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CERTIFICATE OF CORRECTION

PATENT NO.	: 10,933,370 B2
APPLICATION NO.	: 15/951970
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INVENTOR(S)	: Olson et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the Title Page

In "Related U.S. Application Data", in Column 1, Line 1, delete "(60)" and insert --(63)-- therefor

On page 5, in Column 2, under "Other Publications", Line 21, delete "MaY" and insert --May-- therefor

On page 6, in Column 2, under "Other Publications", Line 59, delete "Actioin" and insert --Action-- therefor

On page 7, in Column 1, under "Other Publications", Line 67, delete "ay" and insert --May.-- therefor

On page 8, in Column 2, under "Other Publications", Line 71, delete ""Effectsof" and insert --"Effects of-- therefor

On page 8, in Column 2, under "Other Publications", Line 72, delete "Reducton" and insert --Reduction-- therefor

On page 9, in Column 2, under "Other Publications", Line 5, delete "Removil" and insert --Removal-- therefor

On page 10, in Column 2, under "Other Publications", Line 62, delete "SHeet"" and insert --Sheet"-- therefor

On page 10, in Column 2, under "Other Publications", Line 64, delete ""Fluegas" and insert --"Flue gas-- therefor

In the Specification

In Column 3, Line 13, delete "halides." and insert --halides,-- therefor

Signed and Sealed this
Twenty-eighth Day of December, 2021

Drew Hirshfeld
Performing the Functions and Duties of the Under Secretary of Commerce for Intellectual Property and Director of the United States Patent and Trademark Office

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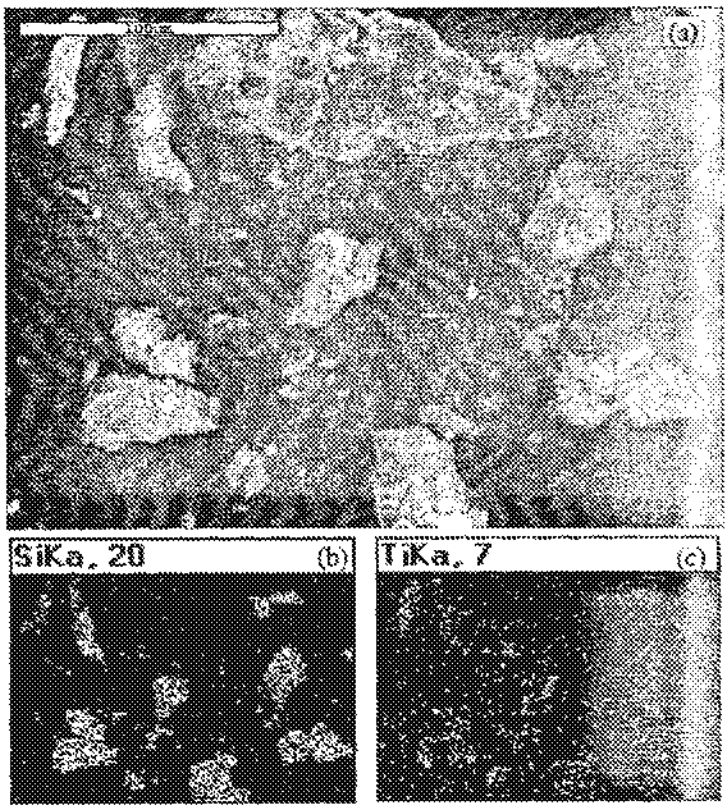
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[Continued on next page]

(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

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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).

BHE et al. EXHIBIT 1023
Page 4

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

BHE et al. EXHIBIT 1023
Page 5

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 ($OH^{\cdot}$), 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

BHE et al. EXHIBIT 1023
Page 6

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.

BHE et al. EXHIBIT 1023
Page 7

[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).

BHE et al. EXHIBIT 1023
Page 8

[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.

[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,

BHE et al. EXHIBIT 1023
Page 10

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

BHE et al. EXHIBIT 1023
Page 11

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.

BHE et al. EXHIBIT 1023
Page 12

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.

BHE et al. EXHIBIT 1023
Page 13

[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.

BHE et al. EXHIBIT 1023
Page 14

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

BHE et al. EXHIBIT 1023
Page 15

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

BHE et al. EXHIBIT 1023
Page 16

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.

BHE et al. EXHIBIT 1023
Page 17

[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.

BHE et al. EXHIBIT 1023
Page 18

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.

BHE et al. EXHIBIT 1023
Page 19

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.

BHE et al. EXHIBIT 1023
Page 20

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.

BHE et al. EXHIBIT 1023
Page 21

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% .

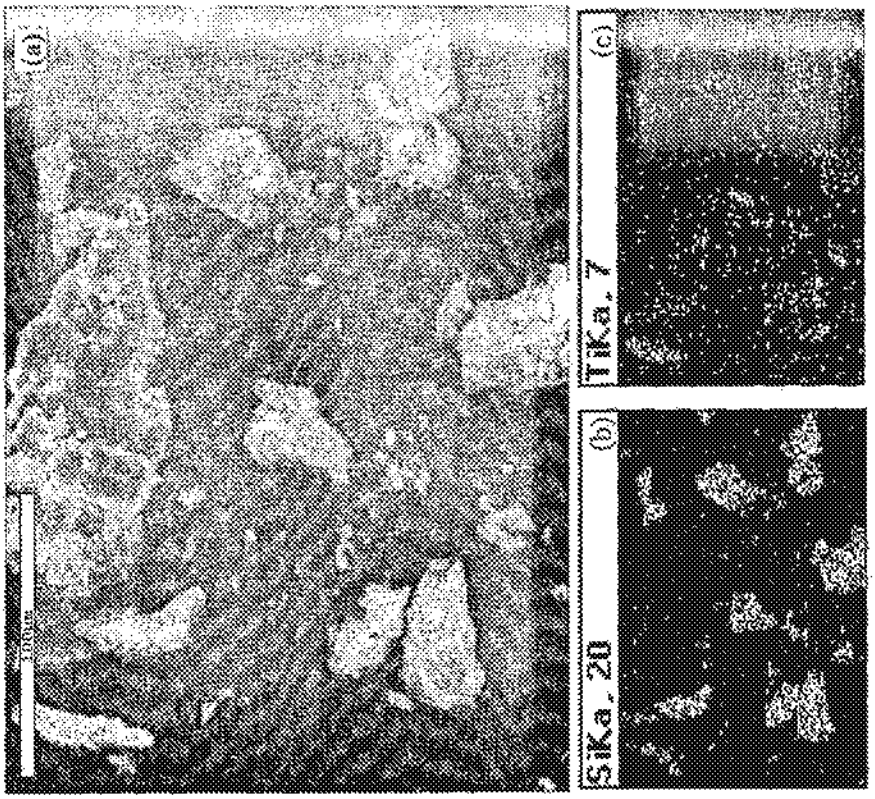


FIG 1

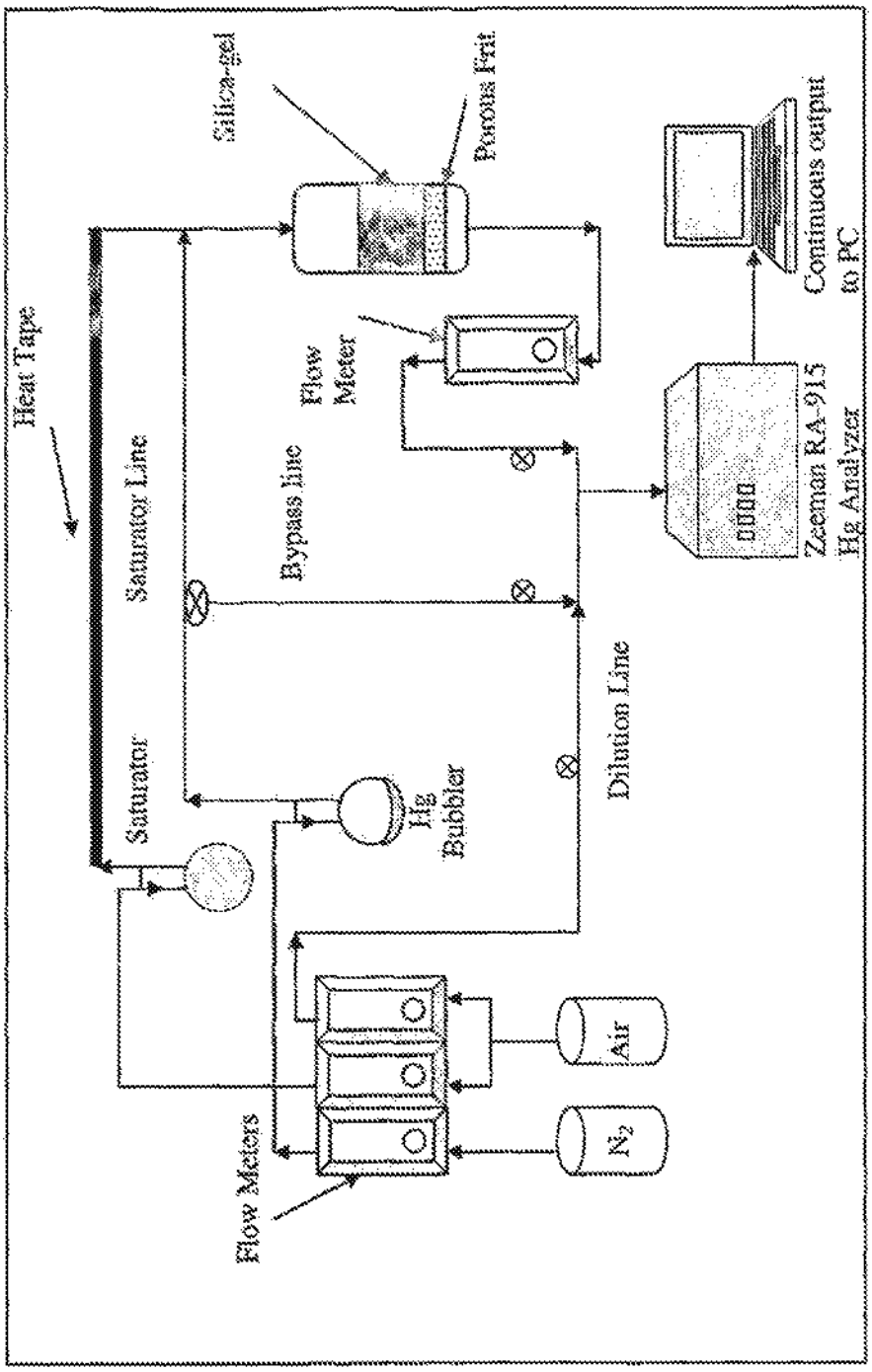

Heat Tape
Saturator Line
Saturator
Silica-gel
Porous Frit
Flow Meter
Bypass line
Hg Bubbler
Dilution Line
Flow Meters
Air
N_2
Zeeman RA-915 Hg Analyzer
Continuous output to PC

FIG 2

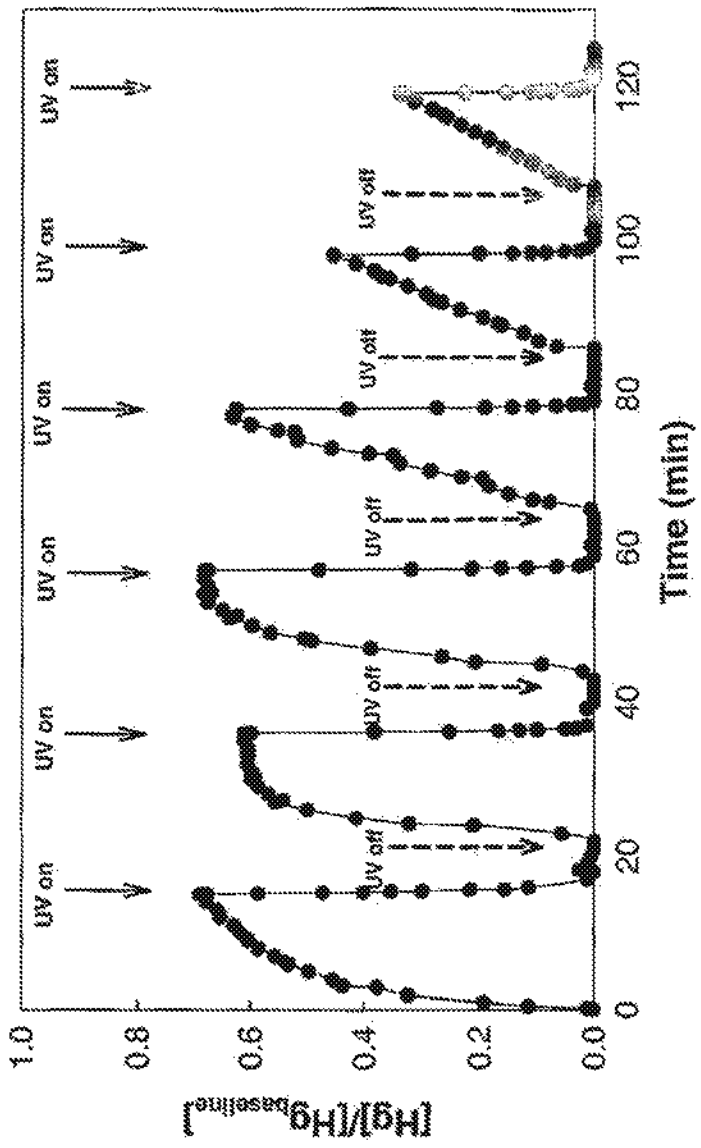

UV on
UV off
[Hg]/[Hg$_{baseline}$]
Time (min)
0.0
0.2
0.4
0.6
0.8
1.0
0
20
40
60
80
100
120

