorbent, typically exceeding that of both the untreated base sorbent and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

[0089] It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio on-site in order to overcome and optimize for a given set of site conditions.

[0090] The synergy that can be gained when coinjecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e., sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants, thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully

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consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury-binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than AC; thus more of it can be used, still resulting in overall lower costs.

In-Flight Sorbent Preparation

[0091] As stated previously, the halogen promoted sorbent can be readily produced in-flight. This is accomplished by, for example, contacting the vapors of any combination of halogens and, optionally, a second component, in-flight, with base sorbent particles. The particles may be dispersed in a stream of transport air (or other gas, such as the flue gas itself), which also conveys the halogen/halide-promoted sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

[0092] Referring to Figures 5A and 5B, process flow diagrams are shown as examples of the process for mercury removal from a mercury containing gas, such as a flue gas. In an embodiment shown at Figure 5A, gas inlet stream 501 passes through chamber 301 and enters air heater 302 as stream 502; then it exits air heater 302 as stream 503 and passes through particulate control device 303 and enters scrubber 304 as stream 504; finally it exits scrubber 304 as stream 505. As shown, chamber 301 is a boiler, however, one skilled in the art will appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection streams 401, 402, 403 and 404, in addition to stream 501, are multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

[0093] Figure 5B shows an embodiment similar to that of FIG. A, but with the position of the scrubber and particulate control device switched. Specifically, gas inlet stream 501' passes through chamber 301' and enters air heater 302' as stream 502'; then it exits air heater 302' as stream 503' and passes through scrubber 304' and enters particulate control device 303' as stream 504'; finally it exits particulate control device 303' as stream 505'. As shown, chamber 301 is a boiler, however, one skilled in the art will

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appreciate that chamber 301 can also be the combustion chamber of a coal fired boiler, a stand alone combustion chamber or any other chamber in which mercury containing gas is either generated or passed through. Injection stream locations 401', 402', 403' and 404', in addition to stream 501', represent multiple locations wherein promoter, base sorbent, or a combination of promoter and base sorbent may be introduced.

[0094] At each of the aforementioned injection stream locations 401, 401', 402, 402', 403, 403', 404 and 404', 501, 501' multiple injection points are contemplated so that promoter and base sorbent may be injected as a single injection stream or as separate injection streams, as further illustrated in the following exemplary embodiments.

[0095] In an embodiment, a promoter is introduced to chamber 301 at location 401. A base sorbent (carbon, non-carbon, or their combination) is introduced at location 402 upstream of air heater 302. In a further embodiment, a promoter is introduced to at location 402 upstream of air heater 302. A base sorbent (carbon, non-carbon, or their combination) is also introduced at location 402 either as a separate stream or as a mixed single stream with the promoter. In another embodiment, a promoter is introduced at locations 401 and 402. A base sorbent (carbon, non-carbon, or their combination) is introduced at location 402 either as a separate stream or as a mixed single stream with the promoter.

[0096] With the aid of this disclosure, one of ordinary skill in the art will be able to configure the process in many different fashions for mercury removal using the promoted sorbent. All these configurations are considered equivalents of the disclosed process and therefore are within the scope of the claimed invention.

Advantages of On-Site Preparation

[0097] In-flight preparation of the halogen/halide-promoted sorbent on location produces certain advantages. For example, the treatment system can be combined with the base sorbent injection system at the end-use site. With this technique, the halogen/halide is introduced to the base sorbent air (or other gas, including to the flue gas or other mercury containing gas) mixture in a transport line (or flue gas duct part of the base sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.

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- The inventive process uses existing hardware and operation procedures.
- The inventive technology ensures that the sorbent is always fresh and, thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- The inventive process allows rapid on-site tailoring of additive–sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when fuels are changed or loads are reduced, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

[0098] With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide-promoted sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g., bromine) to the base sorbent structure.

Sorbent Injection Location

[0099] Some of the preferred embodiments contemplate the use of a halogen-promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen-promoted sorbent comprise a powdered modified AC prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base AC and/or with the use of a halogen-based sorbent and any other combinations of the sorbent technologies provided in this patent. Other embodiments allow for in-flight preparation of promoted sorbents by using and combining the promoters and base sorbents. Alternatively, embodiments include methods wherein the base sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

[00100] Any of the above embodiments of the halogen/halide-promoted carbon and/or non-carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed, and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon and/or non-carbon itself contrasts with the earlier, more expensive, conventional methods of

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adding a reagent (such as peroxide, gold, triiodide, etc.) to a base sorbent. The halogen/halide-promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in copending, commonly owned PCT Patent Application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT," which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

[00101] Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

EXAMPLES

[00102] To more clearly illustrate the present invention, an example is presented below. This example is intended to be illustrative, and no limitations to the present invention should be drawn or inferred from the example presented herein.

Example 1 – Non-carbon-Promoted Sorbent Tests at Full-Scale Plants

[00103] Full-scale commercial tests were conducted at several coal-burning facilities equipped with ESPs wherein three types of pre-cursers were injected upstream of an ESP at 325°F. In all, more than thirty tests were performed with variations in base sorbent material, base sorbent material injection rates and promoter injection rates. Promoters were halogen-based materials. Base sorbents were clay-based materials such as perlite and pumacite, which are vesicular forms of tectosilicates comprising silicates and aluminate tetrahedra with alkali metals in the interstitual spaces. Each base sorbent was injected upstream from the ESP.

[00104] The flue gas flow rate for the test was approximately 23 million $dsft^3/hr$ with a corresponding mercury flow rate of 0.0097 lbs Hg/hr. Initial mercury concentration in

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the flue gas prior to the introduction of the base sorbent or promoted sorbent was approximately 0.000417 lbs Hg/million dsft^3.

[00105] As shown in Table 1, each base sorbent was injected at three different test rates: about 100 lb/hr ("Low"), about 150 lb/hr ("Ave.") and about 200 lb/hr ("High"). At each test rate, the mercury removal rate was measured both with and without the use of a promoter to show the relative benefit of introducing the promoter into the flue gas stream. For the tests where promoter was injected into the flue gas stream, promoter was injected at about 20 lb/hr for the "Low" tests, at about 25 lb/hr for the "Ave." tests and from about 30 to about 50 lb/hr for the "High" tests. The percent mercury removal for each test was calculated based on measurements taken from the inlet flue gas and the outlet flue gas. The results as shown in Table 1 clearly show a significant improvement in mercury capture when a promoter and base sorbent are injected, as compared to the injection of a base sorbent alone.

Table 1. Test Data for Non Carbon-Promoted Sorbents

Base Sorbent Material	Base Sorbent Injection Rate (lb/hr)			Promoter Injection Rate (lb/hr)			Percent Removal of Mercury (%)		
	Low	Ave.	High	Low	Ave.	High	Low	Ave.	High
Perlite	100	150	200	0	0	0	37	40	43
	100	150	200	20	25	35	55	72	74
Pumacite	100	150	200	0	0	0	25	25	25
	100	150	200	20	25	50	52	60	65
Clay-Based Mix of Silica and Alumina	100	150	200	0	0	0	50	52	54
	100	150	200	20	25	30	58	65	74

[00106] While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

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Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

[00107] The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

[00108] The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

[00109] Although the invention is described herein as a promoted sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

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CLAIMS

What is claimed is:

1. A method for separating mercury from a mercury containing gas comprising:

(a) providing a sorbent material;

(b) providing a halogen or halide promoter;

(c) promoting at least a portion of the sorbent material by chemically reacting the sorbent material with the halogen or halide promoter to form a promoted halogenated sorbent;

(d) chemically reacting elemental mercury in the mercury containing gas with the promoted halogenated sorbent to form a mercury/sorbent chemical composition; and

(e) separating particulates from the mercury containing gas to form a cleaned gas, the particulates including ash and the first mercury/sorbent chemical composition.

2. The method of claim 1, further comprising the step of injecting the sorbent material and the halogen or halide promoter into the mercury containing gas.

3. The method of claim 2, wherein said halogen or halide promoter and the sorbent material are injected into the mercury containing gas at the same location.

4. The method of claim 2, wherein said halogen or halide promoter and the sorbent material are injected into the mercury containing gas at separate locations.

5. The method of claim 4, wherein said halogen or halide promoter is injected into the mercury-containing gas upstream of the injection of said sorbent.

6. The method of claim 5, wherein said halogen or halide promoter is injected into a combustion chamber that produces a mercury-containing gas, and the sorbent is injected downstream of the combustion chamber.

7. The method of claim 6, wherein said halogen or halide promoter is additionally

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injected downstream of the combustion chamber.

8. The method of claim 6, wherein said combustion chamber is a boiler and the mercury-containing gas is a flue gas.

9. The method of claim 3, wherein said halogen or halide promoter and sorbent are injected downstream of a chamber that produces a mercury-containing gas.

10. The method of claim 9, wherein said chamber is a boiler and the mercury-containing gas is a flue gas.

11. The method of claim 2, wherein the rate at which said sorbent is injected or the rate at which said promoter is injected or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially a desired level.

12. The method of claim 1, wherein said sorbent comprises carbon based materials.

13. The method of claim 12, wherein said sorbent comprises activated carbon.

14. The method of claim 1, wherein said sorbent is selected from the group consisting of non-carbon based materials, including porous felsic materials, vesicular felsic materials, porous basaltic materials, vesicular basaltic materials, clay-based compounds, alkaline compounds, calcium hydroxide compounds, sodium acetate compounds, bicarbonate compounds, and combinations thereof.

15. The method of claim 13, wherein said sorbent is an activated carbon base material that reacts with oxidized mercury in the mercury-containing gas to form a second mercury/sorbent chemical composition.

16. The method of claim 14, wherein said sorbent is a non-carbon base material that reacts with oxidized mercury in the mercury-containing gas to form a second mercury/sorbent chemical composition.

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17. The method of claim 1, wherein said sorbent is a non-carbon material that comprises Lewis basic groups.

18. The method of claim 1, wherein said sorbent is a carbon material that comprises Lewis acid groups.

19. The method of claim 1, wherein said sorbent includes both a carbon material and a non-carbon material.

20. The method of claim 14, wherein said non-carbon material comprises amorphous forms of tectosilicates comprising nanoscale cavities lined with Lewis basic oxygen associated with alkaline-earth metals.