FIG 3

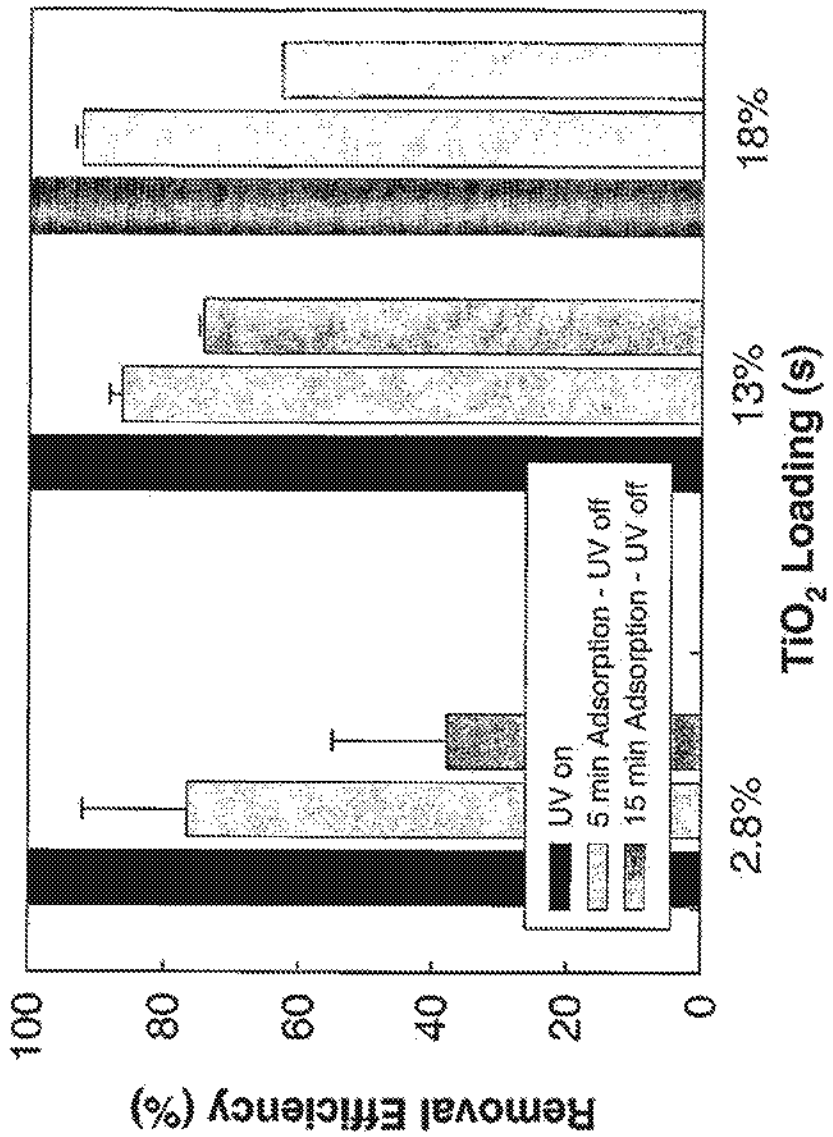

Removal Efficiency (%)
100
80
60
40
20
0
UV on
5 min Adsorption - UV off
15 min Adsorption - UV off
2.8%
13%
18%
TiO2 Loading (s)

FIG 4

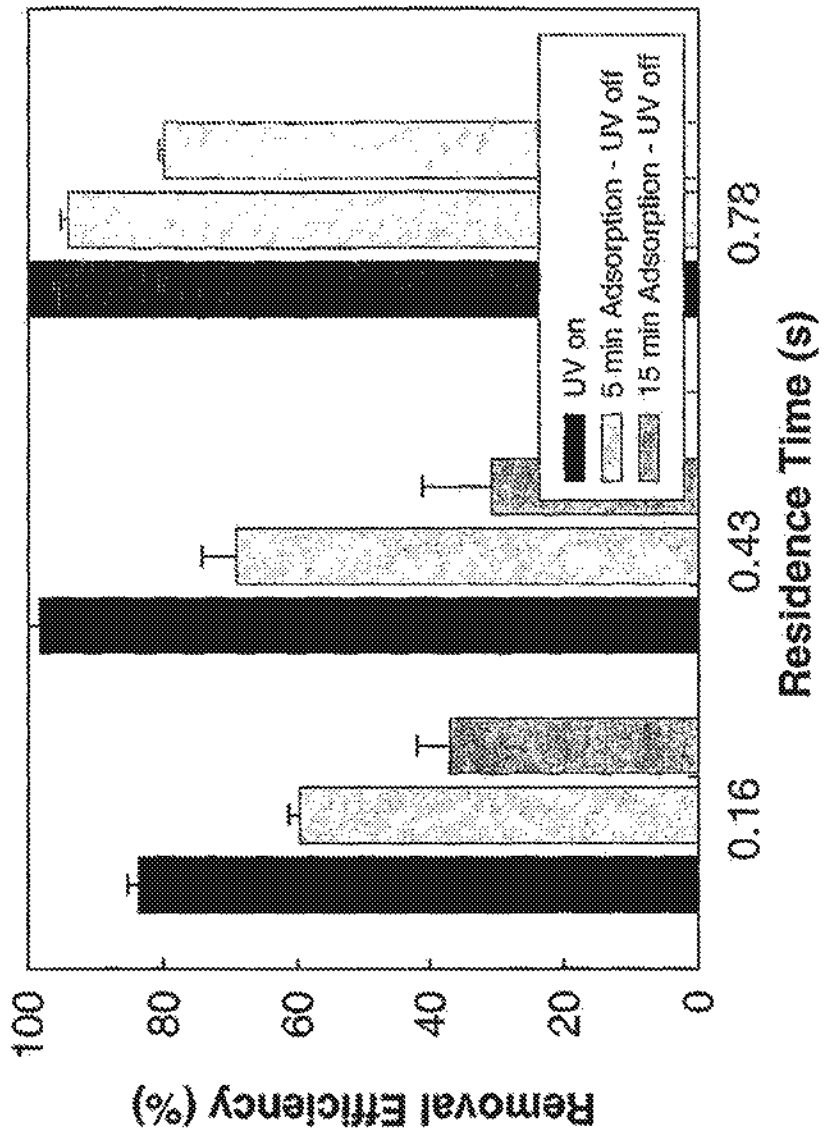

Removal Efficiency (%)
100
80
60
40
20
0
0.16
0.43
0.78
Residence Time (s)
UV on
5 min Adsorption - UV off
15 min Adsorption - UV off

FIG 5

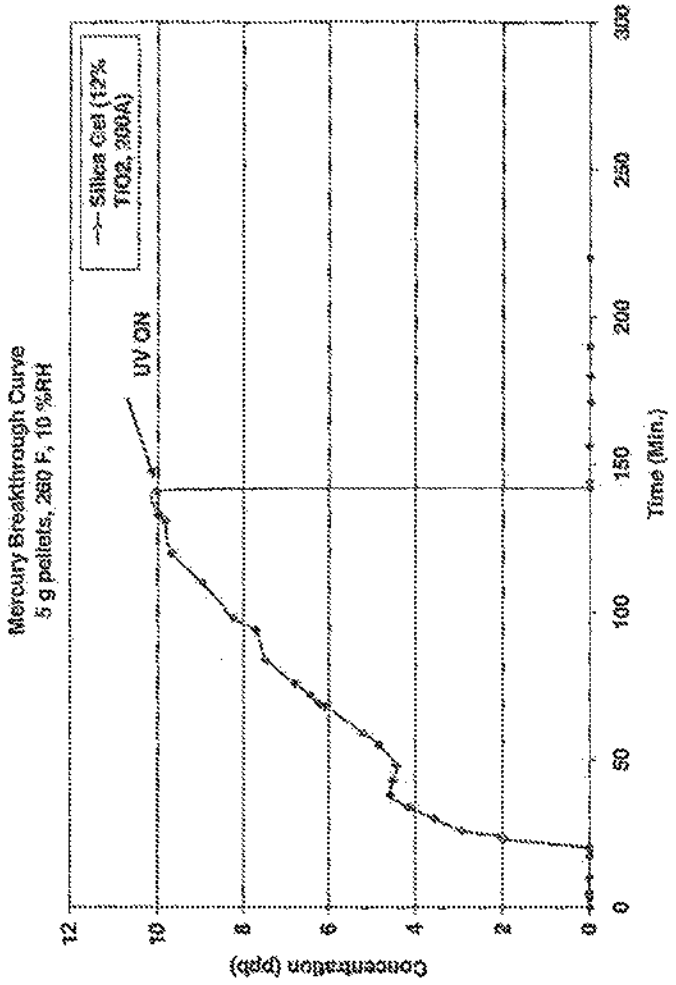

Mercury Breakthrough Curve
5 g pellets, 250 F, 10 %RH
UV ON
Silica Gel (12% TiO2, 280A)
Concentration (ppb)
Time (Min.)
0
2
4
6
8
10
12
0
50
100
150
200
250
300

FIG 6

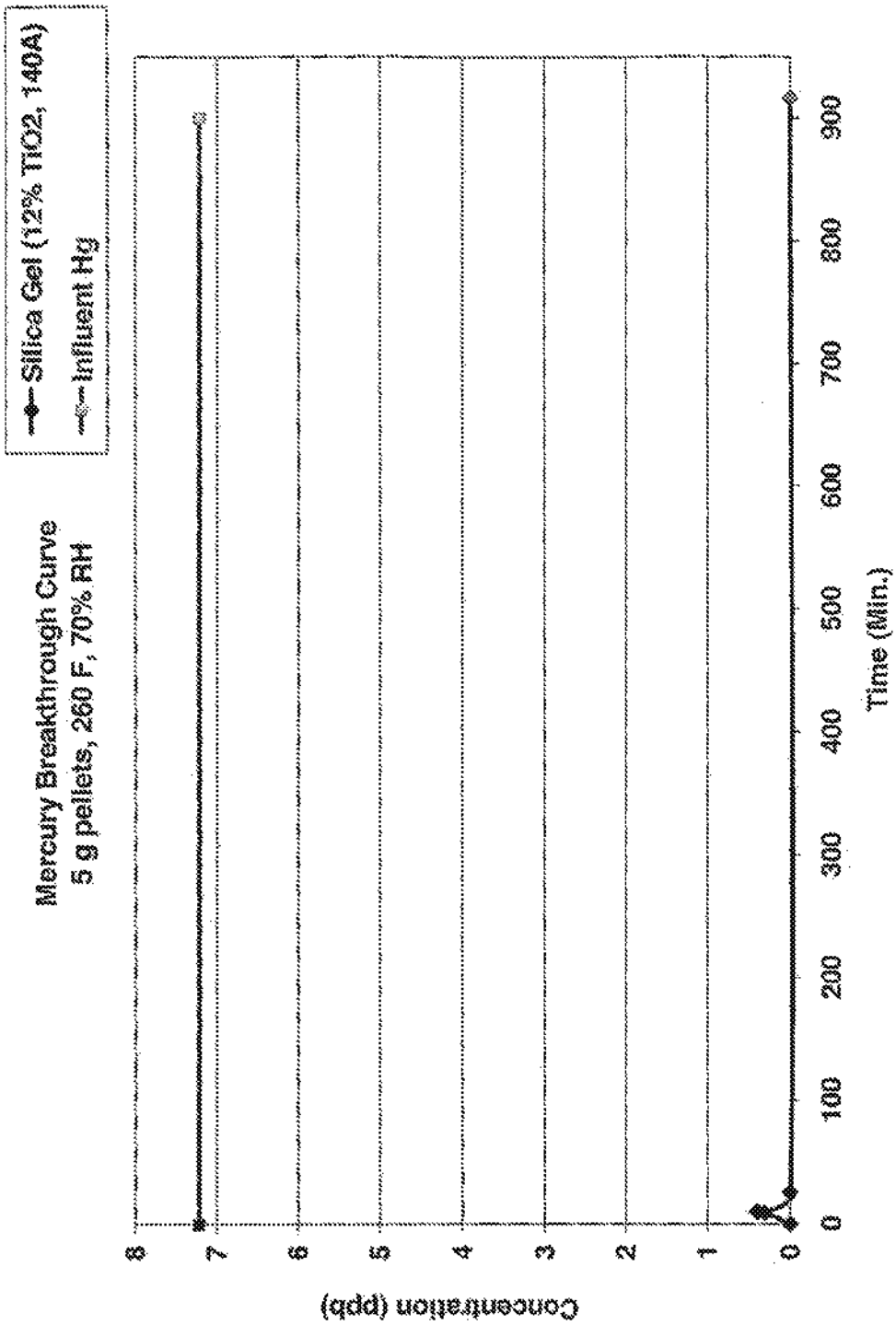

Mercury Breakthrough Curve
5 g pellets, 260 F, 70% RH
Silica Gel (12% TiO2, 140A)
Influent Hg
Concentration (ppb)
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
700
800
900
Time (Min.)

FIG 7

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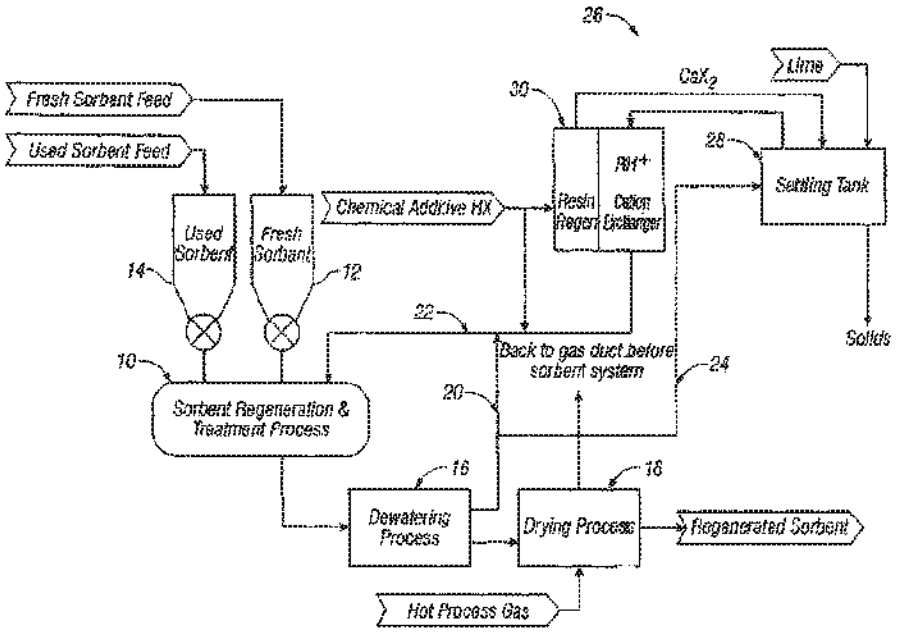
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[Continued on next page]

(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 elementary 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.