21. The method of claim 20, wherein said alkaline-earth metals comprise Group I and Group II alkaline-earth metals.

22. The method of claim 13 wherein said non-carbon material comprises amorphous forms of phyllosilicates comprising nanoscale cavities lined with Lewis basic oxygen.

23. The method of claim 1, wherein said promoted sorbent comprises metastable complexes formed between said promoter and inorganic species on a non-carbon sorbent.

24. The method of claim 23 wherein said inorganic species is selected from the group consisting of sodium compounds, calcium compounds, magnesium compounds, aluminum compounds, iron compounds, and combinations thereof.

25. The method of claim 1, wherein said promoted sorbent comprises metastable complexes formed between said promoter and metal-oxygen-metal structures on a non-carbon sorbent.

26. The method of claim 25, wherein said promoter after being complexed with the metal-oxygen-metal structures is in the form selected from the group consisting of a dihalogen group, a halogen atom, a hydrohalogen group, a Group V halide, a Group VI halide, and combinations thereof.

27. The method of claim 1, wherein said promoted sorbent comprises activated Lewis basic groups or activated Lewis acid groups or combination thereof.

28. The method of claim 1, wherein said interaction between promoted sorbent and said mercury-containing gas stream comprises:

mercury diffusing from the gas phase onto said promoted sorbent surface; and

reacting with activated Lewis basic groups or activated Lewis acid groups or combination thereof to cause chemisorption on the sorbent surface.

29. The method of claim 1 further comprising pretreating said sorbent to increase the number of Lewis basic groups or Lewis acid groups or combination thereof on said sorbent.

30. The method of claim 29, wherein pretreating said sorbent comprises chemical treatment, thermal treatment, vacuum treatment, and combinations thereof.

31. The method of claim 30, wherein said chemical treatment comprises acid treatment and alkaline treatment.

32. The method of claim 1 further comprising introducing an alkali component into the mercury-containing gas.

33. The method of claim 1, wherein a carbon sorbent is reacted with said promoter to produce a promoted carbon sorbent.

34. The method of claim 33, wherein said carbon sorbent or said promoter or combination thereof are introduced into the mercury-containing gas at one or more locations.

35. The method of claim 34, wherein the rate at which said carbon sorbent is introduced or the rate at which said promoter is introduced or combination thereof is adjusted according to a monitored mercury content in the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially a desired level.

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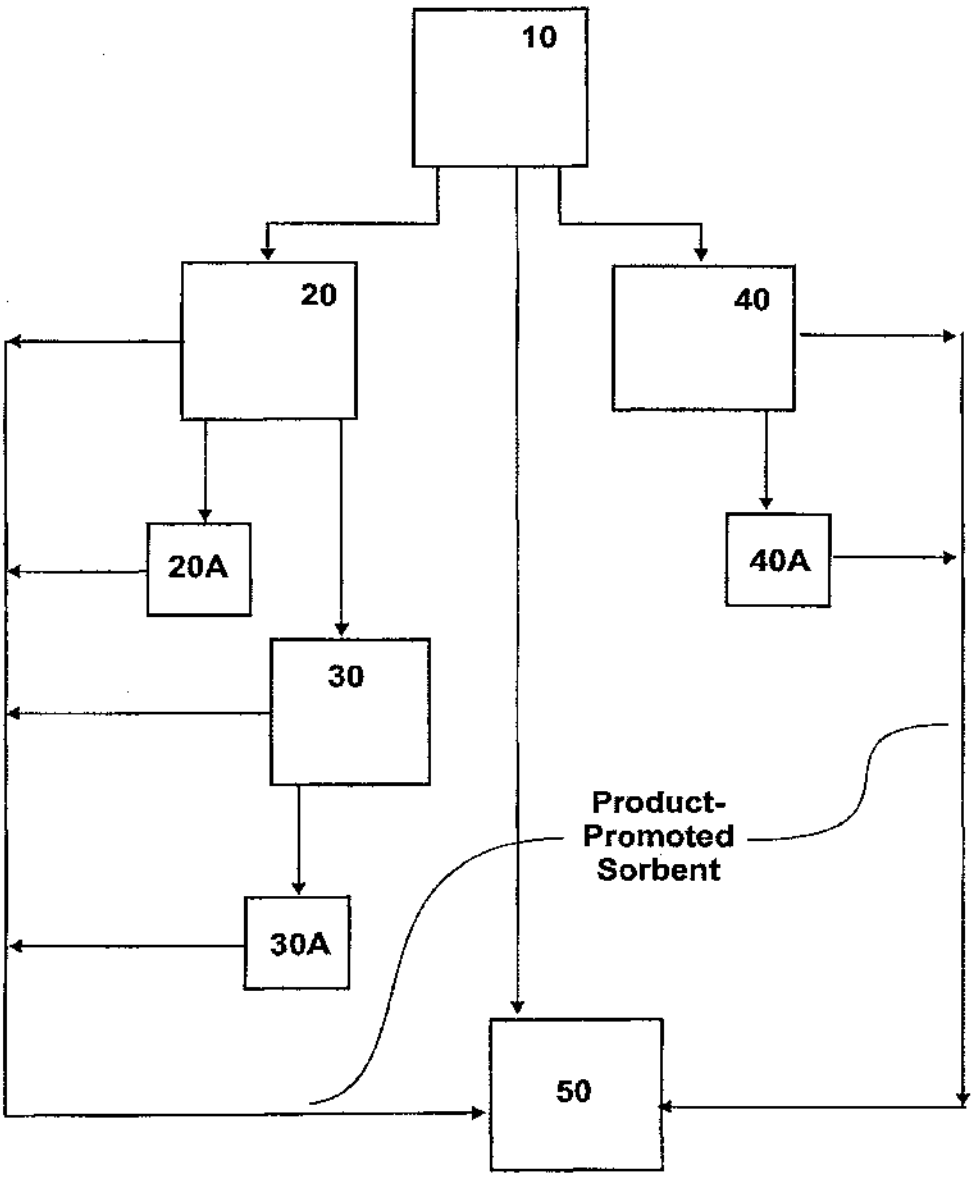


FIG. 1

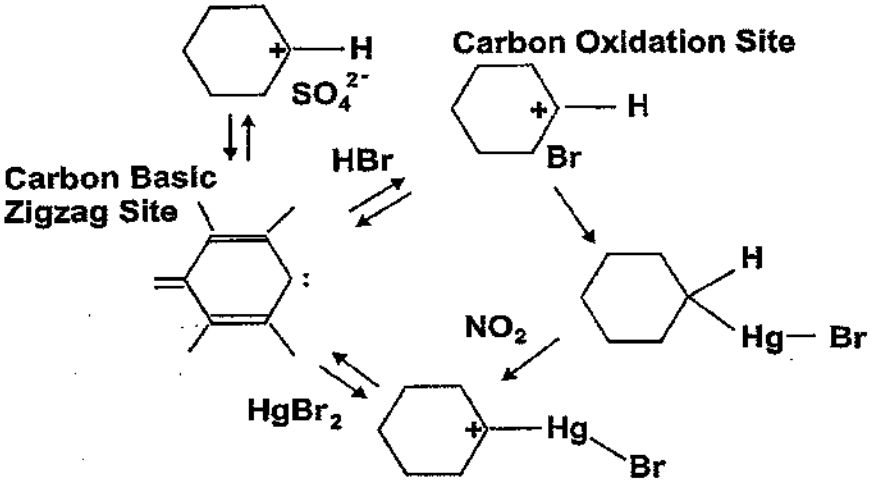

Carbon Oxidation Site
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SO_4^{2-}
HBr
Carbon Basic
Zigzag Site
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Br
H
Hg— Br
NO_2
$HgBr_2$
Hg
Br

FIG. 2

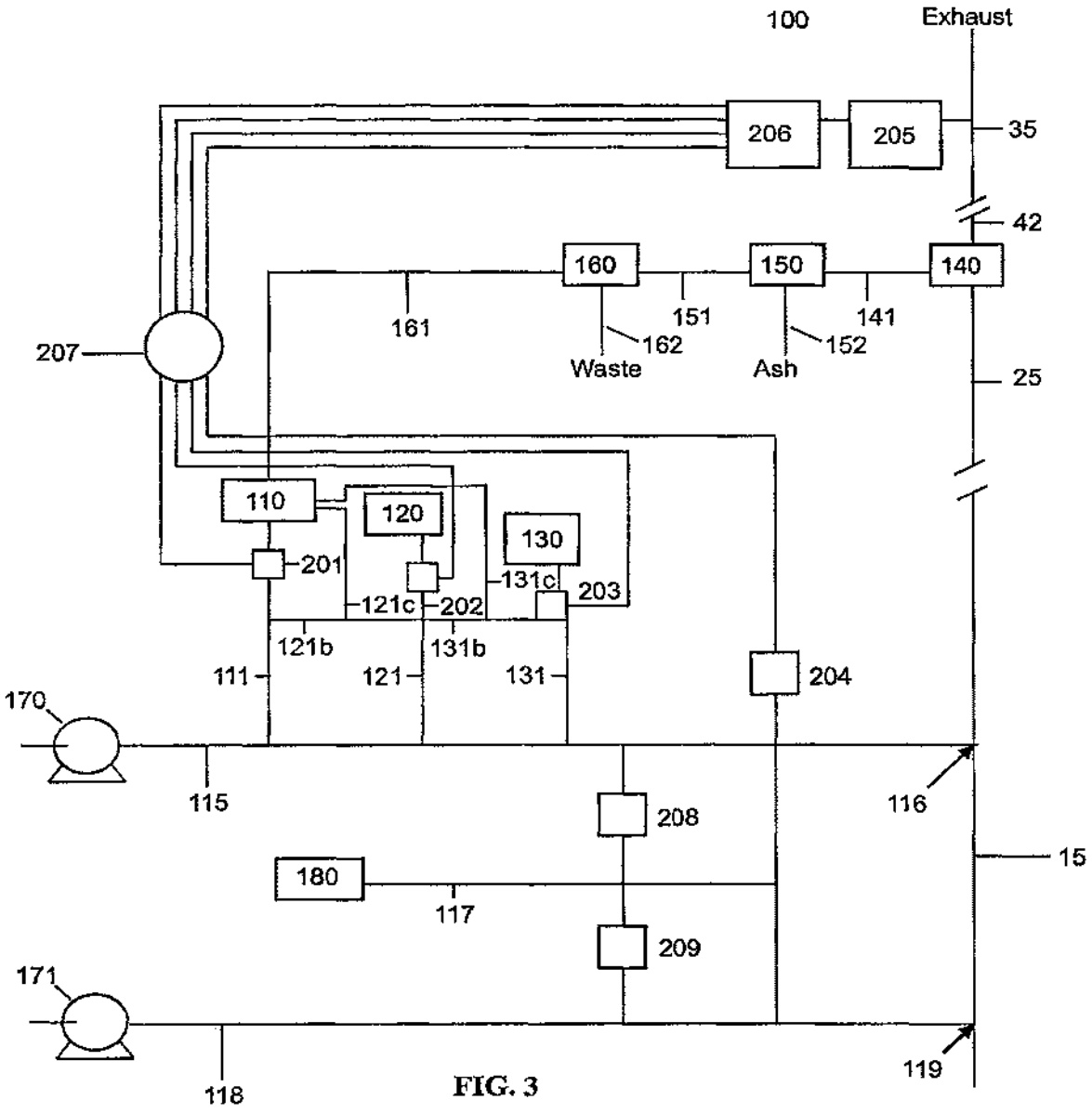

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Exhaust
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205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
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201
131c
203
121c
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FIG. 3

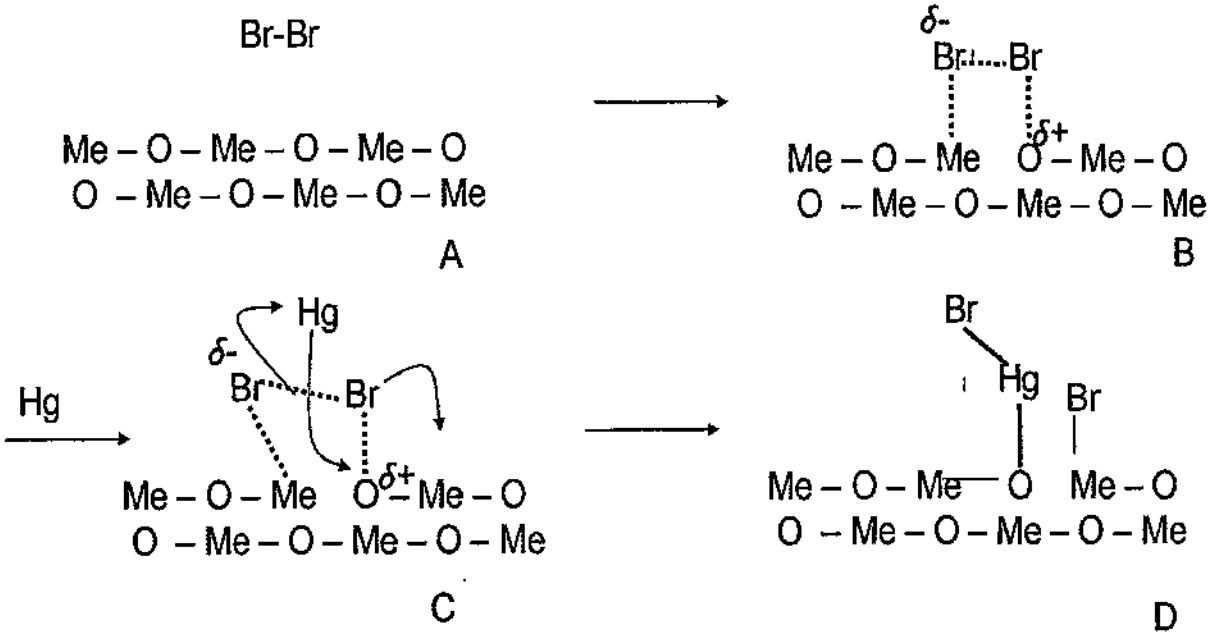

Br-Br
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O – Me – O – Me – O – Me
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δ-
Br
Br
δ+
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B
Hg
Hg
δ-
Br
Br
δ+
Me – O – Me O – Me – O
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D

FIG. 4

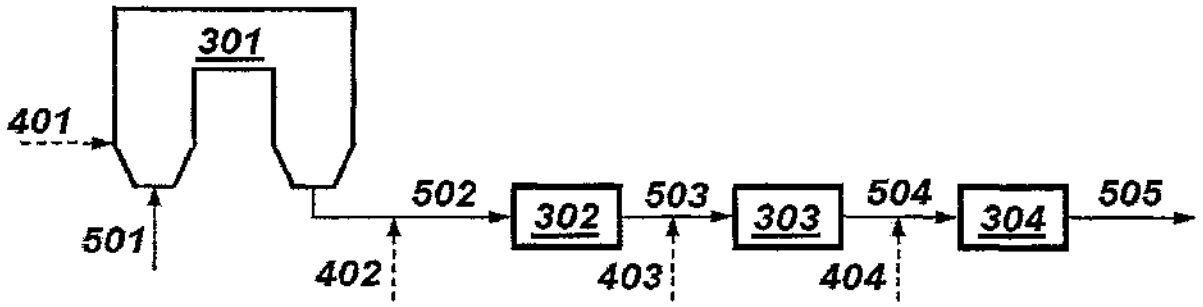

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FIG. 5A

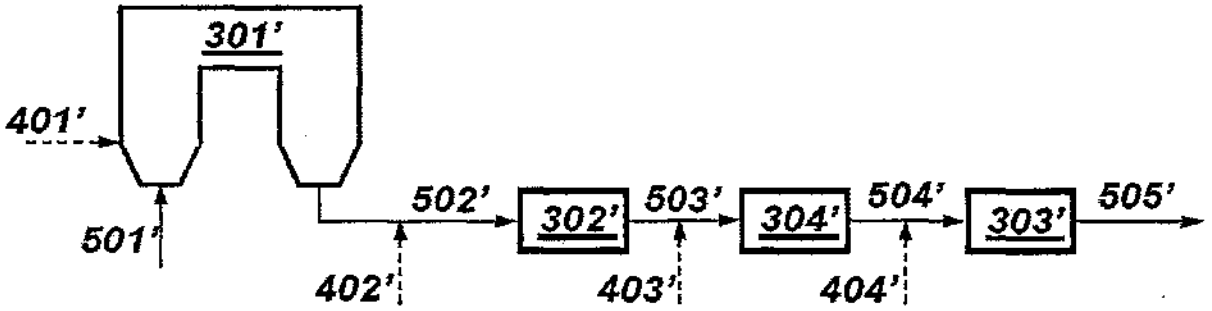

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FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/022807

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/02(2006.01)i, B01D 53/64(2006.01)i, F23J 15/00(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)
B01D 53/02; C01B 31/08; B01J 8/00; B01J 20/00

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: sorbent, mercury, flue gas, halogen promoter

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009-0062119 A1 (OLSON EDWIN S. et al.) 05 March 2009 See the abstract, fig. 1-10, Paragraph [10] ~ Paragraph [134], whole claims	1-35
A	US 2006-0204428 A1 (CHIEN-CHUNG CHAO et al.) 14 September 2006 See the abstract, Paragraph [33] ~ Paragraph [191]	1-35
A	US 2007-0234902 A1 (DAVID FAIR et al.) 11 October 2007 See the whole document	1-35

☐ 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 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
13 SEPTEMBER 2010 (13.09.2010)	**13 SEPTEMBER 2010 (13.09.2010)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	JO Soo Ik Telephone No. 82-42-481-5893

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2010/022807

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009-0062119 A1	05.03.2009	None	
US 2006-0204418 A1	14.09.2006	CA 2600876-A1	21.09.2006
		CN 101175692 A0	07.05.2008
		EP 1866245 A2	19.12.2007
		KR 10-2007-0113287 A	28.11.2007
		MX 2007011233 A	08.11.2007
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		WO 2006-099291 A3	21.09.2006
US 2007 0234902 A1	11.10.2007	WO 2007 112248 A2	04.10.2007
		WO 2007-112248 A3	13.12.2007
		WO 2007-112248 A3	04.10.2007

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17 April 2013 (17.04.2013)

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(74) Agents: **MADDEN, Robert, B.** et al.; Schwegman, Lundberg & Woessner, P.A., P.O. Box 2938, Minneapolis, Minnesota 55402 (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, 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,

[Continued on next page]

(54) Title: CARBON NANOCOMPOSITE SORBENT AND METHODS OF USING THE SAME FOR SEPARATION OF ONE OR MORE MATERIALS FROM A GAS STREAM

(57) Abstract: The present invention relates to carbon nanocomposite sorbents. The present invention provides carbon nanocomposite sorbents, methods for making the same, and methods for separation of a pollutant from a gas that includes that pollutant. Various embodiments provide a method for reducing the mercury content of a mercury-containing gas.

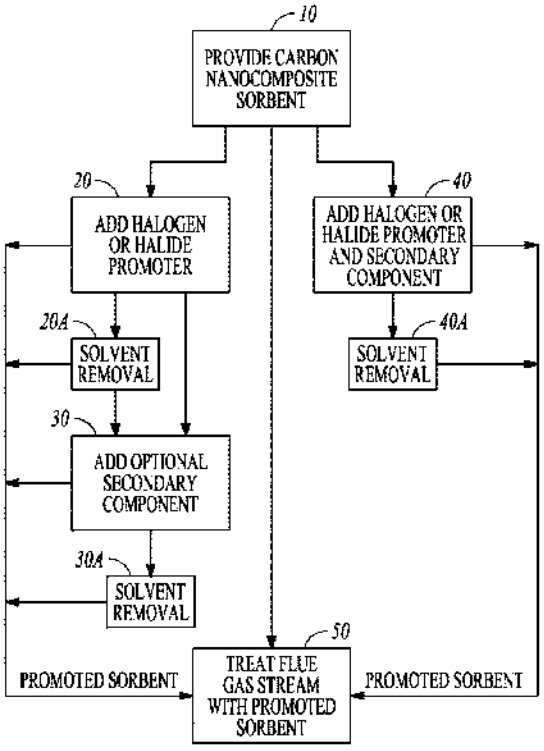


FIG. 1

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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).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

CARBON NANOCOMPOSITE SORBENT AND METHODS OF USING THE SAME FOR SEPARATION OF ONE OR MORE MATERIALS FROM A GAS STREAM

CLAIM OF PRIORITY

[0001] This patent application claims the benefit of priority of U.S. Patent Application Serial Number 13/453,274 filed on April 23, 2012, which is hereby incorporated by reference in its entirety.