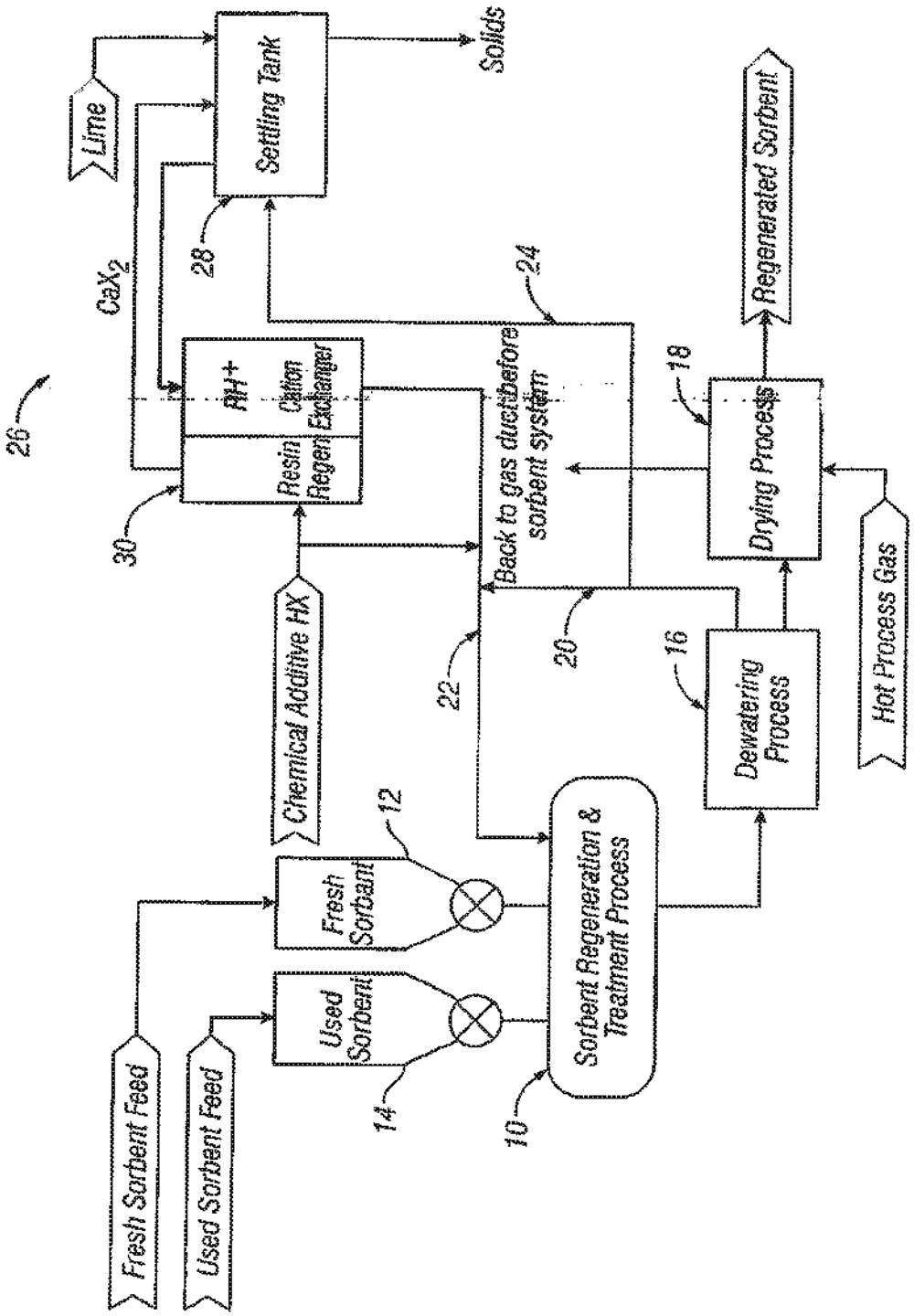


FIG. 1

BHE et al. EXHIBIT 1023
Page 53

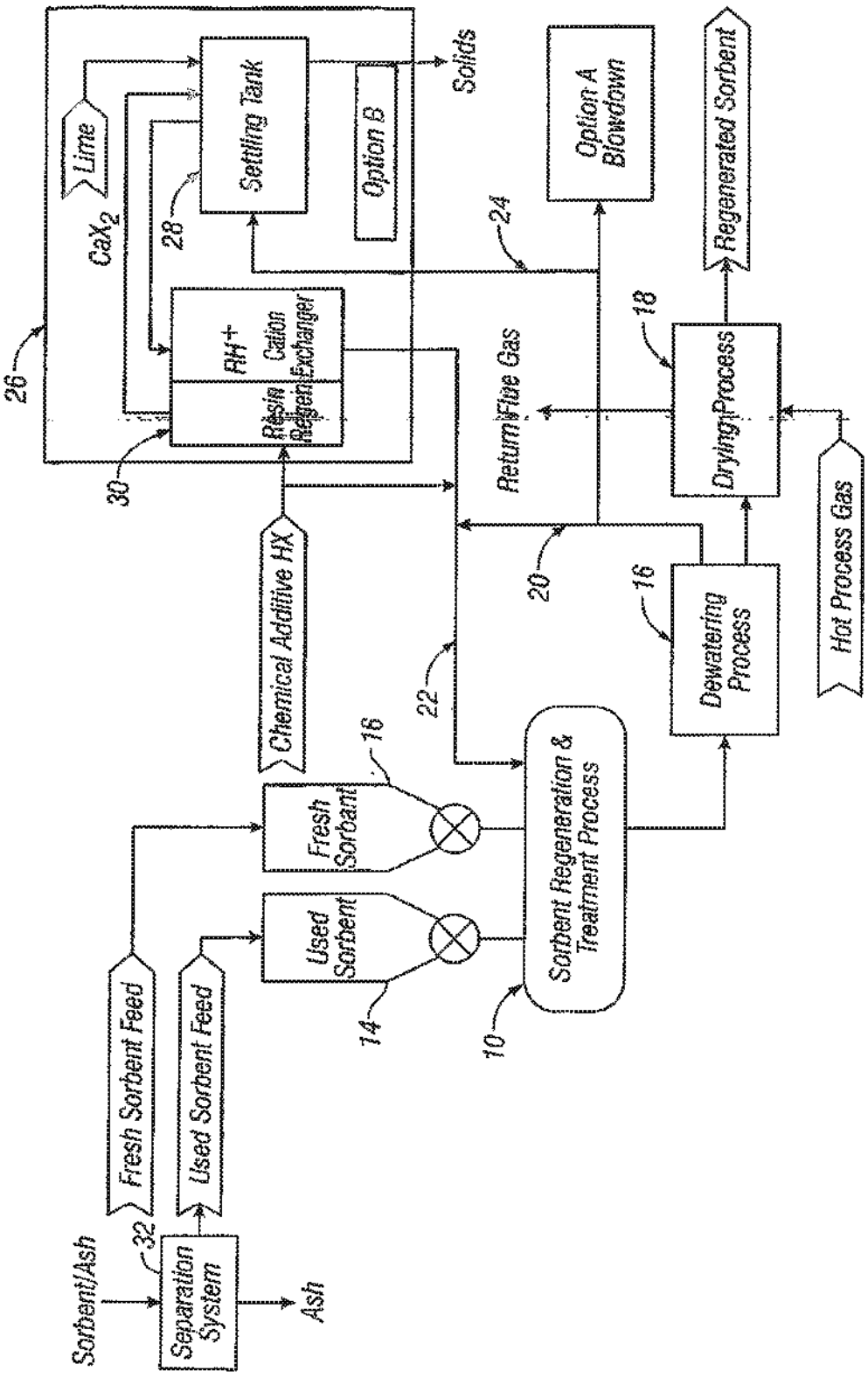

Sorbent/Ash
Separation System
32
Ash
Fresh Sorbent Feed
Used Sorbent Feed
Fresh Sorbent
Used Sorbent
16
14
Chemical Additive HX
26
30
Lime
CaX_2
28
Settling Tank
Option B
Solids
RH+ Cation Exchanger
Resin Regen
Sorbent Regeneration & Treatment Process
10
22
20
Return Flue Gas
24
Option A Blowdown
Dewatering Process
16
18
Drying Process
Regenerated Sorbent
Hot Process Gas

FIG. 2

3/3

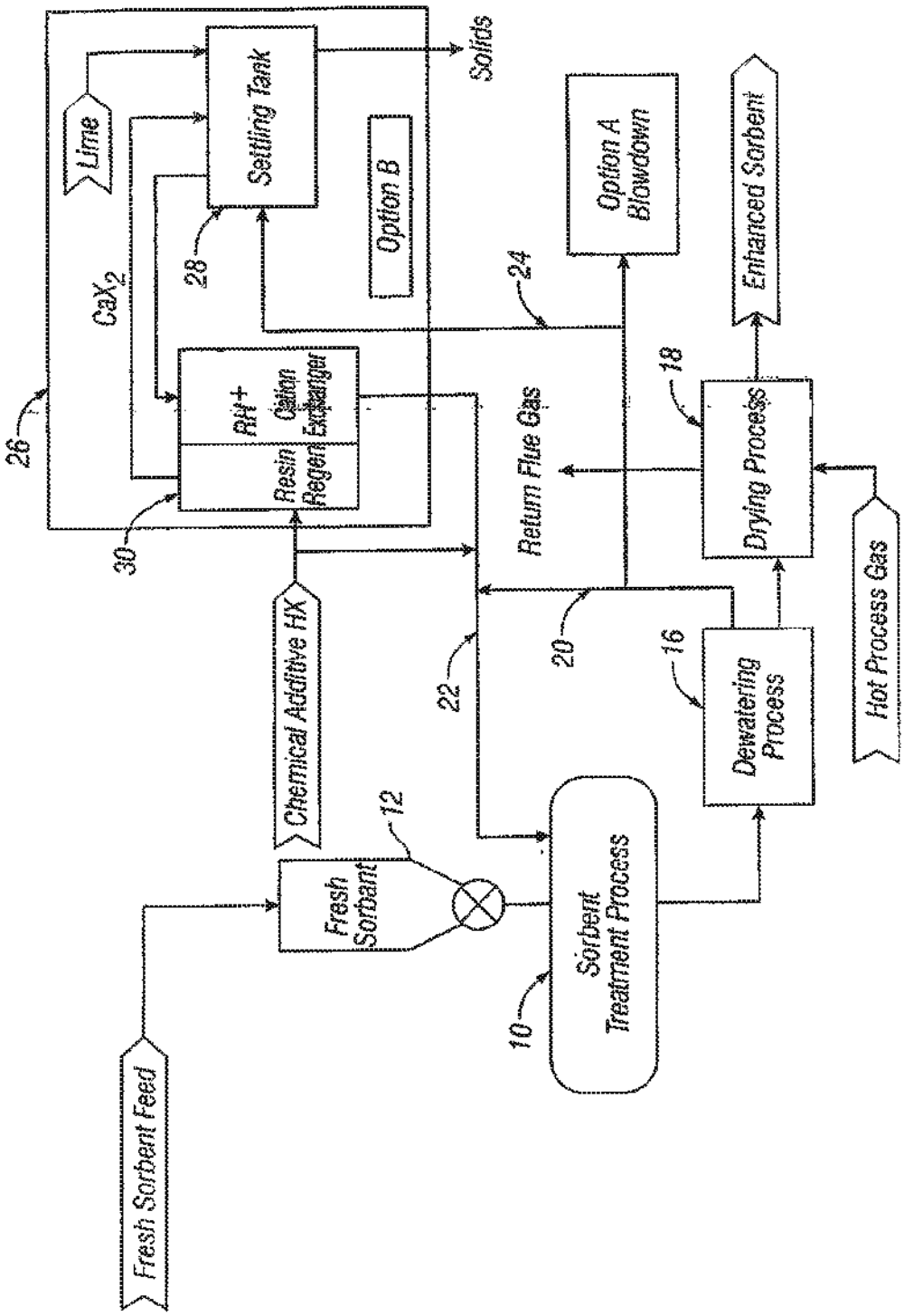


FIG. 3

BHE et al. EXHIBIT 1023
Page 55

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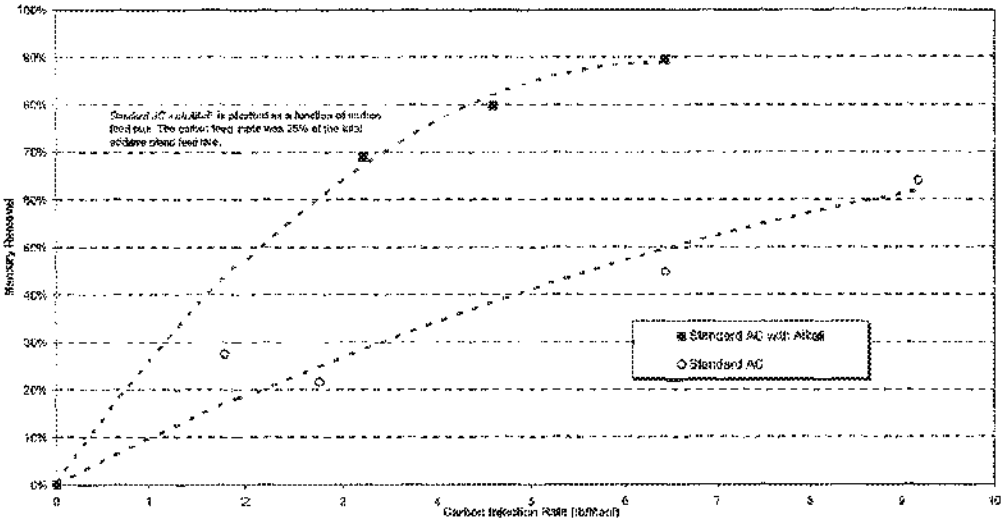
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(54) Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY



(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,

BHE et al. EXHIBIT 1023
Page 58

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

BHE et al. EXHIBIT 1023
Page 59

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.

BHE et al. EXHIBIT 1023
Page 60

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-

BHE et al. EXHIBIT 1023
Page 61

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.

BHE et al. EXHIBIT 1023
Page 62

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

BHE et al. EXHIBIT 1023
Page 63

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.

BHE et al. EXHIBIT 1023
Page 64

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

BHE et al. EXHIBIT 1023
Page 65

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

BHE et al. EXHIBIT 1023
Page 66

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

BHE et al. EXHIBIT 1023
Page 67

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.

BHE et al. EXHIBIT 1023
Page 68

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

BHE et al. EXHIBIT 1023
Page 69

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).

BHE et al. EXHIBIT 1023
Page 70

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

BHE et al. EXHIBIT 1023
Page 71

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

BHE et al. EXHIBIT 1023
Page 72

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

BHE et al. EXHIBIT 1023
Page 73

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

BHE et al. EXHIBIT 1023
Page 74

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

BHE et al. EXHIBIT 1023
Page 75

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

BHE et al. EXHIBIT 1023
Page 76

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.

BHE et al. EXHIBIT 1023
Page 77

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 12.5 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

BHE et al. EXHIBIT 1023
Page 78

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

BHE et al. EXHIBIT 1023
Page 79

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

BHE et al. EXHIBIT 1023
Page 80

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

BHE et al. EXHIBIT 1023
Page 81

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

BHE et al. EXHIBIT 1023
Page 82

(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

BHE et al. EXHIBIT 1023
Page 83

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.

BHE et al. EXHIBIT 1023
Page 84

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

BHE et al. EXHIBIT 1023
Page 85

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.

BHE et al. EXHIBIT 1023
Page 86

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.

BHE et al. EXHIBIT 1023
Page 87

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

BHE et al. EXHIBIT 1023
Page 88

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.