STATEMENT OF GOVERNMENT SUPPORT

[0002] This invention was made with government support awarded by the U.S. Department of Energy (DOE) under DOE Cooperative Agreement Number DE-FC26-08NT43291 entitled "EERC-DOE Joint Program on Research and Development for Fossil Energy-Related Resources"; Subtask 4.8 entitled "Fate and Control of Mercury and Trace Elements"; EERC Fund Number 14990. The U.S. government has certain rights in this invention.

BACKGROUND OF THE INVENTION

[0003] Mercury (Hg) emissions have become a health and environmental concern because of their toxicity and ability to bioaccumulate. The U.S. Environmental Protection Agency (EPA) has issued regulations for the control of Hg emissions from waste-to-energy, cement production, and coal-fired power plants. Mercury in flue gas from industrial sources (e.g., power plants) can be captured by injection of sorbents such as activated carbon, which can then be removed by particulate collection devices. The amount of standard sorbents (e.g., activated carbon) needed to serve the market is large. Standard sorbents are not always effective and become more expensive as injection rates increase.

[0004] A nanocomposite is a multiphase solid material in which one of the phases has at least one dimension of less than about 1000 nm or in which less than an about 1000 nm repeat distance separates the phases that make up the material. Nanocomposites in which one or more of the phases is a bulk matrix

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and one or more other materials is a nanodimensional phase can have unique properties, with the mechanical, electrical, thermal, optical, chemical, or catalytic properties of the nanocomposite material differing significantly from that of the individual component materials.

[0005] The first examples of carbon nanocomposites were prepared by intercalating monomers into interlamellar spaces in clays, polymerizing the monomer, and carbonizing the polymer. The minimum thickness of the carbon layer was 1.1 nm (Kyotani-1988). In the next two decades, a variety of monomers were employed with several clays and other porous support materials. In some cases, the inorganic part of the composite was removed to study the graphite-like carbon structures. In 2004, Bakandritsas et al. produced carbon-clay nanocomposites using sucrose as the carbon source (Bakandritsas-2004). The thickness of each layer was about 1 nm and 0.4 nm for the clay and graphene layers, respectively. Later, this group described the use of these for adsorption of gases (CO_2, CH_4, N_2) and organic solutes in aqueous solutions (Bakandritsas-2005). Because they can be easily shaped, have high surface-areas, and conduct electricity, carbon-clay nanocomposites from sucrose were used to produce electrodes and sensors (Darder-2005, Gomez-Aviles-2007, Fernandez-Saavedra-2008, Gomez-Aviles-2010). The porous carbon-clay nanocomposites from sucrose also have been utilized for catalyst supports (Nguyen-Thanh-2006a. Nguyen-Thanh-2006b, Ikeue-2008).

[0006] Several applications of composite materials for adsorption of metal ions such as Hg^{2+} have been described in the literature. These include the following materials: chitosan-coated ceramic (Boddu-2002), polypyrrole film on clay (Eisazadeh-2007), mercapto-functionalized polysiloxane film on diatoms (Wang-2007), polyaniline film on ash (Ghorbani-2011), and polyaniline composite with humic acid (Zhang). None of these is a carbon nanocomposite; rather, they are typically a polymer film deposited on a support and suffer limitations from stability and difficulty of recycling and processing.

[0007] Separation of elemental or oxidized mercury from a gas stream has been conducted with several types of nanocomposites made with non-carbon materials. A SiO_2-TiO_2 nanocomposite was used for Hg capture under UV radiation (Li-2008). This technology suffers from the difficulty of having to

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effectively irradiate combustion effluent containing fine particulate. A magnetite- and Ag-impregnated zeolite nanocomposite was described (Dong-2009). It is suspected that the Ag nanocomposite represents a significant environment risk in itself, as well as being a high-cost sorbent. Capture of Hg in flue gas with a CeO_2-WO_3/TiO_2 nanocomposite was reported (Wan-2011). These non-carbon sorbents have higher cost and slower kinetics than desirable.

SUMMARY OF THE INVENTION

[0008] In various embodiments, the present invention provides a method for separating a material from a gas that includes the material. In some embodiments, the material can be a pollutant or an unwanted constituent of the gas. The method includes providing or obtaining a carbon nanocomposite sorbent. The method also includes contacting at least some of the material with the sorbent to form a material-sorbent composition. The method also includes separating at least some of the material-sorbent composition from the material-containing gas. The separation gives a separated or partially separated gas.

[0009] In various embodiments, the present invention provides a method for reducing the pollutant content of a pollutant-containing gas. The method includes providing or obtaining a carbon nanocomposite sorbent. The method includes providing or obtaining a halogen or halide promoter. The method includes promoting at least a portion of the sorbent material. The promoting of the sorbent material includes chemically reacting the portion of the sorbent material with the halogen or halide promoter. The promoting of the sorbent material gives a promoted sorbent. The method includes contacting at least part of the promoted sorbent with the pollutant. In some embodiments, the method can also include contacting the pollutant with sorbent that is unpromoted. Contacting the promoted sorbent with the pollutant forms a pollutant-sorbent composition. The method also includes separating at least some of the pollutant-sorbent composition. The separation gives a cleaned gas, having a lower pollutant content than the starting material (e.g., uncleaned) pollutant-containing gas. In various embodiments, the pollutant can be mercury.

[0010] In various embodiments, the present invention provides a method of forming a carbon nanocomposite material. The method includes obtaining or

providing a carbon precursor material. The method includes providing or obtaining a substrate material. The method includes contacting the carbon precursor and the substrate material to provide a nanocomposite starting material. The method also includes heating the nanocomposite starting material to provide the carbon nanocomposite sorbent. In various embodiments, the present invention provides the carbon nanocomposite that is generated by the method. In some examples, the present invention provides the nanocomposite in combination with various materials the nanocomposite encounters during performance of the method, such as the nanocomposite in combination with mercury, with oxidized mercury, or with a mercury-containing gas. In some embodiments, the method can include adding a halogen or halide promoter and allowing the promoter to react with the sorbent to form a promoted carbon nanocomposite sorbent.

[0011] Surprisingly, despite activated carbons being routinely used to capture pollutants in flue gas streams, carbon nanocomposites have not been used before for gas-phase mercury capture. Traditional thinking is that an excess of inorganic support such as clay in the carbon nanocomposite hinders the sorption of the pollutant on the carbon. However, surprisingly, in accord with some embodiments of the present invention, the non-carbon parts can enhance the sorption of pollutant on the proximate carbon graphene layer. The basal planes of the carbon portions of the nanocomposites are indeed largely hindered within carbon nanocomposite structures. However, the carbon edge structures are very well exposed in the structures, and these are the part of the carbon that is active for pollutant capture (e.g., mercury, selenium, arsenic, and the like). As described herein, the graphene edge structures can be promoted by reaction with a halogen, hydrogen halide, or ammonium halide to produce a carbocation edge structure that is highly reactive for oxidation and capture of pollutants such as mercury.

[0012] Since support materials such as clays are by themselves inert, the promotion of oxidation of pollutants by the carbon layer caused by certain support materials is also unexpected. However, in accord with some embodiments of the present invention, a polyanionic aluminosilicate layer (e.g., from clay) can stabilize the development of cationic sites on the proximate

graphene carbon structures that are essential for oxidation of pollutants such as mercury. The same stabilizing effect can occur with a carbon-diatom (silicate) nanocomposite or other nanocomposites composed of graphene layers and polar inorganic structures.

[0013] In embodiments that include a nanocomposite that is promoted via hydrogen halide compound obtained from degradation or reaction of the corresponding ammonium halide, another advantageous role for the inorganic portion can be in providing a binding site for the ammonia that is released from either the decomposition or reaction of the ammonium salt. The bound ammonia forms a complex with basic character that reacts with SO_2 in the flue gas and prevents their interference with the capture on the edge structure of pollutants such as mercury.

[0014] In another advantage of inorganic support in embodiments that include clay as the support, the clay is stabilized to dispersion in an aqueous medium. Clays are usually difficult to filter or separate from an aqueous medium, but in the form of a nanocomposite with carbon, the material can be easily separated from an aqueous medium by filtration. Thus, the nanocomposite can be conveniently utilized to capture mercury in an aqueous environment.

[0015] The present invention advantageously can separate a material (e.g., a pollutant) from a gas that includes that material more efficiently than other methods. The present invention provides certain advantages over other methods and materials for the removal of mercury from mercury-containing gas. The method and materials of various embodiments of the present invention can capture and remove mercury from a gas more efficiently than other methods of mercury removal. The method and materials of various embodiments of the present invention can operate more efficiently than other methods of mercury removal. For example, the method and materials of various embodiments can remove a given amount of mercury for a smaller amount of financial expenditure, as compared to other methods. For example, the method and materials of various embodiments can remove a larger amount of mercury for a given mass of carbon, as compared to other methods of removing mercury, including as compared to other methods of removing mercury that include a carbon sorbent. Thus, the method and materials of various embodiments can

result in the use of less sorbent material (e.g., less carbon overall), as well as the disposal of less used sorbent material, than other methods of mercury removal.

[0016] In various embodiments, the present invention provides a method for reducing the mercury content of a mercury-containing gas. The method includes providing or obtaining a carbon nanocomposite sorbent. The carbon nanocomposite sorbent is made by steps including providing or obtaining a carbon precursor and providing or obtaining a substrate material. The steps also include contacting the carbon precursor and the substrate material. The contacting provides a nanocomposite starting material. The steps also include heating the nanocomposite starting material. The heating provides the carbon nanocomposite sorbent. The method for reducing mercury content of the mercury-containing gas also includes providing or obtaining a halogen or halide promoter. The method includes promoting at least a portion of the sorbent material. The promoting of the sorbent material includes chemically reacting the portion of the sorbent material with the halogen or halide promoter. The promoting of the sorbent material gives a promoted sorbent. The method includes contacting at least part of the promoted sorbent with the mercury. Contacting the promoted sorbent with the mercury forms a mercury-sorbent composition. The method also includes separating at least some of the mercury-sorbent composition from the gas. The separation gives a cleaned gas, having a lower mercury content than the uncleaned gas.