BHE et al. EXHIBIT 1023
Page 89

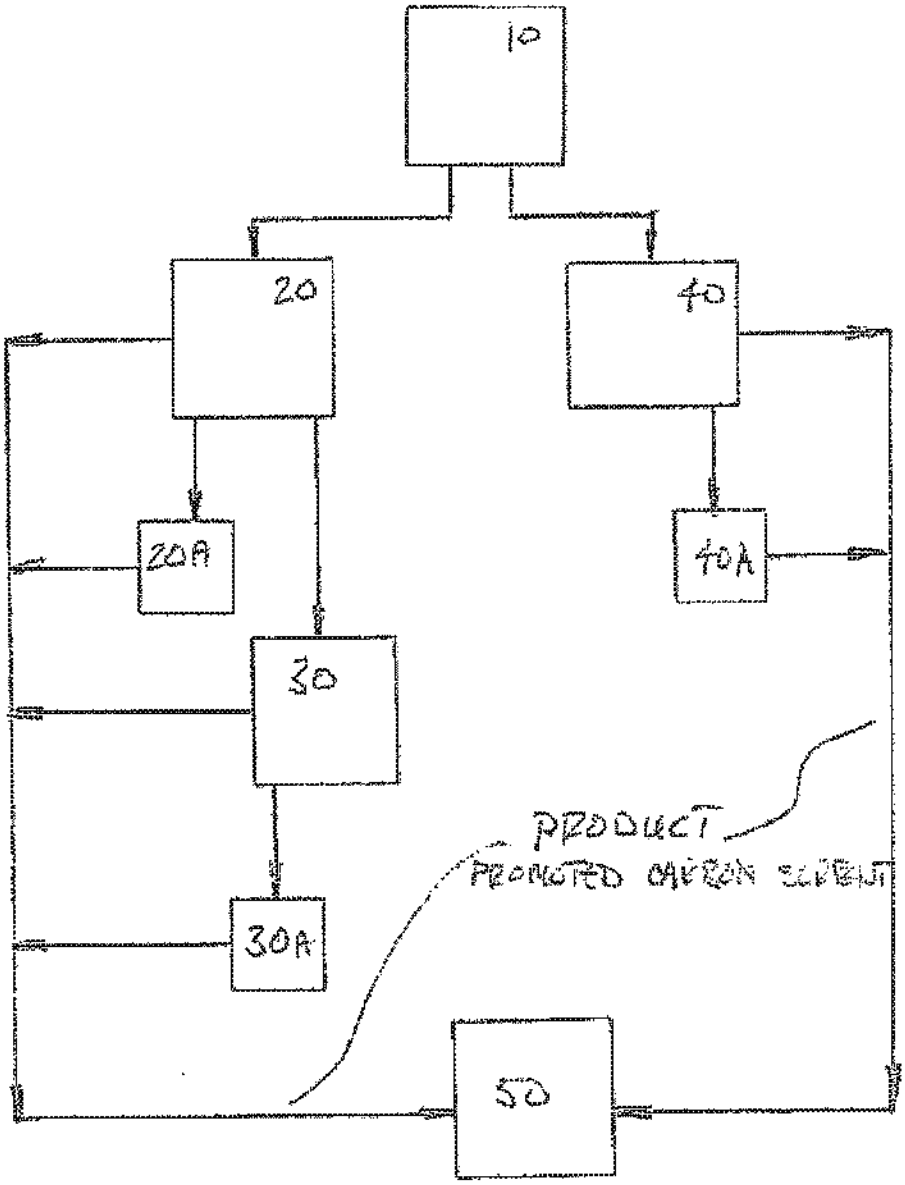


FIG. 1

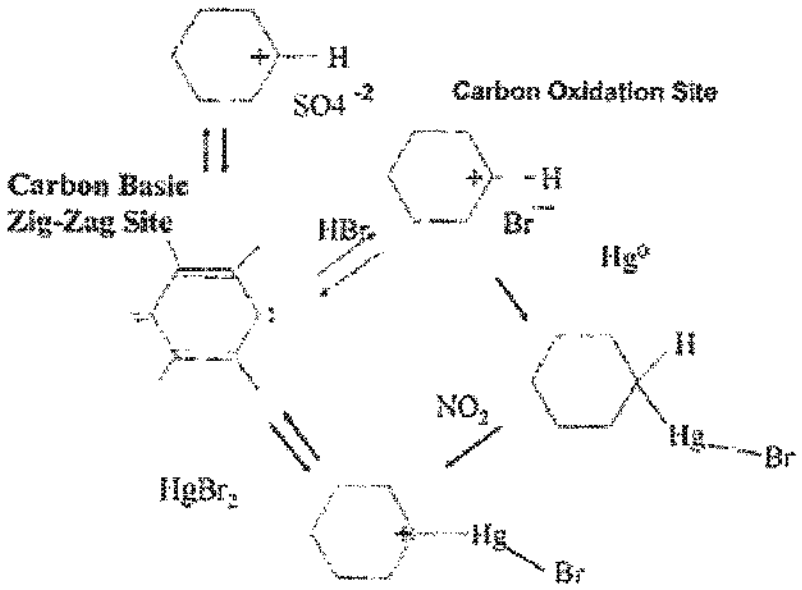

H
SO4 -2
Carbon Oxidation Site
Carbon Basic
Zig-Zag Site
HBr
H
Br
Hg°
H
NO2
Hg
Br
HgBr2
Hg
Br

FIG. 2

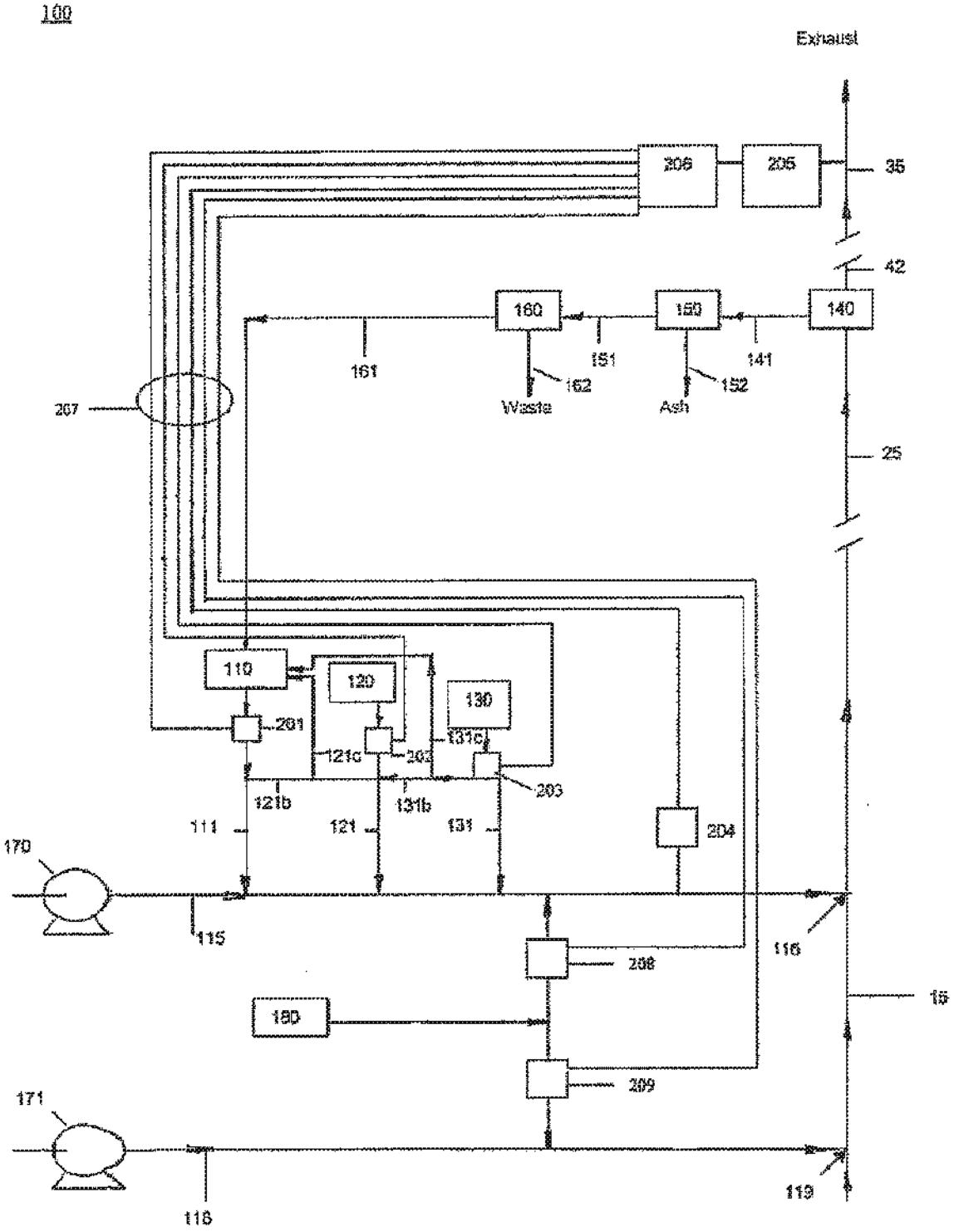

100
Exhaust
206
205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
25
110
120
130
201
121c
203
131c
203
121b
131b
111
121
131
204
170
115
116
208
15
180
209
171
118
119

FIG. 3

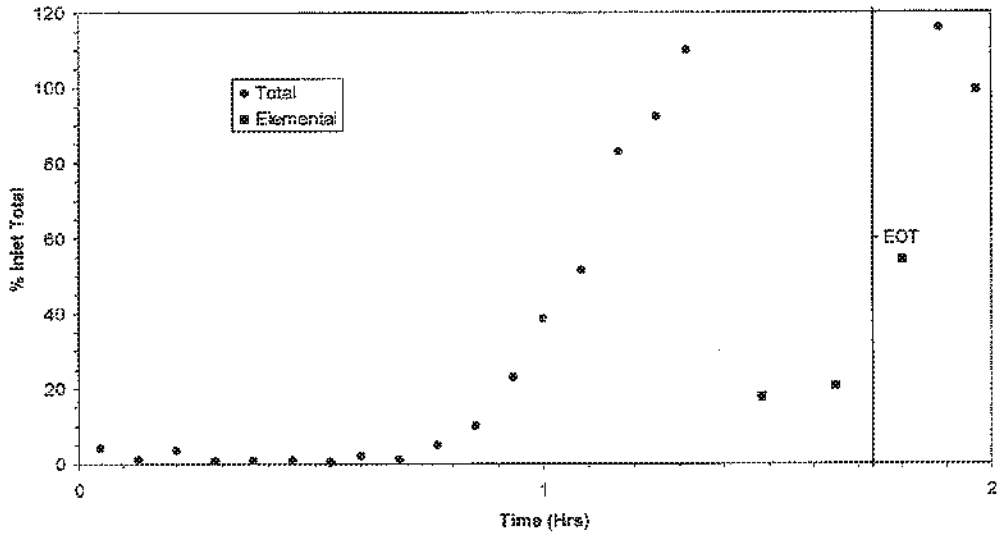

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
2
Time (Hrs)

FIG. 4

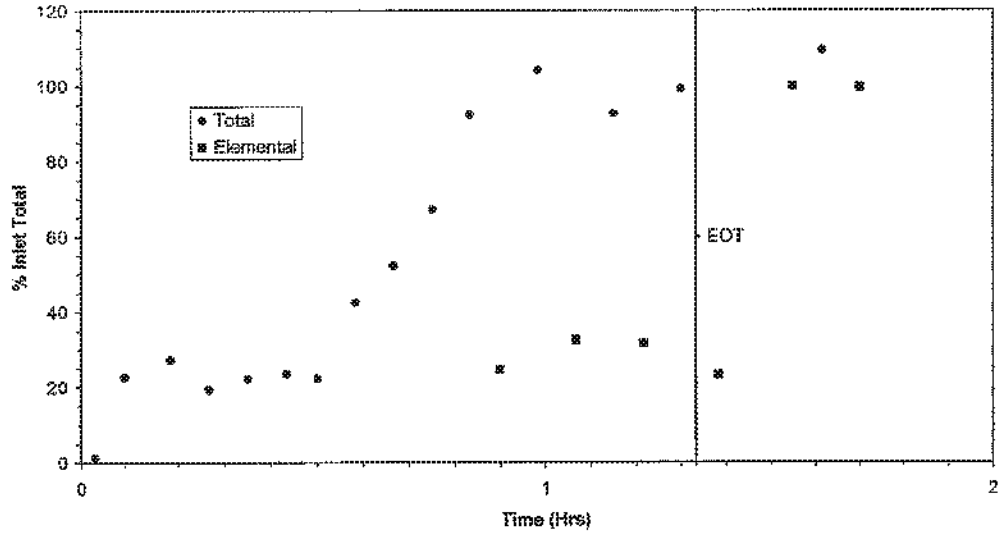

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
2
Time (Hrs)

FIG. 5

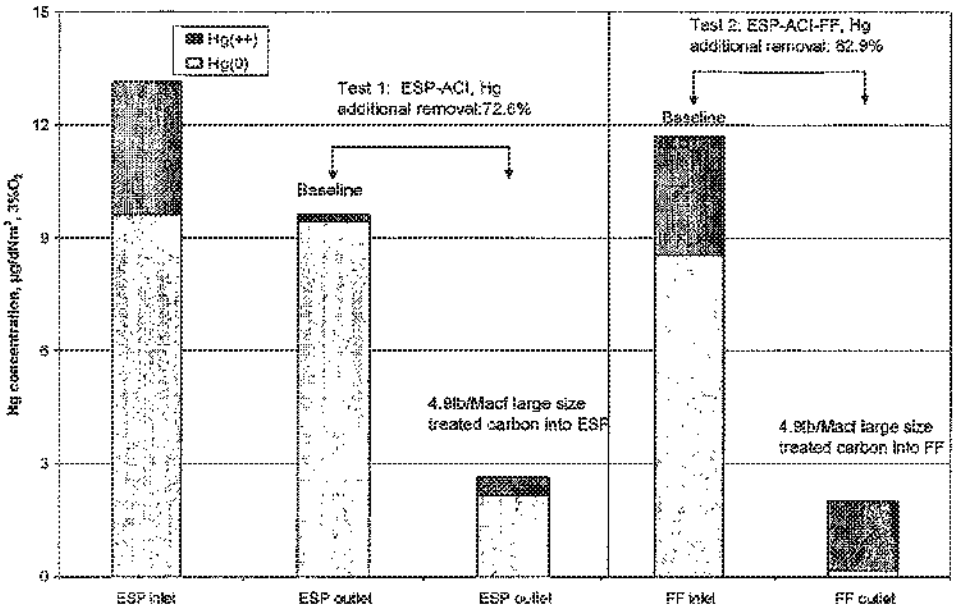

Hg(++)
Hg(0)
Test 1: ESP-ACI, Hg additional removal:72.6%
Baseline
4.9lb/Macf large size treated carbon into ESP
Test 2: ESP-ACI-FF, Hg additional removal: 82.9%
Baseline
4.9lb/Macf large size treated carbon into FF
Hg concentration, µg/dNm³, 3%O₂
ESP inlet
ESP outlet
ESP outlet
FF inlet
FF outlet

FIG. 6

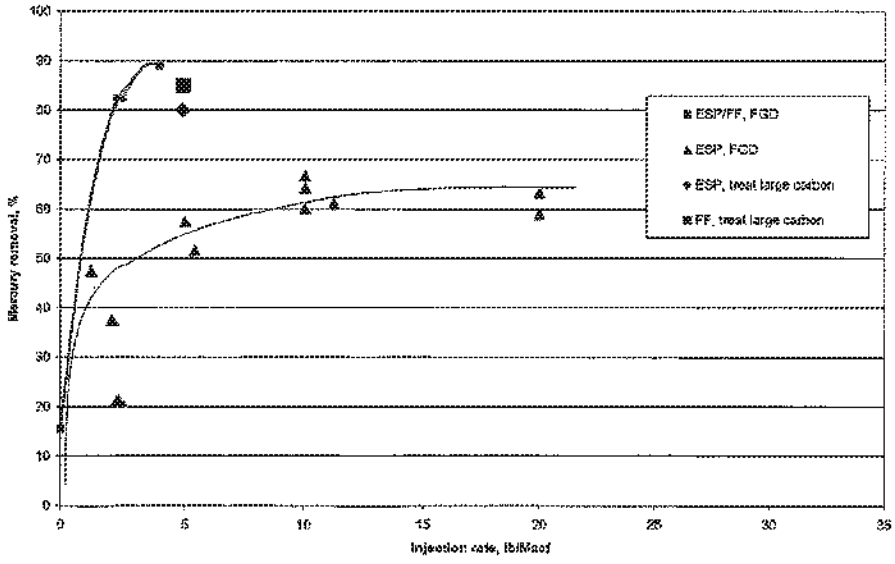

ESP/FF, FGD
ESP, FGD
ESP, treat large carbon
FF, treat large carbon
Mercury removal, %
Injection rate, lb/Macf