[0017] In various embodiments, the present invention provides a method of making a carbon nanocomposite sorbent. The method includes providing or obtaining a carbon precursor. The method includes providing or obtaining a substrate material. The method includes contacting the carbon precursor and the substrate material. Contacting the carbon precursor and the substrate material provides a nanocomposite starting material. The method also includes heating the nanocomposite starting material. Heating the nanocomposite starting material provides the carbon nanocomposite sorbent.

BRIEF DESCRIPTION OF THE FIGURES

[0018] In the drawings, which are not necessarily drawn to scale, like numerals describe substantially similar components throughout the several

views. Like numerals having different letter suffixes represent different instances of substantially similar components. The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.

[0019] FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents, in accordance with various embodiments.

[0020] FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury, in accordance with various embodiments.

[0021] FIGS. 3A and 3B schematically illustrate preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases (e.g. from combustion) and/or product gases from a gasification system, in accordance with various embodiments.

[0022] FIG. 4 illustrates particulate test combustor (PTC) results for NanoG-CM testing, in accordance with various embodiments.

[0023] FIG. 5 illustrates PTC results for NanoG-CM testing, in accordance with various embodiments.

[0024] FIG. 6 illustrates model results for in-flight mercury capture with a composite sorbent in a high-sulfur flue gas, in accordance with various embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Reference will now be made in detail to certain claims of the disclosed subject matter, examples of which are illustrated in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that they are not intended to limit the disclosed subject matter to those claims. On the contrary, the disclosed subject matter is intended to cover all alternatives, modifications, and equivalents, which can be included within the scope of the presently disclosed subject matter as defined by the claims.

[0026] References in the specification to "one embodiment," "an embodiment," "an example embodiment," etc., indicate that the embodiment described can include a particular feature, structure, or characteristic, but every

embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to effect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

[0027] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also the individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range.

[0028] In this document, the terms "a," "an," or "the" are used to include one or more than one unless the context clearly dictates otherwise. The term "or" is used to refer to a nonexclusive "or" unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. Furthermore, all publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0029] In the methods of manufacturing described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited.

[0030] Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

Definitions

[0031] The term "about" can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range. When a range or a list of sequential values is given, unless otherwise specified, any value within the range or any value between the given sequential values is also disclosed.

[0032] The term "hydrocarbon" as used herein refers to a functional group or molecule that includes carbon and hydrogen atoms. The term can also refer to a functional group or molecule that normally includes both carbon and hydrogen atoms but wherein all the hydrogen atoms are substituted with other functional groups.

[0033] The term "pore" as used herein refers to a depression, slit, or hole of any size or shape in a solid object. A pore can run all the way through an object or partially through the object. A pore can intersect other pores.

[0034] The term "solvent" as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Nonlimiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

[0035] The term "air" as used herein refers to a mixture of gases with a composition approximately identical to the native composition of gases taken from the atmosphere, generally at ground level. In some examples, air is taken from the ambient surroundings. Air has a composition that includes approximately 78% nitrogen, 21% oxygen, 1% argon, and 0.04% carbon dioxide, as well as small amounts of other gases.

[0036] The term "room temperature" as used herein refers to ambient

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temperature, which can be, for example, between about 15°C and about 28°C.

[0037] As used herein, "substantially" refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

[0038] As used herein, "nanocomposite" refers to a multiphase solid material in which one of the phases has at least one dimension of less than about 1000 nm or in which less than an about 1000 nm repeat distance separates at least some of the phases that make up the material. In some embodiments, one of the phases has at least one dimension in the range of about 1 nm - 1000 nm or in which an about 1 - 1000 nm repeat distance separates at least some of the phases that make up the material; in other embodiments, the lower limit of the range can be less than about 1 nm.

[0039] As used herein, "phase" refers to a region of space throughout which all physical properties of a material are essentially uniform, such as physical state, structure, and chemistry. For example, a liquid and a gaseous state can be two different phases. For example, a carbon material distributed on a substrate can be two different phases. For example, a carbon material distributed on a porous substrate can be two different phases.

[0040] As used herein, "mineral" refers to a naturally occurring solid chemical substance formed through biogeochemical processes, having, for example, characteristic chemical composition, highly ordered atomic structure, and specific physical properties.

Description

[0041] Various embodiments of the present invention provide methods and materials for the separation of a material from a gas. In some embodiments, the material can be a pollutant or an undesired constituent. In other embodiments, the material can be any suitable material. The gas includes the material; for example, the material can be dissolved or suspended in the gas. The material includes a carbon nanocomposite sorbent. The method includes providing or obtaining the carbon nanocomposite sorbent. The method includes contacting at least some of the material in the gas with the sorbent to form a material-sorbent composition. The method also includes separating particulates

from the gas. The particulates include at least some of the material-sorbent composition. The separating gives a separated gas having a lower amount of the material therein than the starting material gas. Herein many specific examples of embodiments are given wherein the material separated is mercury, wherein the carbon nanocomposite sorbent is treated (e.g., promoted) with halides or halogens, or wherein the carbon nanocomposite sorbent is treated with other materials. However, one of ordinary skill in the art will extrapolate from the examples and appreciate that embodiments encompass separation of any suitable material (such as, for example, any suitable pollutant, e.g., arsenic, selenium, and the like) from a gas using any suitable carbon nanocomposite material.

[0042] In various embodiments, the material separated from the gas is a pollutant (e.g., an unwanted or undesirable constituent), and the material is desired to be removed from the gas to purify the gas. The pollutant can include mercury. The pollutant can include elemental mercury. The pollutant can include oxidized mercury. In various embodiments, the method can include providing a promoter. The promoter can be allowed to chemically react with at least a portion of the sorbent material, forming a promoted sorbent. The sorbent that contacts the pollutant can include the promoted sorbent. In various embodiments, the promoter can be a halogen or halide promoter.

Reducing the Mercury Content of a Mercury-Containing Gas

[0043] In various embodiments, the present invention provides methods and materials for reducing the mercury content of a mercury-containing gas. The method includes providing or obtaining a carbon nanocomposite sorbent. The method can include providing or obtaining a halogen or halide promoter. The method can include promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent. The method includes contacting at least part of the promoted sorbent with the mercury to form a mercury-sorbent composition. In various embodiments, the sorbent contacted with the mercury can also include unpromoted sorbent. The method also includes separating at least some of the mercury-sorbent composition from the mercury-containing gas. The separation gives a cleaned gas having a lower mercury content than the

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starting material gas. The mercury in the mercury-containing gas can be any suitable form of mercury, such as, for example, elemental mercury. The mercury can be suspended or dissolved in the gas. In some embodiments, the promoter can be HBr or NH_4Br, and in some examples, the HBr can be provided via degradation or reaction of ammonium bromide, NH_4Br. In some embodiments, the promoter (e.g., HBr) or promoter precursor (e.g., NH_4Br) can be injected at an injection rate in the flue gas separately from the carbon nanocomposite sorbent or with the carbon nanocomposite sorbent (e.g., can be applied to the sorbent pre-injection).

Carbon Nanocomposite Sorbent

[0044] The methods provided by embodiments of the present invention use a carbon nanocomposite sorbent to remove a material from a gas, for example, to remove mercury from a mercury-containing gas. Nanocomposites are composed of two of more phases such that the phases are intimately connected to each other at nanoscale dimensions (e.g., 1000 nm or less). When these nanocomposites are highly porous, especially microporous or nanoporous, the intimate connectivity of the two nanocomposites can result in high surface-areas as well as correspondingly high catalytic activities. This can especially be the case when a catalytically active material, such as certain forms of carbon, is dispersed on a bulk substrate having a high surface-area. Carbon nanocomposites can include a thin layer of graphene sheet coated on or intercalated into an inorganic support.

[0045] In some embodiments, the carbon nanocomposite sorbent can be about 50% or less carbon, or about 3 wt% to about 50 wt% carbon, or about 5 wt% to about 10 wt% carbon. In some embodiments, the carbon nanocomposite sorbent can be about 1 wt% to about 99.5 wt% bulk substrate, or about 50 wt% to about 97 wt% bulk substrate, or about 90 wt% to about 95 wt% bulk substrate (e.g., diatomaceous earth, smectite clays, and the like).

[0046] The nanocomposite of the present invention can be any suitable carbon nanocomposite. In some examples, the nanocomposite can be a suitable form of carbon distributed on a suitably porous or suitably high surface-area substrate. The nanocomposite can be produced or can be commercially obtained.

In some embodiments, the nanocomposite is commercially obtained, and further processing steps may be required to suitably activate the carbon for separation of the material, such as separation of the mercury. Further processing steps to suitably activate the nanocomposite can include treatment with heat (e.g., calcining), treatment with base, treatment with a halide or halogen (e.g., promoting), or combinations thereof. For example, in some embodiments, treatment of the nanocomposite with a halide or halogen can promote the nanocomposite to form active sites in the nanocomposite which can transform mercury from elemental mercury into oxidized mercury (e.g., mercury oxide). In some embodiments, no promotion of the nanocomposite is used. For example, in some embodiments, treatment of the nanocomposite with an acid or base can prepare the nanocomposite for promotion using a halide or halogen or can prepare the nanocomposite such that suitable reactivity is obtained. In other embodiments, no treatment with acid or base is used prior to promotion using a halide or halogen or prior to using the sorbent to remove mercury or other materials from the gas.

[0047] The method can include contacting at least part of the nanocomposite sorbent with the material in the gas, such as mercury, to form a composition, such as a mercury-sorbent composition. The present invention is not dependent on any particular mechanism of action; so long as the material is removed from the gas using the carbon nanocomposite sorbent, the method is encompassed as an embodiment of the present invention. In some embodiments, the mercury is absorbed in its elemental form by the sorbent; the mercury-sorbent composition can include the sorbent and the elemental form of mercury. In some embodiments, the mercury is converted by the sorbent via a chemical reaction, such as oxidation, such that the mercury from the gas is transformed into an oxide of mercury (e.g., HgO); the mercury-sorbent composition can include the sorbent and a transformed form of the mercury such as a mercury oxide. In some embodiments, the mercury-sorbent composition can include a combination of elemental mercury and transformed mercury, such as mercury oxide. In some examples, the absorbing of elemental mercury or the transformation of mercury can modify the sorbent, such that the sorbent is at least slightly different after the composition is formed; e.g., after transformation

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of a particular atom of mercury to mercury oxide, the active location of the sorbent that caused the transformation can be unreactive or less reactive.

[0048] In some examples, elemental mercury or transformed mercury can remain absorbed to the sorbent until the mercury-sorbent composition has been removed in a later separation step. For example, elemental mercury or transformed mercury can be absorbed, or reacted and absorbed, into or onto the sorbent composition, such that at least about 1 wt%, 3 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%, 99.9 wt%, 99.99 wt%, or about 99.999 wt% or more of the mercury in the mercury-containing gas stream is absorbed, or reacted and absorbed, into or onto the sorbent composition. In some embodiments, elemental mercury or transformed mercury can be released from the mercury-sorbent composition; for example, less than about 1 wt%, 3 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, or less than about 99 wt% of the mercury can be released from the mercury-sorbent composition prior to separation of the mercury-sorbent composition from the gas. In some examples, the majority of absorbed elemental or transformed mercury can remain part of the mercury-sorbent composition until the mercury-sorbent composition is removed in a later separation step. In some examples, transformed mercury that is released from the mercury-sorbent composition can be later removed from the gas via the separation step. In some examples, elemental or transformed mercury that has been released from the mercury-sorbent composition can contact carbon nanocomposite sorbent to form a mercury-sorbent composition, to be removed later via the separation step.

[0049] In various embodiments, the carbon nanocomposite sorbent includes binding sites that bind with mercury in the mercury-containing gas. In some examples, the sorbent material includes carbon that is reacted or impregnated with halogens or halides to form mercury binding sites in the promoted sorbent. In some examples, the sorbent material can include carbon that is activated at least in part by treatment with a base, wherein the base-activated carbon can react or become impregnated with halogens, hydrogen halides, and Group V or VI halides to form mercury-binding sites in the promoted sorbent. In some examples, the biding sites in the carbon react with

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mercury in the mercury-containing gas to form the mercury-sorbent composition. In some examples, at least a portion of the binding sites of the carbon react with oxidized mercury in the mercury-containing gas to form a mercury-sorbent composition.

[0050] In some embodiments, at least some of the carbon in the carbon nanocomposite is in the graphene form of carbon. The graphene form of carbon can, in some embodiments, include higher concentrations of locations suitable as the active sites of the nanocomposite. In some examples, certain parts of graphene carbon can have the highest concentrations of locations suitable as the active sites of the nanocomposite: in some examples at the edges, in some examples in non-edge locations. Such locations suitable as active sites may be activated via treatment with halide or halogen, as described herein. In various embodiments, the carbon in the carbon nanocomposite can be at least about 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%, 99.9 wt%, 99.99 wt%, or more than about 99.999 wt% graphene form of carbon.

[0051] In some embodiments, the carbon nanocomposite sorbent has a mean particle diameter greater than 40 micrometers, or greater than 60 micrometers, or a particle size distribution greater than that of fly ash or entrained ash in a flue gas stream to be treated, such that the carbon nanocomposite sorbent and ash can be separated by physical means in the separation step.

[0052] In one example, the nanocomposite can be a carbon nanocomposite that is promoted for gas-phase Hg oxidation when a halide salt contained in the porous structure is decomposed during injection into a heated duct. In some examples, the halide salt can be ammonium bromide. In some examples, the carbon nanocomposite can include graphene. In some examples, the non-carbon part of the nanocomposite includes a high surface-area, porous, inorganic matrix.

Method of Forming a Carbon Nanocomposite Sorbent

[0053] The carbon nanocomposite sorbent can be obtained, it can be synthesized, or any combination thereof. For example, an obtained carbon

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nanocomposite material may need further treatment before it is suitable for use in an embodiment of the method of the present invention. Various embodiments provide a method of forming the carbon nanocomposite sorbent, a carbon nanocomposite sorbent formed thereby, or a combination of the carbon nanocomposite sorbent with a mercury-containing gas. For example, the method of making the carbon nanocomposite sorbent can include providing or obtaining a carbon precursor, wherein the carbon precursor provides the carbon in the carbon nanocomposite sorbent. The method can include providing or obtaining a substrate material, wherein the substrate material provides the bulk substrate in the carbon nanocomposite sorbent. The method can include contacting the carbon precursor and the substrate material to provide a nanocomposite starting material. The method can include heating the nanocomposite starting material. Heating the nanocomposite starting material provides the nanocomposite sorbent. Before use, the nanocomposite sorbent can optionally be subjected to processing steps, such as treatment with base, or such as treatment with a halogen or halide, which can allow formation of active sites on the carbon nanocomposite that can react with elemental mercury to transform the mercury, for example, into oxidized mercury (e.g., mercury oxide).

[0054] In some examples, using a substrate such as a clay (e.g., the substrate allowing for an open and porous substructure), a carbohydrate (e.g., carbon precursor) can be contacted with the substrate. The resulting mixture can be heated, which creates a carbon layer with a low carbon density that covers the open porous structure of the substrate material. In some embodiments, as the mixture is heated, the substrate can swell. The carbon layer can be created by chemical reactions of the carbon precursor caused by the heating step, including decomposition reactions, including for example pyrolysis, dehydration, or decarboxylation reactions. In some embodiments, the carbon layer created includes the graphene form of carbon, for example as graphene ribbons. The graphene form of carbon, especially at its edges, can, in some embodiments, include higher concentrations of locations suitable as the active sites of the nanocomposite. The carbon coats the surfaces of the clay particles, which can be randomly stacked in a highly porous matrix. In examples, a halide or halogen can be introduced to the sorbent, promoting the carbon and enhancing the

reactivity of the sorbent to mercury. The halide or halogen can be introduced in various forms.

[0055] In some embodiments, a promoted sorbent can be produced "in-flight." This can be accomplished by, for example, contacting the vapors of any combination of halogens, in-flight, with the carbon nanocomposite sorbent. In-flight promotion of the carbon nanocomposite sorbent can be accomplished by contacting the vapors of any combination of halogens with the carbon nanocomposite sorbent in a stream of transport air or a polluted gas stream containing mercury from which mercury is to be removed. The particles can be dispersed in a stream of transport air (or other gas), which also conveys the halogen-/halide-promoted carbon sorbent particles to the flue gas duct, or other polluted gas stream, from which mercury is to then be removed. In some embodiments, the particles can be dispersed directly in a flue gas stream.

[0056] The simplicity and resulting cost savings of in-flight promotion can be advantageous. Capital equipment costs, operation costs, and transportation costs of a treatment facility can be eliminated. In-flight preparation can use existing hardware and operation procedures and can help to ensure the promoted sorbent is always fresh and, thus, more reactive. In-flight preparation allows for rapid on-site tailoring of the degree of promoting the sorbent in order to ensure adequate reactivity to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics and effectiveness of mercury capture.

Carbon Precursor

[0057] The method of making the carbon nanocomposite sorbent can include providing or obtaining a carbon precursor, wherein the carbon precursor provides the carbon in the carbon nanocomposite sorbent. The carbon layer in the nanocomposite can be created by chemical reactions of the carbon precursor caused by the heating step, including decomposition reactions, including for example pyrolysis, dehydration, or decarboxylation reactions.

[0058] The carbon precursor can include any suitable carbon precursor, such that the heating step transforms the carbon precursor and the substrate into a suitable carbon nanocomposite sorbent. For example, the carbon precursor can

be any sugar source such as a carbohydrate (saccharide), including, for example, brown sugar, barley sugar, caramel, cane sugar, corn syrup, molasses, sugar or sugar processing wastes such as beet sugar waste, cane sugar waste, and the like. The carbon precursor can be any suitable starch or source of starch.

[0059] In some examples, the carbon precursor can be present in from about 1 wt% to about 99 wt%, about 20 wt% to about 80 wt%, or about 40 wt% to about 60 wt% of the starting material for the carbon nanocomposite sorbent. In some examples, the carbon precursor can be present in from about 50% or less carbon, or about 3 wt% to about 50 wt% carbon, or about 5 wt% to about 10 wt% carbon of the starting material for the carbon nanocomposite sorbent. Wt% in this paragraph refers to the percentage by weight based on the total weight of the carbon precursor and the substrate material.

Substrate Material

[0060] The method of making the carbon nanocomposite sorbent can include providing or obtaining a substrate material, wherein the substrate material provides the bulk substrate in the carbon nanocomposite sorbent.

[0061] The substrate material can include any suitable substrate material, such that the heating step transforms the carbon precursor and the substrate material into a suitable carbon nanocomposite sorbent. The substrate can include any suitable porous material. For example, the substrate material can be diatomaceous earth, zeolites, porous minerals (e.g., clays) including, for example, smectites (e.g., montmorillonite, bentonite, nontronite, saponite), kaolins, illites, chlorites, sepiolite, or attapulgites. In some examples, the substrate can include polymers, non-metals, metals, metalloids, ceramics or mixtures, and blends, as well as composites and alloys thereof. The materials can be synthetic or naturally occurring or naturally derived materials. Examples of synthetic polymers include any common thermoplastics and thermosetting materials. Examples of metals include aluminum, titanium, copper, steel, and stainless steel. Examples of ceramics include any form of alumina, zirconia, titania, and silica. Examples of naturally occurring or naturally derived materials include wood, wood composites, paper, cellulose acetate, and geologic formations such as granite or limestone. Examples of non-metals include various

forms of carbon such as graphite or carbon. Examples of metalloids include silicon or germanium. The porous material can be a construction material such as concrete or asphalt.

[0062] In some examples, the substrate material can be present in from about 1 wt% to about 99 wt%, about 20 wt% to about 80 wt%, or about 40 wt% to about 60 wt% of the starting material for the carbon nanocomposite sorbent. Wt% in this paragraph refers to the percentage by weight based on the total weight of the carbon precursor and the substrate material.

Contacting and Heating

[0063] The method of making the carbon nanocomposite sorbent can include contacting the carbon precursor and the substrate material to provide a nanocomposite starting material. The method can include heating (e.g., providing energy to) the nanocomposite starting material. Heating (or other means of providing energy to) the nanocomposite starting material provides the nanocomposite sorbent.

[0064] The contacting can take place in any suitable fashion. The contacting mixes the carbon precursor and the substrate material, such that when the conglomeration is heated (or subjected to any other suitable source of energy), the carbon nanocomposite sorbent is formed. The contacting can be performed such that the carbohydrate is approximately evenly distributed on the substrate. In some examples, water or another solvent can be added to help distribute the carbon precursor on the substrate. In examples where water is included in the mixture of the carbon precursor and the substrate, the conglomeration can be dried prior to the heating. The drying can occur in any conventional manner (e.g., convective, conductive, microwave, and the like), including by heating near or above the boiling point of the solvent, in the case of water (e.g., 50°C-120°C or higher), at atmospheric pressure, under pressure, or under a vacuum.