FIG. 7

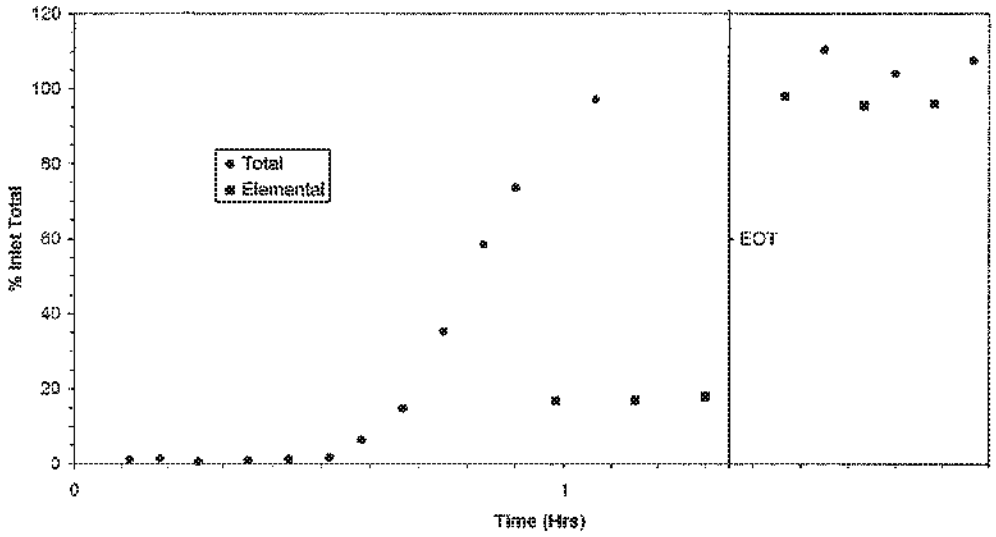

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
Time (Hrs)

FIG. 8

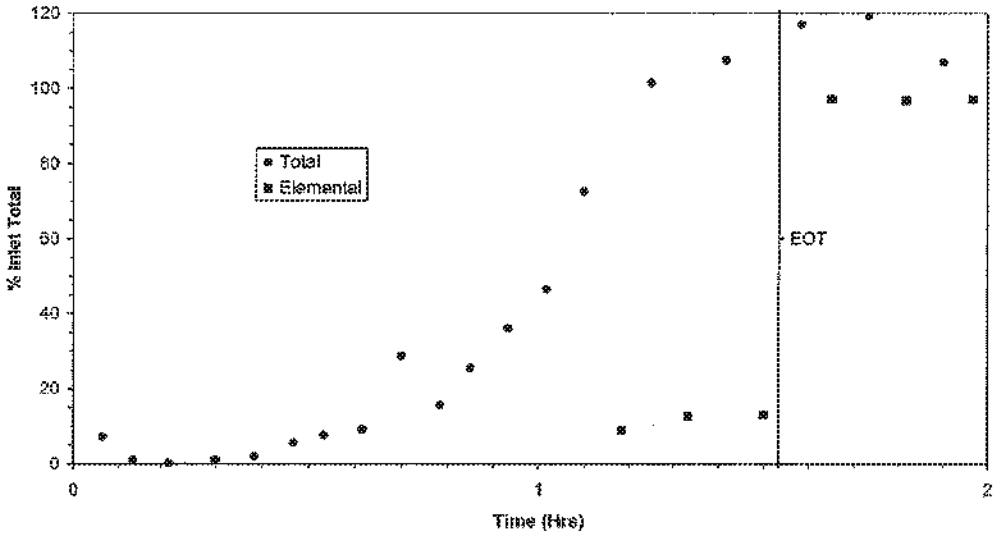

120
100
80
60
40
20
0
% Inlet Total
Total
Elemental
EOT
0
1
2
Time (Hrs)

FIG. 9

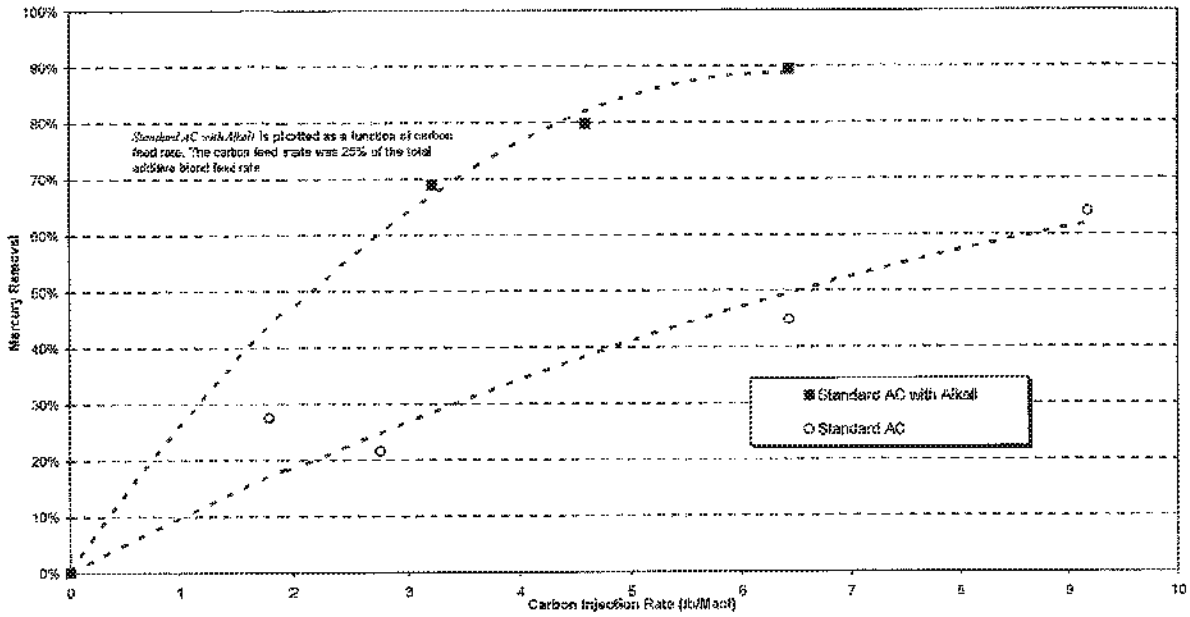

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
Mercury Removal
0
1
2
3
4
5
6
7
8
9
10
Carbon Injection Rate (lb/Macf)
Standard AC with Alkali is plotted as a function of carbon feed rate. The carbon feed rate was 25% of the total additive blend feed rate
Standard AC with Alkali
Standard AC

FIG. 10

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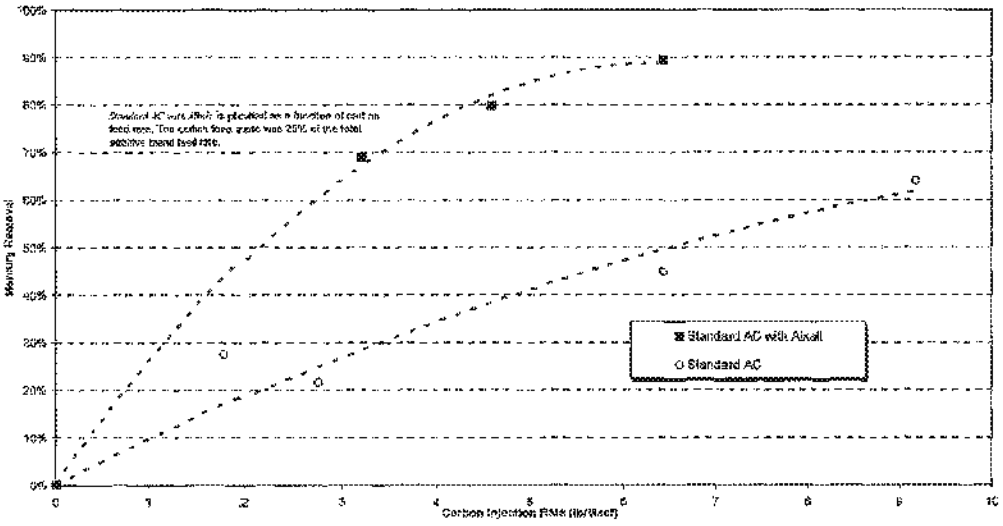
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(54) Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY



(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.

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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,

BHE et al. EXHIBIT 1023
Page 100

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

BHE et al. EXHIBIT 1023
Page 101

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.

BHE et al. EXHIBIT 1023
Page 102

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-

BHE et al. EXHIBIT 1023
Page 103

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.

BHE et al. EXHIBIT 1023
Page 104

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

BHE et al. EXHIBIT 1023
Page 105

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.

BHE et al. EXHIBIT 1023
Page 106

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

BHE et al. EXHIBIT 1023
Page 107

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

BHE et al. EXHIBIT 1023
Page 108

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

BHE et al. EXHIBIT 1023
Page 109

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.

BHE et al. EXHIBIT 1023
Page 110

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

BHE et al. EXHIBIT 1023
Page 111

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).

BHE et al. EXHIBIT 1023
Page 112

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

BHE et al. EXHIBIT 1023
Page 113

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

BHE et al. EXHIBIT 1023
Page 114

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

BHE et al. EXHIBIT 1023
Page 115

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

BHE et al. EXHIBIT 1023
Page 116

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

BHE et al. EXHIBIT 1023
Page 117

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

BHE et al. EXHIBIT 1023
Page 118

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.

BHE et al. EXHIBIT 1023
Page 119

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

BHE et al. EXHIBIT 1023
Page 120

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

BHE et al. EXHIBIT 1023
Page 121

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

BHE et al. EXHIBIT 1023
Page 122

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

BHE et al. EXHIBIT 1023
Page 123

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

BHE et al. EXHIBIT 1023
Page 124

(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

BHE et al. EXHIBIT 1023
Page 125

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.

BHE et al. EXHIBIT 1023
Page 126

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

BHE et al. EXHIBIT 1023
Page 127

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.

BHE et al. EXHIBIT 1023
Page 128

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.

BHE et al. EXHIBIT 1023
Page 129

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

BHE et al. EXHIBIT 1023
Page 130

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.