[0065] The contacted composition of the carbon precursor and the substrate can then be heated to form the carbon nanocomposite sorbent. The heating is sufficient to cause the chemical reactions that transform the carbon precursor into the form of carbon present in the carbon nanocomposite (e.g.,

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decomposition reactions) including, for example, pyrolysis, dehydration, or decarboxylation reactions. The heating can take place at any suitable temperature, such that the carbon nanocomposite is sufficiently formed, for example about 50°C, 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C, or about 1200°C. The heating can take place for any suitable time, such that the carbon nanocomposite is sufficiently formed, for example, greater than about 1 min, 2 min, 5 min, 10 min, 30 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 5 h, 10 h, or greater than about 24 h. The heating can take place in any suitable apparatus, for example, a unit that allows heated air to flow around the mixture being heated or a furnace. The heating can be accelerated, or lengthened, depending on the apparatus and the nanocomposite material.

Halogen or Halide Promoter

[0066] A "halogen" is defined as a member of the elements included in Group VIIA of the periodic table (Group VIIA [CAS] corresponds to Group VIIB [IUPAC]). The molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, can be relatively uncreative with elemental mercury in a hot flue gas. Any halogen ion, gas, or compound can be a promoter.

[0067] Embodiments of the method for reducing the mercury content of a mercury-containing gas include providing or obtaining a halogen or halide promoter. The method includes promoting at least a portion of the sorbent material. The promoting of the sorbent material includes chemically reacting or impregnating the portion of the sorbent material with the halogen or halide promoter. The halogen or halide promoter can be derived from reaction or degradation of another compound (e.g., a promoter precursor). The promoting of the sorbent material gives a promoted sorbent. The promoting of the sorbent material can occur before injection into a gas stream, during injection into a gas stream, after injection into a gas stream, or a combination thereof, wherein the gas stream can be a mercury-containing gas stream, a transport stream, or a combination thereof. In some examples, the promoter can be added to the sorbent before the promoter and the sorbent react, such that the heat of the gas stream into which the promoter is added causes the promoting of the sorbent. For example, the promoter can be added as a gas, as a gas dissolved in a liquid, or as

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a solid such as a salt, or other substance (e.g., acid) dissolved in liquid (e.g., water). In examples wherein the promoter is added in a liquid such as water, the water can be allowed to dry, which can allow the promoter to adhere to, impregnate, or react with the nanocomposite sorbent, or a combination thereof. In some examples, a pre-added promoter can be an ammonium salt, such as an ammonium chloride, an ammonium bromide, or an ammonium iodide, including, for example, mono-, di-, tri-, or tetraalkyl ammonium halides, or NH_4^+ halide salts. In some examples, the promoter can be added to the sorbent near to or at the time of promoting; for example, the promoter can be added to a gas stream with the sorbent or such that it contacts the sorbent within a heated gas stream, such as a mercury-containing gas stream or a feed gas stream. In some examples, the promoter can be NH_4Br.

[0068] In some embodiments, the promoter can be HBr, and in some examples, the HBr can be provided via degradation or reaction of a promoter precursor such as ammonium bromide, sodium bromide, or calcium bromide. The promoter can be HCl, and in some examples, the HCl can be provided via degradation or reaction of a promoter precursor such as ammonium chloride, sodium chloride, or calcium chloride. The promoter can be HF, and in some examples, the HF can be provided via degradation or reaction of a promoter precursor such as ammonium fluoride, sodium fluoride, or calcium fluoride. In some examples, the promoter (e.g., HBr or HCl) or promoter precursor (e.g., NH_4Br, NaBr, $CaBr_2$, NH_4Cl, NaCl, $CaCl_2$) can be injected in the flue gas separately from the carbon nanocomposite sorbent or with the carbon nanocomposite sorbent (e.g., can be applied to the sorbent pre-injection, injected simultaneously at the same location, or injected simultaneously at different locations).

[0069] Not intending to limit embodiments to any particular mechanism of action, in various embodiments, adding a halogen, or a proton from a hydrogen halide acid, to a basic carbene site on the carbon edge structure forms a carbocation that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site can also generate reactive halogen radicals or carbon radicals at the active sites on the carbon. Thus the carbon nanocomposite sorbent provides a highly reactive

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halogen-containing reagent that can oxidize the mercury and promote its capture on the carbon nanocomposite sorbent. In some embodiments, a sorbent that contains bromine or that is promoted by bromine or a bromine reagent is expected to be more reactive than the corresponding sorbent promoted by chlorine or a chlorine reagent and less expensive than the sorbent promoted by iodine or an iodine reagent.

[0070] Reactions of halogens and acidic species with the binding sites on the promoted carbon nanocomposite sorbent can create active sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, Se, or other pollutants, can also react with the oxidation sites on the carbon.

[0071] In some embodiments, the halogen or halide promoter that is added to, and reacts with, the carbon nanocomposite sorbent can include, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (e.g., in water or a non-aqueous solvent such as an alcohol or other organic solvent).

[0072] Embodiments are also provided in which the organic solvent can include a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

[0073] In some embodiments, the method can include adding an additional halogen or halide promoter to the promoted sorbent. The additional halogen or halide can be any halogen or halide described herein as suitable as the first halogen or halide. For example, the additional halogen or halide promoter can include HI, HBr, HCl, a Group V element with halogen, or a Group VI element with halogen.

[0074] In various embodiments, the step of promoting at least a portion of the sorbent material can occur at least partially before the contacting of the mercury-containing gas with the sorbent. In some examples, the step of

promoting at least a portion of the sorbent can occur at least partially during the contacting of the mercury-containing gas with the sorbent. In some examples, the carbon nanocomposite sorbent can be injected into a gas stream at an injection rate, in which at least one promoter is injected separately at an injection rate into a gas stream whereby in-flight reaction produces the promoted sorbent. In some examples, the promoter can be reacted in the gas phase or as a vapor. In some examples, the promoter is added at from about 0.01 g to about 200 g, or about 0.1 g to about 100 g, or about 1 g to about 30 g per 100 grams of carbon nanocomposite sorbent material. In some examples, either one or both of the gas streams into which the sorbent and the promoter are injected can be a transport gas, a flue gas stream (e.g., a mercury-containing gas), or a combination thereof. In some examples, the promoter injection rate and the sorbent injection rate into the gas are determined, at least in part, from the monitored mercury content of the cleaned gas.

Contacting the Sorbent and the Mercury in the Mercury-Containing Gas

[0075] In embodiments of the method for reducing the mercury content of a mercury-containing gas, the method can include contacting at least part of the promoted sorbent with the mercury in the mercury-containing gas. Contacting the promoted sorbent with the mercury in the mercury-containing gas includes contacting the promoted sorbent with the mercury-containing gas. Contacting the promoted sorbent with the mercury forms a mercury-sorbent composition. The contacting can occur in any suitable location. For example, the contacting can occur in the gas. In another embodiment, the contacting can occur in an aqueous liquid. In another example, the contacting can occur in the gas, and subsequently contacting can also occur in an aqueous phase such as a scrubber.

[0076] In various embodiments, measurement of mercury emissions can be used as feedback to assist in controlling the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which can help to ensure mercury removal requirements are met with the minimum promoter and sorbent requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured

downstream of the injection location, for example, in the exhaust gas at the stack. In various embodiments, contacting at least part of the promoted sorbent with the mercury in the mercury-containing gas can occur between particulate control devices.

Separating at Least Some of the Mercury-Sorbent Composition from the Mercury-Containing Gas

[0077] In embodiments of the method for reducing the mercury content of a mercury-containing gas, the method includes separating at least some of the mercury-sorbent composition from the gas. The separation gives a cleaned gas, having a lower mercury content than starting material mercury-containing gas. In some embodiments, separating at least some of the mercury-sorbent composition from the mercury-containing gas comprises separating particulates from the gas, wherein the particulates comprise at least some of the mercury-sorbent composition.

[0078] In some examples, the step of separating particulates from the mercury-containing gas includes separating the particulates from the gas in a particulate separator. The particulate separator can be any suitable separator. The particulate separator can include one or more cyclones, electrostatic precipitators, fabric separators, scrubbers, or other particulate removal devices as are known in the art. In some embodiments, an electrostatic precipitator can be used, followed by a scrubber. In other embodiments, an electrostatic precipitator can be used without a scrubber, or another particulate separator can be used. Some devices that can function as particulate separators can also have other functions, for example a scrubber can also remove SO_2 or SO_3 from the gas stream, as described further below. In embodiments that include contacting of the mercury with a sorbent in an aqueous phase, e.g. in a scrubber, the removal of mercury from the gas that occurs within the aqueous phase by reaction or interaction of the mercury with the sorbent in the aqueous phase can be considered separation of the mercury-sorbent composition from the gas.

[0079] In some examples, by separating the particulates from the mercury-containing gas, at least about 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%,

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99.9 wt%, 99.99 wt%, or about 99.999 wt% or more mercury can be removed from the mercury-containing gas stream. As discussed herein, the mercury can be removed in the form of elemental mercury, in the form of a transformed mercury, such as a oxidized mercury (e.g., mercury oxide).

Scrubber

[0080] In various embodiments of the method for reducing the pollutant content of a pollutant-containing gas, an aqueous scrubber can be used. An aqueous scrubber allows an aqueous liquid or aqueous slurry to contact the gas stream. A scrubber can spray, nebulize, or otherwise distribute aqueous material in the space through which the gas stream flows therein such that the surface area of the liquid that contacts the gas in the scrubber is increased. The aqueous solution can fall to the bottom of the scrubber, where it can be recycled back to the top, or removed to be regenerated, cleaned, or replaced. The aqueous scrubber can be any suitable aqueous scrubber. In some examples, the aqueous scrubber can remove one or more pollutants from the gas stream.