BHE et al. EXHIBIT 1023
Page 131

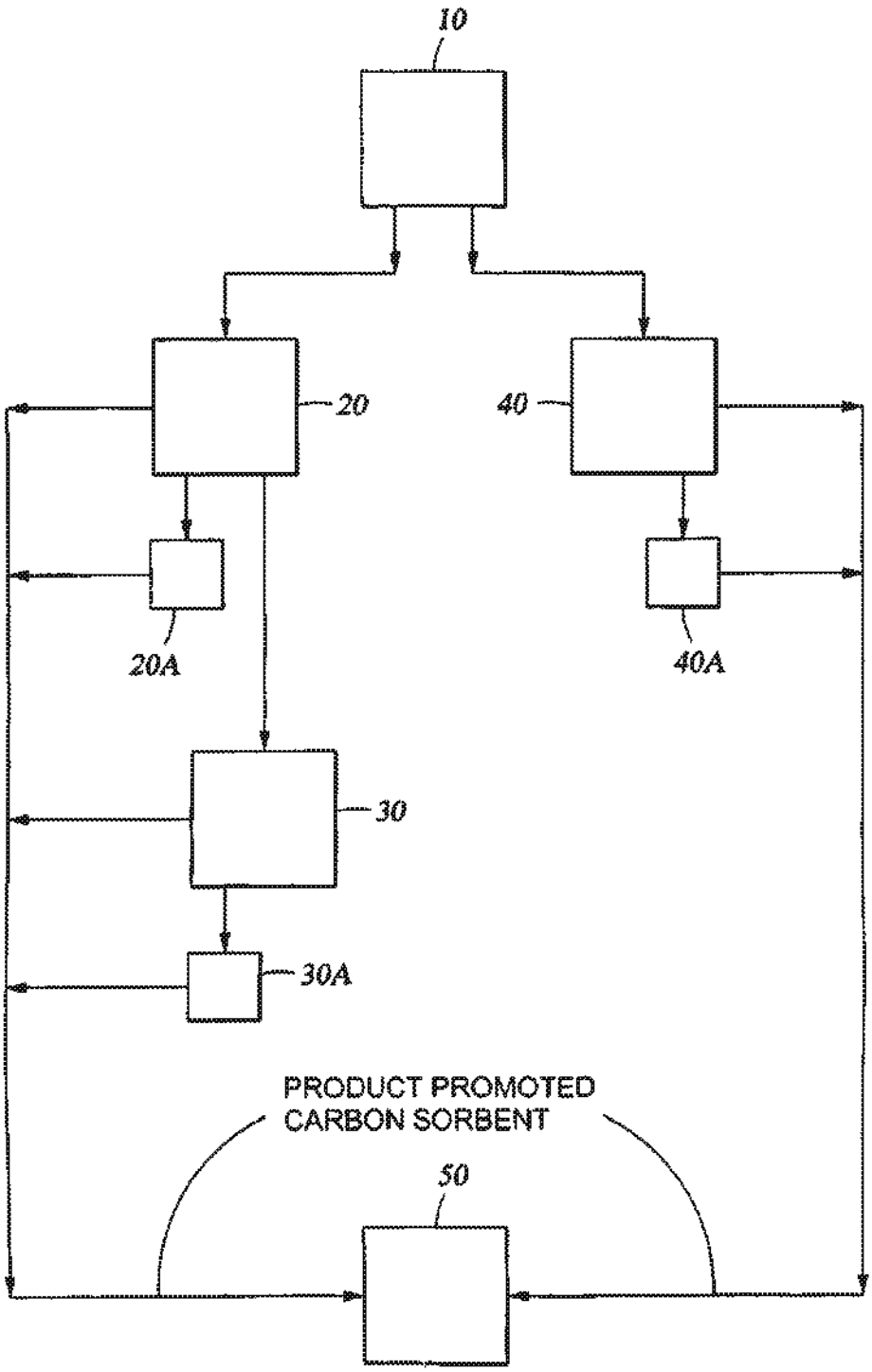


Fig. 1

BHE et al. EXHIBIT 1023
Page 132

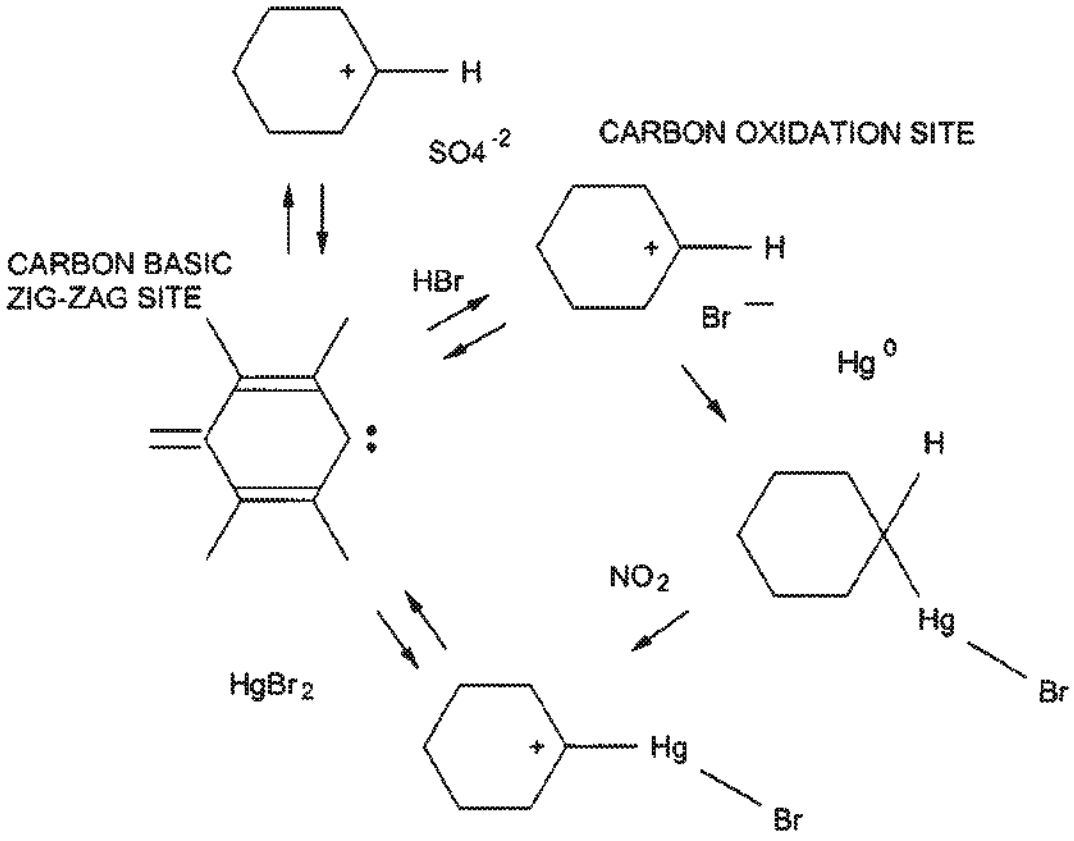


Fig. 2

BHE et al. EXHIBIT 1023
Page 133

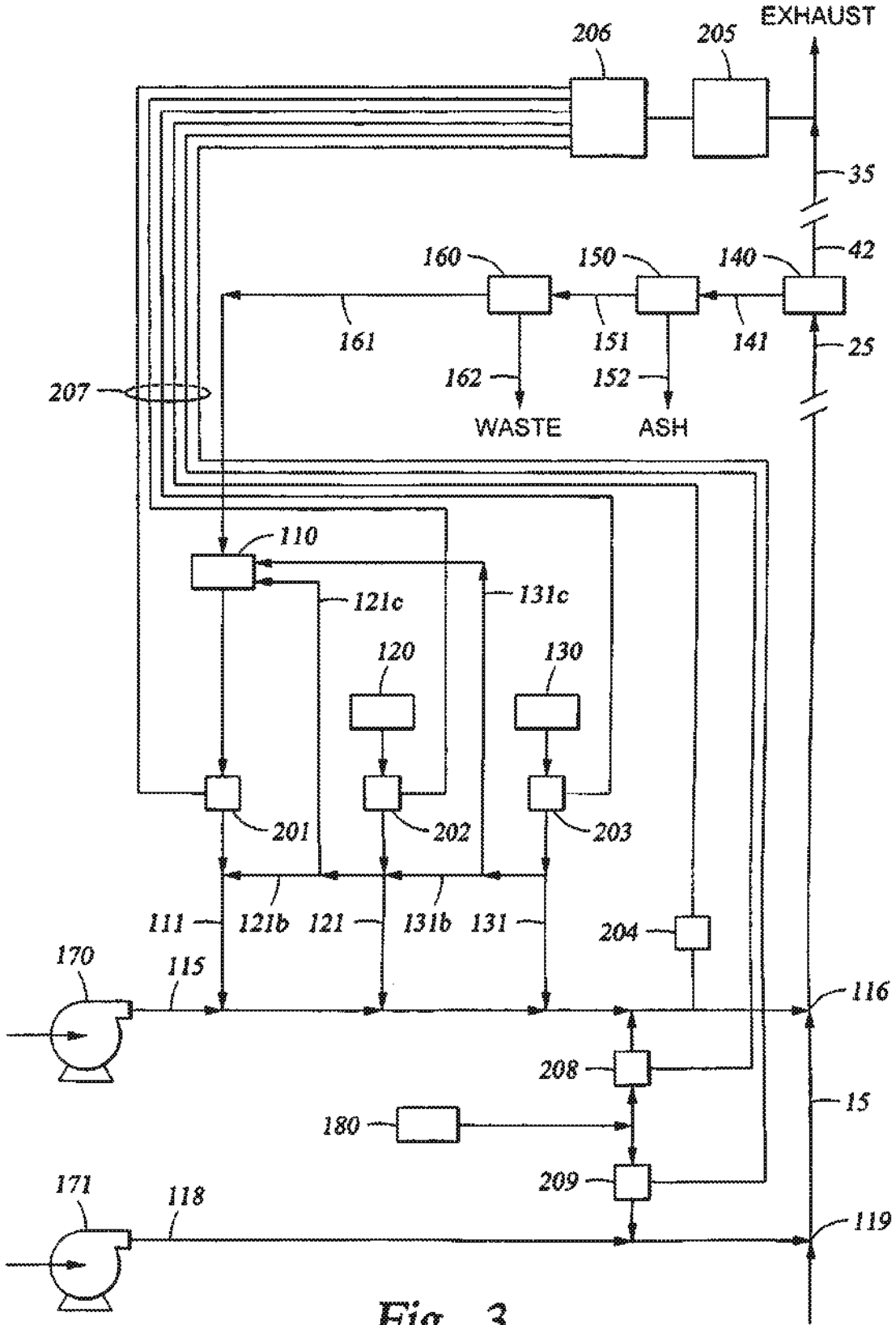


Fig. 3

BHE et al. EXHIBIT 1023
Page 134

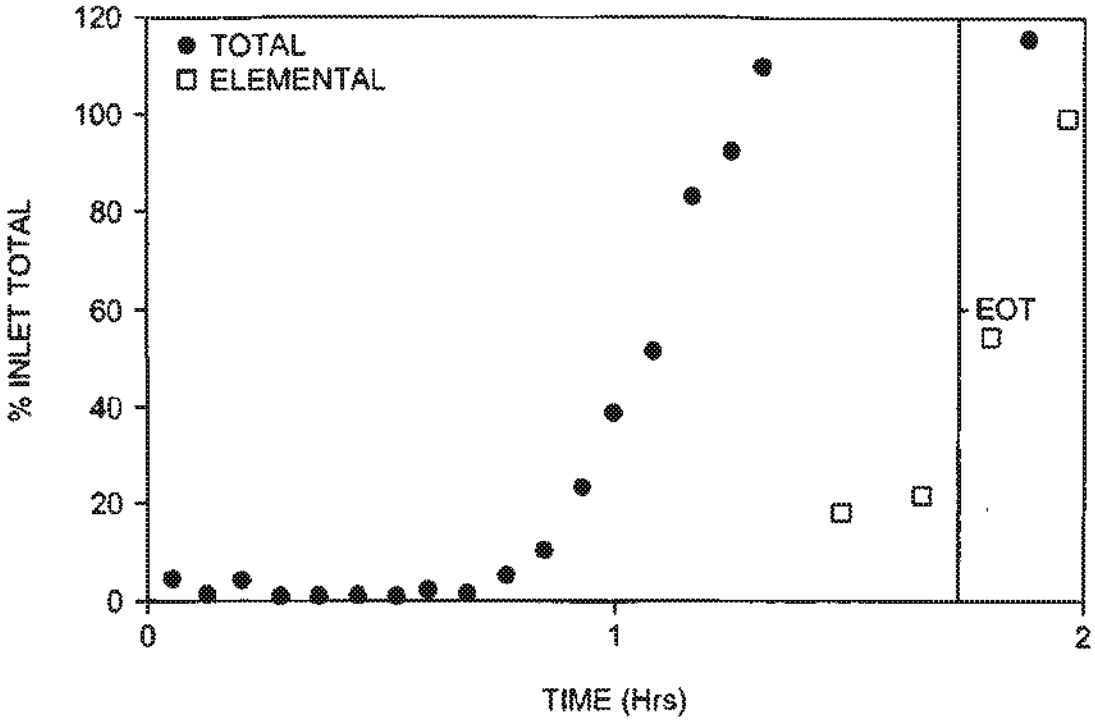


Fig. 4

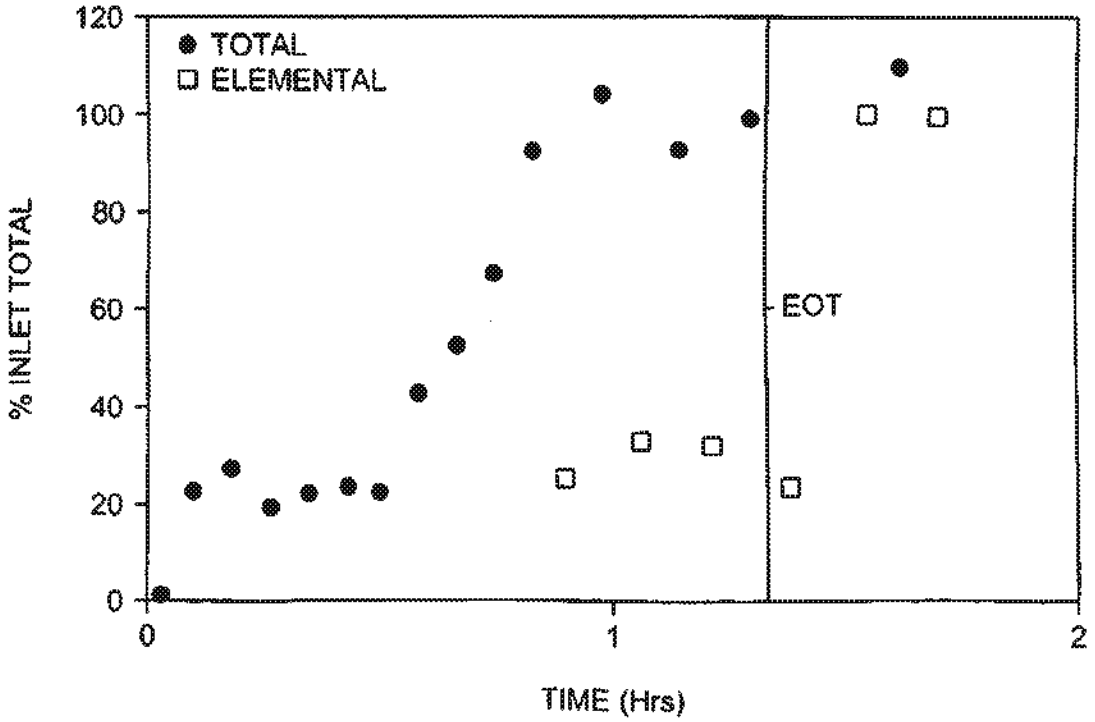


Fig. 5

BHE et al. EXHIBIT 1023
Page 135

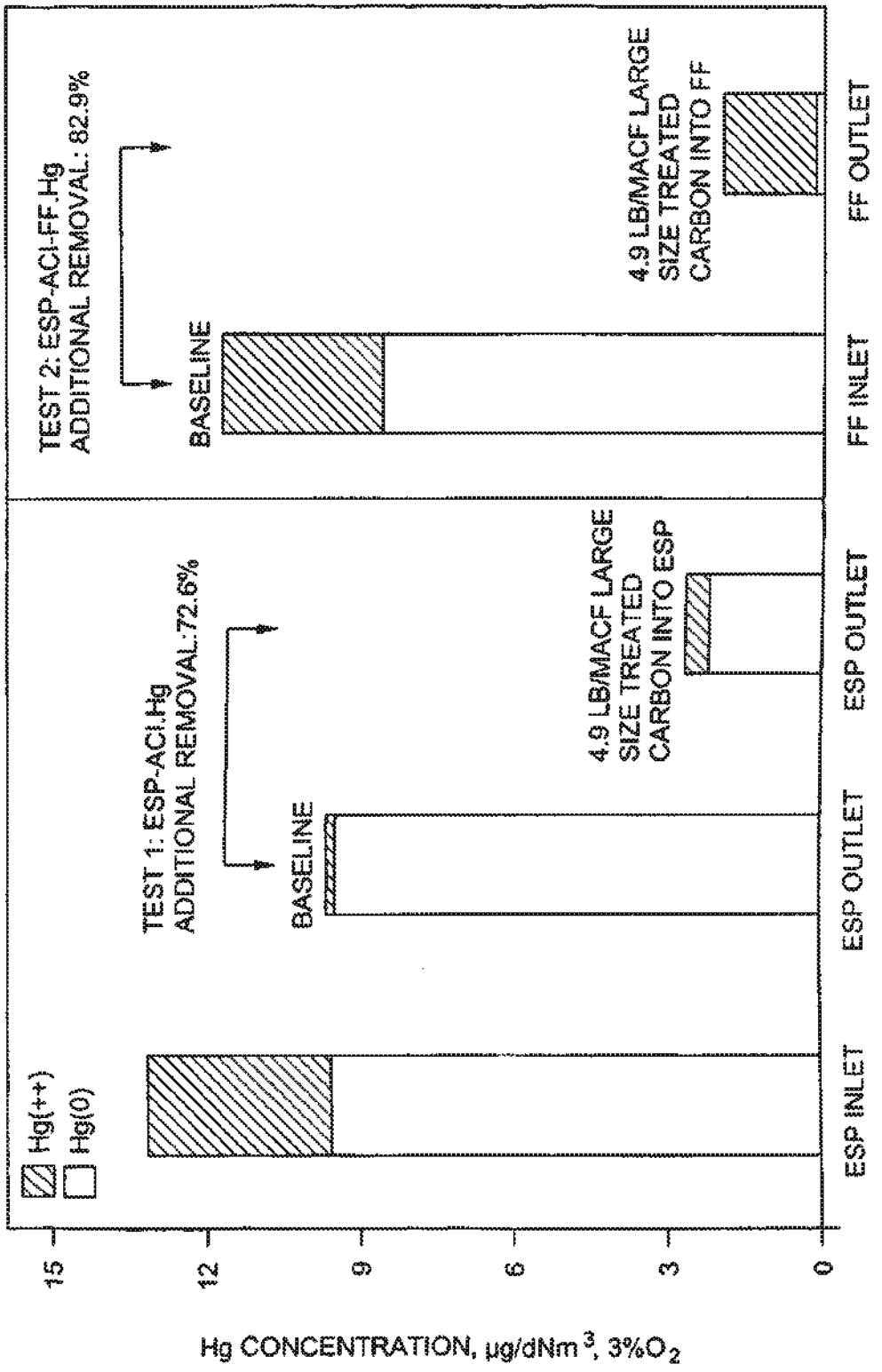


Fig. 6

BHE et al. EXHIBIT 1023
Page 136

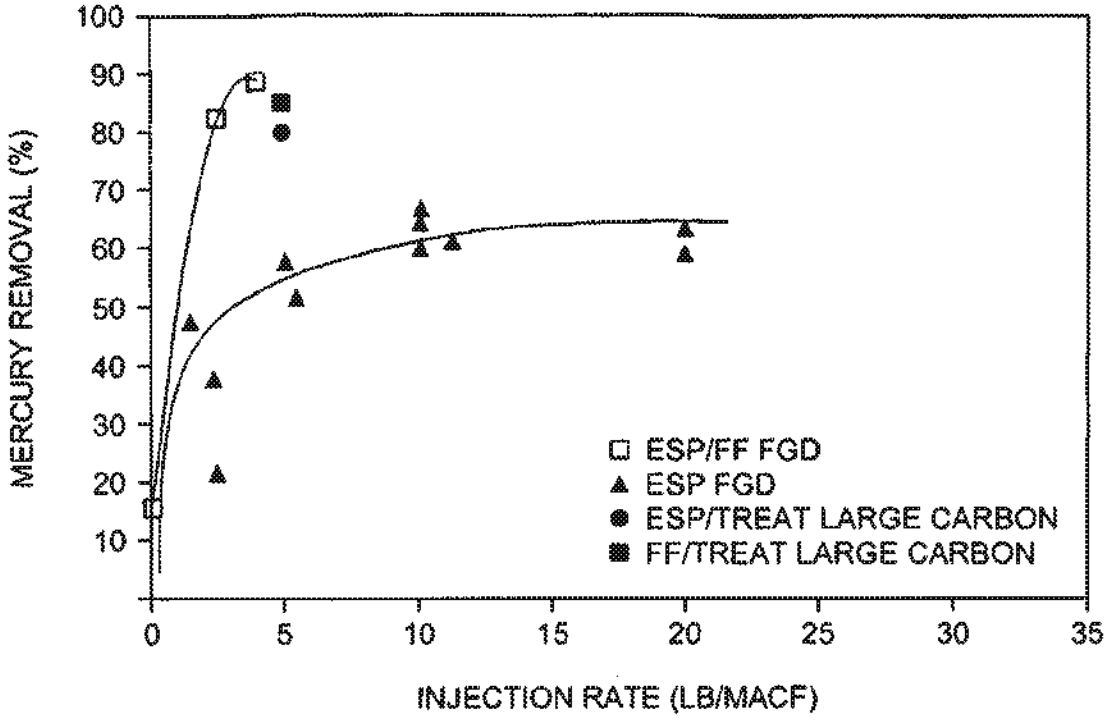


Fig. 7

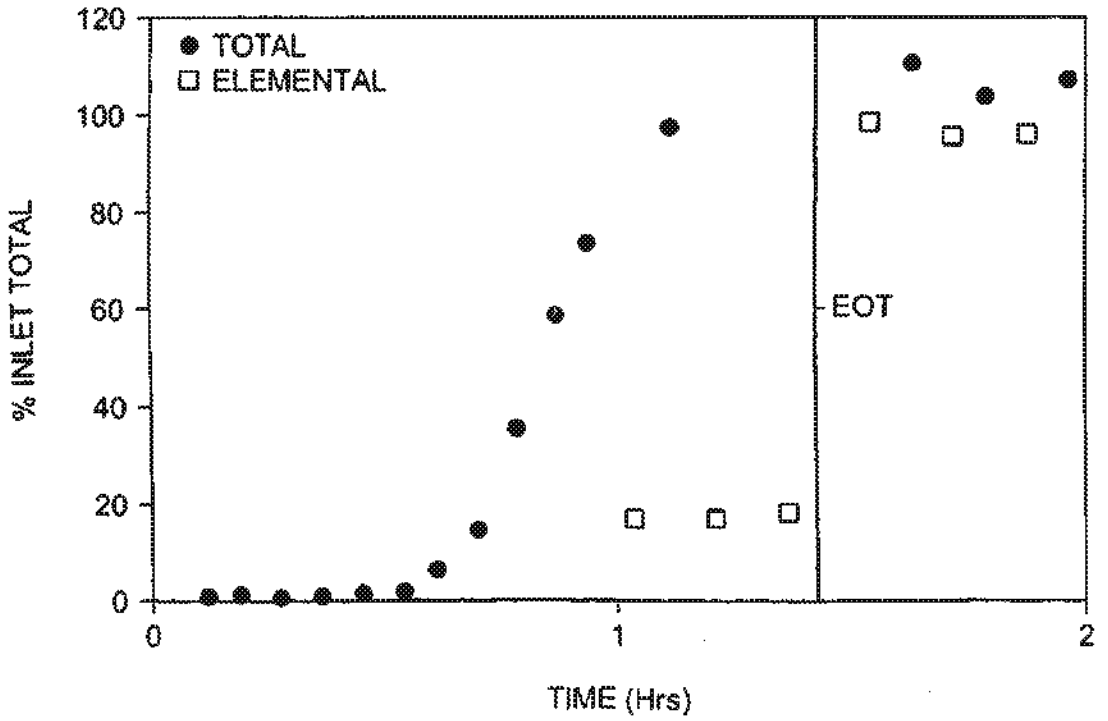


Fig. 8

BHE et al. EXHIBIT 1023
Page 137

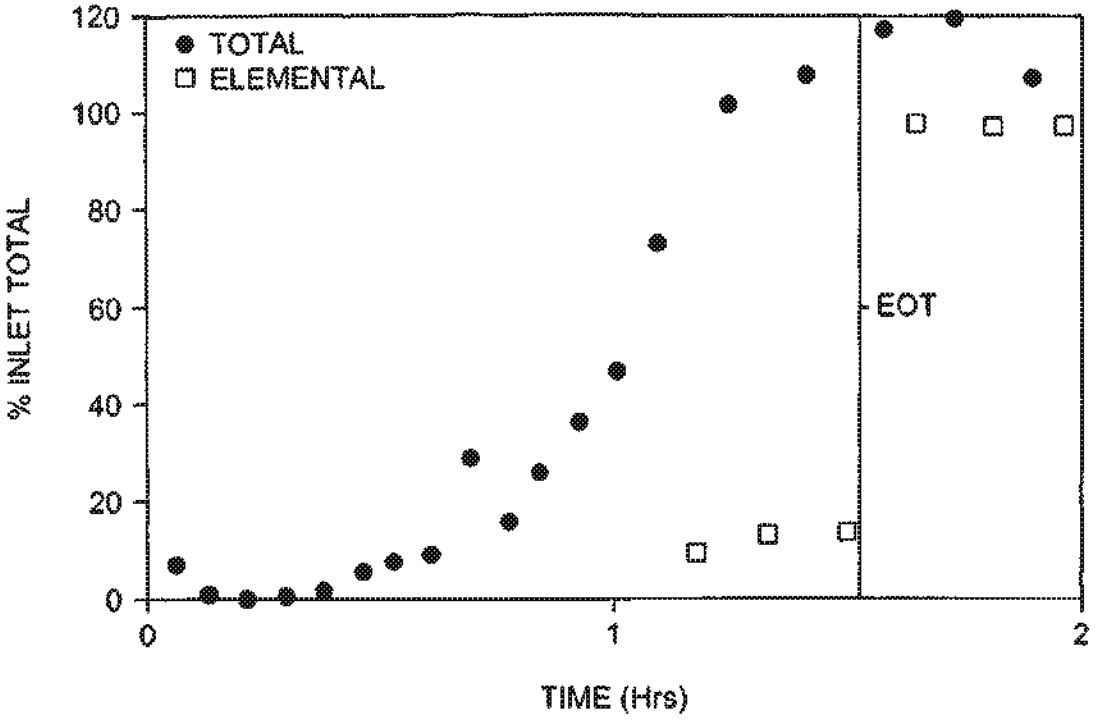


Fig. 9

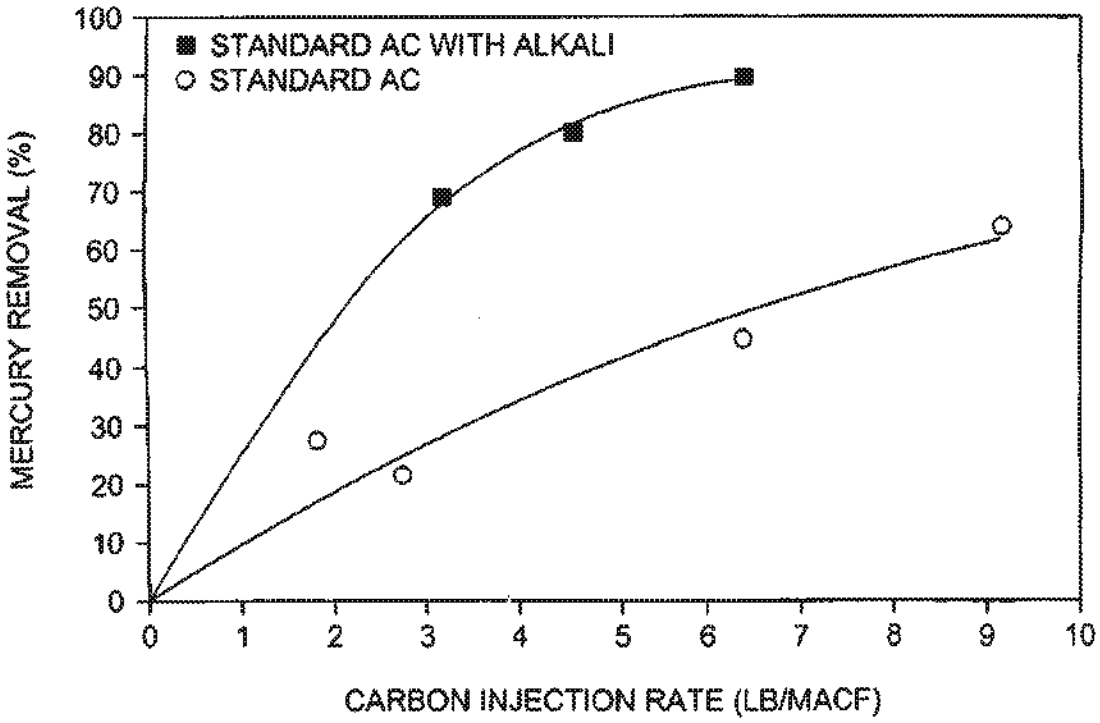


Fig. 10

BHE et al. EXHIBIT 1023
Page 138

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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.

WO 2006/099611 A1

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

BHE et al. EXHIBIT 1023
Page 140

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

BHE et al. EXHIBIT 1023
Page 141

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

BHE et al. EXHIBIT 1023
Page 142

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.

BHE et al. EXHIBIT 1023
Page 143

[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

BHE et al. EXHIBIT 1023
Page 144

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.

BHE et al. EXHIBIT 1023
Page 145

[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.

BHE et al. EXHIBIT 1023
Page 146

[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

BHE et al. EXHIBIT 1023
Page 147

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

BHE et al. EXHIBIT 1023
Page 148

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

BHE et al. EXHIBIT 1023
Page 149

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

BHE et al. EXHIBIT 1023
Page 150

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

BHE et al. EXHIBIT 1023
Page 151

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.

BHE et al. EXHIBIT 1023
Page 152

[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

BHE et al. EXHIBIT 1023
Page 153

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

BHE et al. EXHIBIT 1023
Page 154

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

BHE et al. EXHIBIT 1023
Page 155

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

BHE et al. EXHIBIT 1023
Page 156

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

BHE et al. EXHIBIT 1023
Page 157

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-

BHE et al. EXHIBIT 1023
Page 158

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

BHE et al. EXHIBIT 1023
Page 159

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

BHE et al. EXHIBIT 1023
Page 160

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

BHE et al. EXHIBIT 1023
Page 161

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

BHE et al. EXHIBIT 1023
Page 162

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 ($CaCO_3$·$MgCO_3$) 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

BHE et al. EXHIBIT 1023
Page 163

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

BHE et al. EXHIBIT 1023
Page 164

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

BHE et al. EXHIBIT 1023
Page 165

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

BHE et al. EXHIBIT 1023
Page 166

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

BHE et al. EXHIBIT 1023
Page 167

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.

BHE et al. EXHIBIT 1023
Page 168

[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

BHE et al. EXHIBIT 1023
Page 169

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.

BHE et al. EXHIBIT 1023
Page 170

[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

BHE et al. EXHIBIT 1023
Page 171

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

BHE et al. EXHIBIT 1023
Page 172

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 –

BHE et al. EXHIBIT 1023
Page 173

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.

BHE et al. EXHIBIT 1023
Page 174

[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

BHE et al. EXHIBIT 1023
Page 175

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

BHE et al. EXHIBIT 1023
Page 176

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.

BHE et al. EXHIBIT 1023
Page 177

[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.

BHE et al. EXHIBIT 1023
Page 178

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.

BHE et al. EXHIBIT 1023
Page 179

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

BHE et al. EXHIBIT 1023
Page 180

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

BHE et al. EXHIBIT 1023
Page 181

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

BHE et al. EXHIBIT 1023
Page 182

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).

BHE et al. EXHIBIT 1023
Page 183

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.

BHE et al. EXHIBIT 1023
Page 184

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.

BHE et al. EXHIBIT 1023
Page 185

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.

BHE et al. EXHIBIT 1023
Page 186

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

BHE et al. EXHIBIT 1023
Page 187

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.

BHE et al. EXHIBIT 1023
Page 188

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.

BHE et al. EXHIBIT 1023
Page 189

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.

BHE et al. EXHIBIT 1023
Page 190

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.

BHE et al. EXHIBIT 1023
Page 191

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.

BHE et al. EXHIBIT 1023
Page 192

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.

BHE et al. EXHIBIT 1023
Page 193

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.

BHE et al. EXHIBIT 1023
Page 194

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.

BHE et al. EXHIBIT 1023
Page 195

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.

BHE et al. EXHIBIT 1023
Page 196

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)**

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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 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 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.

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.

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PCT

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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).

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(74) Agents: WESTBY, Timothy, S. et al.; CONLEY ROSE, P.C., P.O. Box 3267, Houston, Texas 77253-3267 (US).