[0081] A scrubber can remove particulate from a gas stream. For example, when a gas stream including particulates passes through the scrubber, particulates that contact droplets or other forms of aqueous solution can become stuck or immersed in the aqueous solution. As the aqueous solution falls to the bottom of the scrubber, the particles can fall with it. The aqueous solution can be recycled back to the top of the scrubber with at least some of the particles in it. The aqueous solution can be any suitable consistency, such as a free-flowing clear liquid, a liquid having suspended solid, or slurry of any suitable viscosity. Continuously or batchwise the aqueous solution in the scrubber can be cleaned or replaced, removing, for example, particles, pollutant, or pollutant-byproduct. In one example, sorbent in the aqueous solution can be separated and regenerated, such as described in US 2007/0167309.

[0082] In various embodiments, the method can include removing at least some SO_2 or SO_3 from the pollutant-containing gas (e.g. reducing the concentration of SO_2 or SO_3). The removal can be done in any suitable way. In some examples, an aqueous scrubber can remove SO_2 or SO_3 from the gas stream, for example, by reaction with SO_2 or SO_3 with chemical compounds

present in the water in the scrubber. Some examples of chemical compounds that can be included in the water in the scrubber that can react with SO_2 or SO_3 include salts that form basic solutions in water, such as, for example, carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), or carbamate ($OCONH_2^-$) salts, having any suitable counterion, such as, for example, ammonium (NH_4^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{+2}), or calcium (Ca^{+2}). For example, the basic salt can be ammonium carbonate ($(NH_4)_2CO_3$), ammonium bicarbonate ($(NH_4)HCO_3$), or ammonium carbamate ($(NH_4)OCONH_2$).

[0083] In various embodiments, a promoter or promoter precursor can be in the aqueous solution of the scrubber. In some embodiments, a promoter (e.g., HBr) can be added directly to the water in the aqueous scrubber. In some examples, a promoter precursor (e.g., NH_4Br) can be added directly to the water in the aqueous scrubber, where it can decompose to form the promoter (e.g., HBr). The promoter precursor can be injected into hot gas (e.g., a hot carrier gas, or the flue gas stream) where it can be converted into the promoter, and subsequently the gas stream can enter the scrubber, where the precursor can be absorbed or dissolved in the water in the scrubber. The promoter or promoter precursor can enter any suitable part of the scrubber in any suitable way, for example, it can enter the flue gas stream prior to entering the scrubber, it can be separately injected into the gas phase of the scrubber, or it can be injected into the aqueous phase of the scrubber.

[0084] In some embodiments, the aqueous solution in the scrubber can include activated carbon nanocomposite sorbent. In such embodiments, the scrubber can remove one or more pollutants from the gas stream, such as mercury, by allowing the activated sorbent in the aqueous phase to react with or absorb one or more pollutants from the gas stream. The nanocomposite can enter the scrubber in any suitable location in any suitable way, for example, it can enter the flue gas stream prior to entering the scrubber, it can be separately injected into the gas phase of the scrubber, or it can be injected into the aqueous phase of the scrubber. Optionally, aqueous solutions that include activated carbon nanocomposite sorbent can include other chemicals that can react with pollutants in the gas stream, such that the scrubber can remove more than one type of pollutant. For example, in addition to activated carbon nanocomposite

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sorbent, an aqueous scrubber solution can also include basic salts that can react with SO_2.

[0085] In some examples, the carbon nanocomposite can be activated in the scrubber, such as in embodiments that include the promoter in the water of the scrubber. The carbon nanocomposite can be added directly to the scrubber (e.g. to the gas phase or liquid phase), or before the scrubber in the gas stream flowing into the scrubber. The carbon nanocomposite can be added at any suitable point between a particulate control device (e.g. ESP) and a scrubber. In some examples, both the carbon nanocomposite and the promoter or promoter precursor can be injected into a hot gas stream (e.g. hot carrier gas, or the flue gas stream) where promoted carbon nanocomposite sorbent can form prior to entry into the scrubber. In some embodiments, a carbon nanocomposite can be coated with a promoter or promoter precursor, and the coated carbon nanocomposite can be injected into a hot gas (e.g., a hot carrier gas, or the flue gas stream) where it can convert into the promoter, and subsequently be absorbed in the water in the scrubber.

[0086] In embodiments including an ESP and a scrubber, optionally carbon nanocomposite can be used for pollutant removal prior to an ESP and also in a wet scrubber. In such an embodiment, the ESP can remove nanocomposite-pollutant. Alternatively, the carbon nanocomposite can be used in the scrubber and not prior to the ESP. Alternatively, the carbon nanocomposite can be used only prior to the ESP and not in the scrubber or not predominantly in the ESP.

Alkaline Component

[0087] In some examples, the method of removing mercury from a mercury-containing gas stream can include injecting an alkaline (e.g., basic) component into the mercury-containing gas. In some examples, the alkaline component includes an oxide, hydroxide, carbonate, or phosphate of an alkali or alkaline-earth element.

[0088] In various examples, the addition of an alkaline component separately or with the carbon nanocomposite sorbent can result in improved mercury capture, in some examples exceeding that of both the promoted and

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unpromoted carbon nanocomposite sorbent. Various factors can impact the effectiveness of the alkaline addition, such as, for example, flue gas pollutants, flue gas constituents (e.g., SO_2, NO_x, HCl, and the like), operating temperature, mercury form, and mercury concentration. In some examples, the alkaline-to-activated-carbon ratio can be adjusted to optimize for a given set of site conditions.

Stabilizing Agent

[0089] In some examples, a stabilizing agent can be added to the promoted sorbent. The stabilizing agent can be a mercury stabilizing agent. In some embodiments, a method is provided whereby a mercury stabilizing agent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing agent(s) can be sequentially added, either before or after the addition and reaction of the halogen/halide. In some embodiments, the halogen/halide includes Br or HBr, and the mercury-stabilizing agent can include S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Regeneration of Sorbent

[0090] In any of the embodiments of the method or the material for separating mercury from a mercury-containing gas stream, the carbon sorbent can be regenerated; sorbent-poisoning pollutants from the flue gas can be removed; and the sorbent can be re-promoted to restore mercury sorption activity. The regenerated sorbent can then be used again in the method. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT," which is hereby incorporated by reference in its entirety.

Example Process

[0091] In various embodiments, the carbon nanocomposite sorbent, method of mercury removal, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas

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streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description can apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

[0092] Referring now to FIG. 1, there is shown a block flow diagram illustrating methods for preparation of promoted carbon sorbents, in accordance with various embodiments. Block 10 illustrates providing carbon nanocomposite sorbent and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a promoted carbon nanocomposite sorbent. In embodiments where a halogen or halide is added in, for example, a solvent, solvent removal can be used as illustrated by block 20A. Block 30 indicates adding an optional secondary component illustrated at block 30 that reacts with the result of block 20 or 20A to produce a promoted carbon nanocomposite sorbent. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, solvent removal can be used as illustrated by block 30A.

[0093] In FIG. 1, the steps leading to step 50 produce promoted sorbent prior to treatment of the flue gas stream with the promoted sorbent. The addition of one or more promoters, and the reactions or interactions with the promoters that lead to promotion of the sorbent, can occur in any suitable location. In some examples, the sorbent can be promoted in a hot-gas stream, such as in a flue gas stream, or such as in a hot carrier gas stream. In some embodiments, the promoter can be added to the sorbent before the sorbent is injected into a hot-gas stream. In some embodiments, the promoter can be added to the hot-gas stream with the sorbent, referred to herein as "in-flight" promotion of the sorbent. Thus, in some embodiments, prior to step 50, the promoter and the sorbent can be injected together or separately into the flue gas stream or another hot-gas stream.

[0094] Referring still to FIG. 1, path 10-40 includes providing a carbon nanocomposite sorbent as illustrated at block 10 and adding a halogen or halide promoter and a secondary component to the sorbent together, with which they can react as illustrated by block 40, producing a promoted carbon nanocomposite sorbent. In embodiments where one or more components are added in solvent, a solvent removal step can be provided as illustrated by block 40A.

[0095] Referring still to FIG. 1, also illustrated are embodiments in which, as illustrated by block 50, a flue gas stream is treated with promoted carbon nanocomposite sorbent prepared as described herein.

[0096] Referring now to FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds, which is not intended to limit embodiments of the present invention to any specific theory of operation. The method of the present invention encompasses any removal of mercury from a gas using a carbon nanocomposite in any suitable way.

[0097] For example, as illustrated in FIG. 2, hydrogen bromide can react with the unsaturated structure of the carbon nanocomposite sorbent. The hydrogen bromide can be provided by, for example, ammonium bromide. The reactive part of the carbon on the carbon nanocomposite sorbent can be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or other bromine compounds can react to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

[0098] The formation of the bromide compound with carbon increases the reactivity of the carbon nanocomposite toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation may result from the promotion effect of the halide exerted on the developing positive charge on the mercury during the oxidation, known in the chemical arts as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons can push in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br_2 to the carbon nanocomposite can form a similar carbon bromide, in which the positive carbon can oxidize the mercury with the assistance of the bromide ion.

[0099] FIG. 3A shows a schematic flow diagram of mercury control system 100 including preparation of promoted carbon sorbents and flue gas mercury reduction, in accordance with embodiments of the present invention.

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There is provided carbon nanocomposite sorbent reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional alkali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 207/208/209, respectively. Reservoirs 110, 120, and 130 with corresponding flow controllers 201, 202, and 203 can be used in conjunction with transport lines 113 and 115 independently, together, or not at all. For example, reservoir 110 with controller 201 can be used with transport line 113 independently and separately to inject material at injection point 114, while at the same time, optional reservoirs 120 and/or 130 with corresponding flow controllers 202 and/or 203 can be used with transport line 115 to independently and separately inject material at injection point 116. In conjunction with the optional alkali component reservoir 180, optional flow control devices 207, 208, and 209 can be used independently, together, or not at all.

[00100] Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport lines 113 and 115. Optional alkali component reservoir 180 can also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 169 to transport line 113 to entrain materials discharged from reservoirs 110, 120, 130, and 180 and to inject such materials, via injection point 114, into polluted flue gas stream 15. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into polluted flue gas stream 15. A source of air, nitrogen, or other transport gas(es) can be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 169, 170, and 171 can be the same or different, as desired. Alternatively, transport gas(es) can be provided to transport lines 113, 115, and 118 by gas source 170 (connection from source 170 to transport line 113 and/or 118 not shown). Although gas sources 169, 170, and 171 are shown in FIG. 3A as compressors or blowers, any source of transport energy known in

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