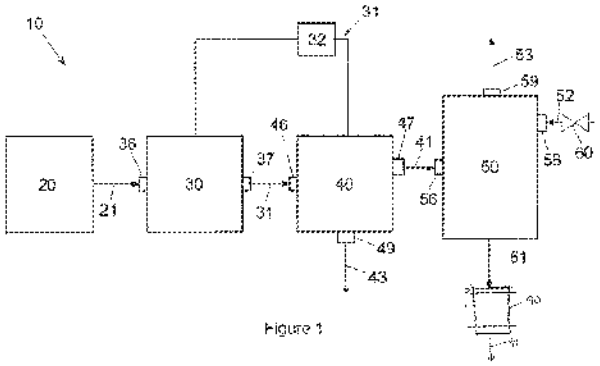
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(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, 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

(54) Title: APPLICATION OF MICROTURBINES TO CONTROL EMISSIONS FROM ASSOCIATED GAS



(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.

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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
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☐ 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
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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	HAN, JAE SEOB
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-5439

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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(71) Applicant *(for all designated States except US)*: **ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION** [US/US]; 15 North 23rd Street, Grand Forks, ND 58202-9018 (US).

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(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, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2010/123609 A1

(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.

BHE et al. EXHIBIT 1023
Page 207

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

BHE et al. EXHIBIT 1023
Page 208

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.

BHE et al. EXHIBIT 1023
Page 209

[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

BHE et al. EXHIBIT 1023
Page 210

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

BHE et al. EXHIBIT 1023
Page 211

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,

BHE et al. EXHIBIT 1023
Page 212

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,

BHE et al. EXHIBIT 1023
Page 213

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

BHE et al. EXHIBIT 1023
Page 214

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

BHE et al. EXHIBIT 1023
Page 215

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

BHE et al. EXHIBIT 1023
Page 216

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

BHE et al. EXHIBIT 1023
Page 217

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.

BHE et al. EXHIBIT 1023
Page 218

[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.

BHE et al. EXHIBIT 1023
Page 219

[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).

BHE et al. EXHIBIT 1023
Page 220

[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

BHE et al. EXHIBIT 1023
Page 221

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

BHE et al. EXHIBIT 1023
Page 222

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

BHE et al. EXHIBIT 1023
Page 223

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

BHE et al. EXHIBIT 1023
Page 224

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.

BHE et al. EXHIBIT 1023
Page 225

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

BHE et al. EXHIBIT 1023
Page 226

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 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.

BHE et al. EXHIBIT 1023
Page 227

[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

BHE et al. EXHIBIT 1023
Page 228

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

BHE et al. EXHIBIT 1023
Page 229

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

BHE et al. EXHIBIT 1023
Page 230

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.

BHE et al. EXHIBIT 1023
Page 231

- 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

BHE et al. EXHIBIT 1023
Page 232

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

BHE et al. EXHIBIT 1023
Page 233

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.

BHE et al. EXHIBIT 1023
Page 234

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.

BHE et al. EXHIBIT 1023
Page 235

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

BHE et al. EXHIBIT 1023
Page 236

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.

BHE et al. EXHIBIT 1023
Page 237

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.

BHE et al. EXHIBIT 1023
Page 238

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.

BHE et al. EXHIBIT 1023
Page 239

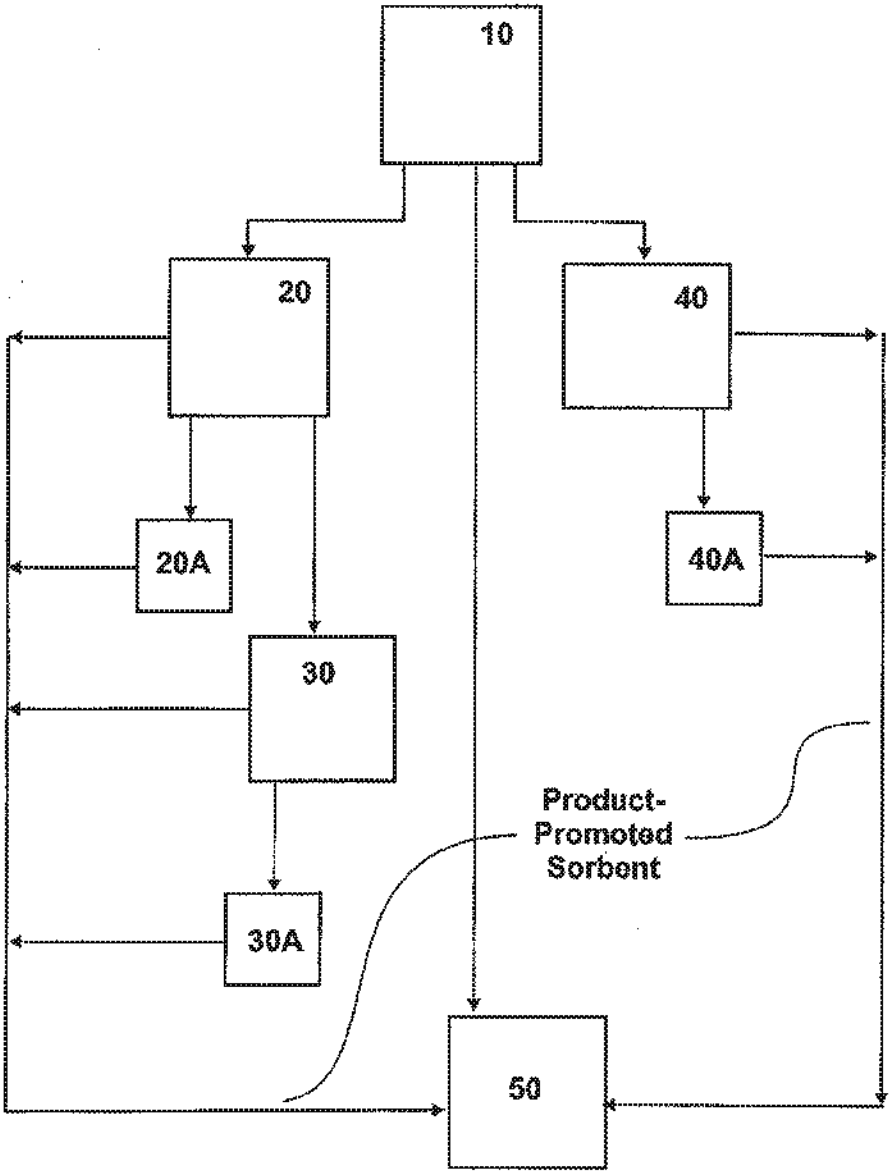


FIG. 1

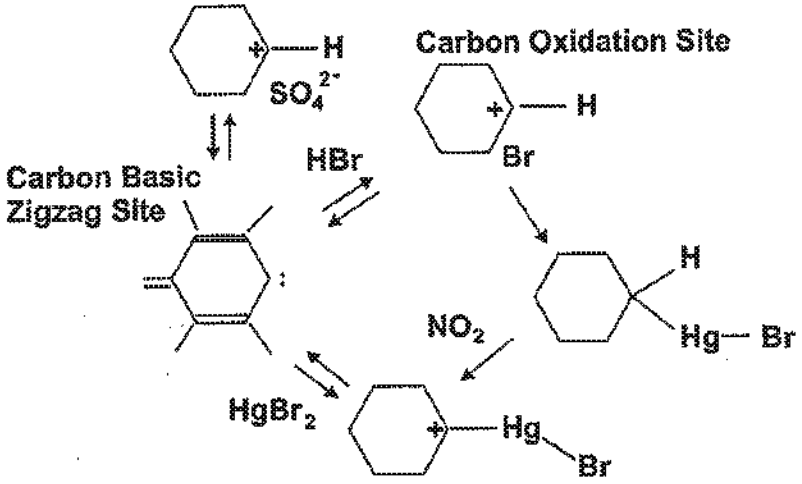

Carbon Oxidation Site
H
SO_4^{2-}
H
Br
HBr
Carbon Basic
Zigzag Site
H
Hg— Br
NO_2
$HgBr_2$
Hg
Br

FIG. 2

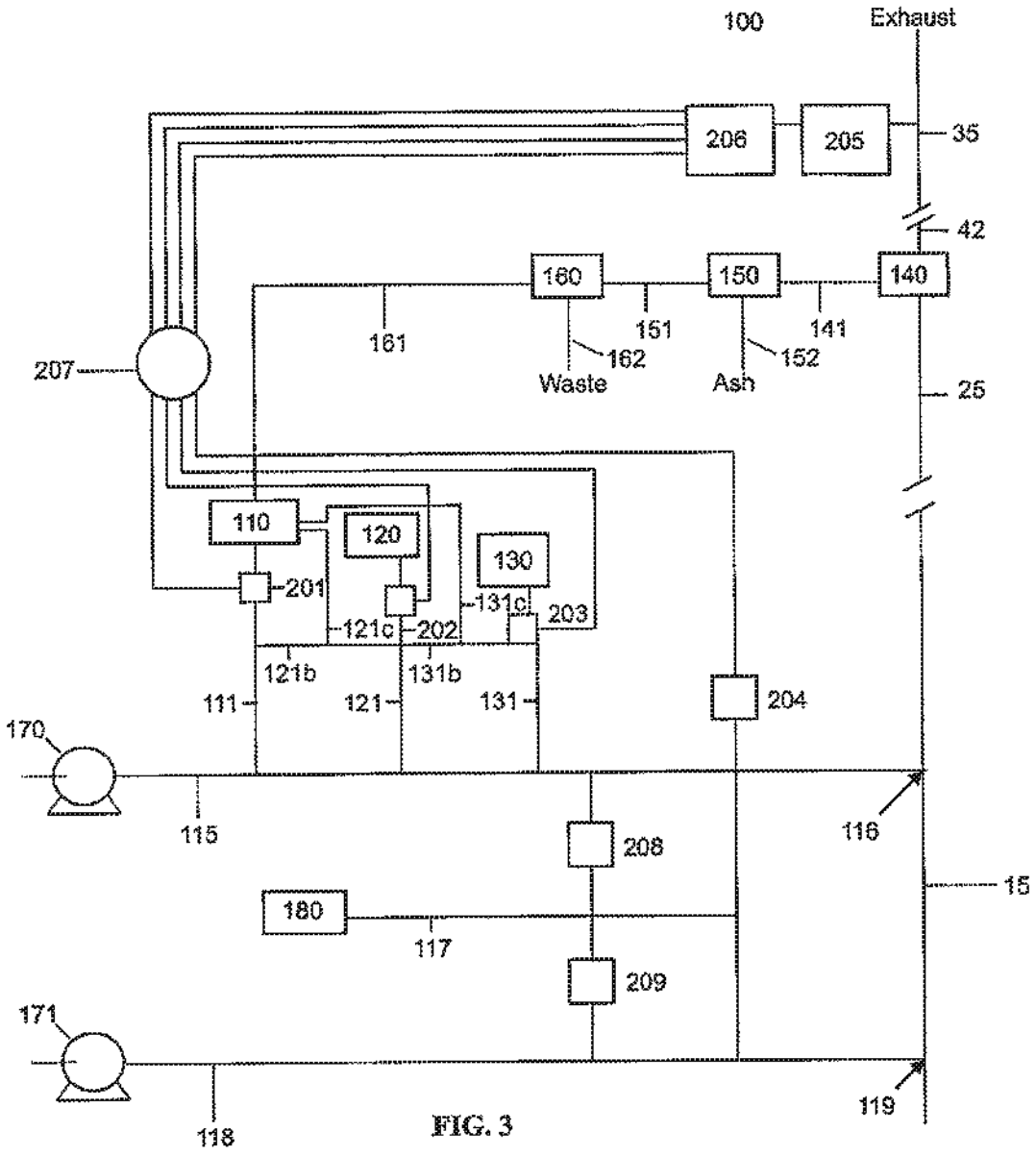

100
Exhaust
206
205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
25
110
120
130
201
131c
203
121c
202
121b
131b
111
121
131
204
170
115
116
208
15
180
117
209
171
118
119

FIG. 3

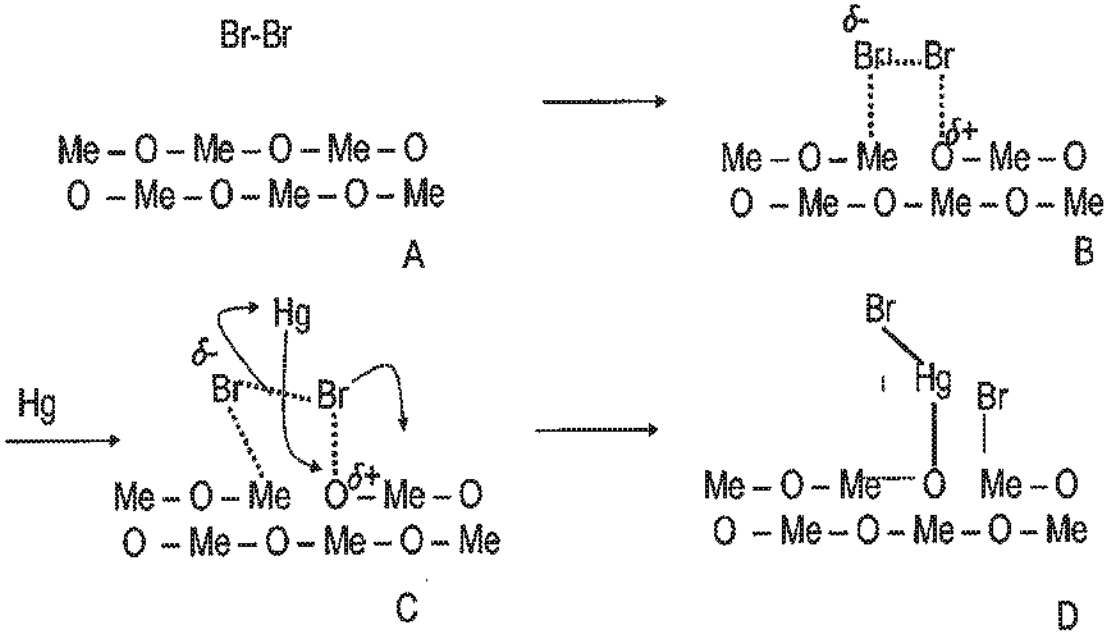


FIG. 4

BHE et al. EXHIBIT 1023
Page 243

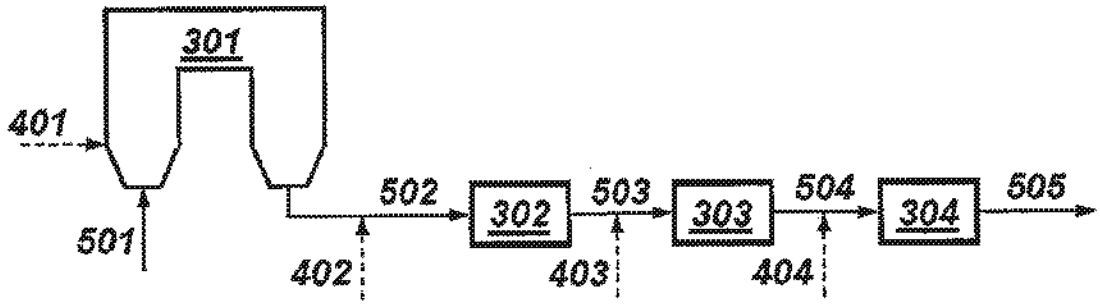


FIG. 5A

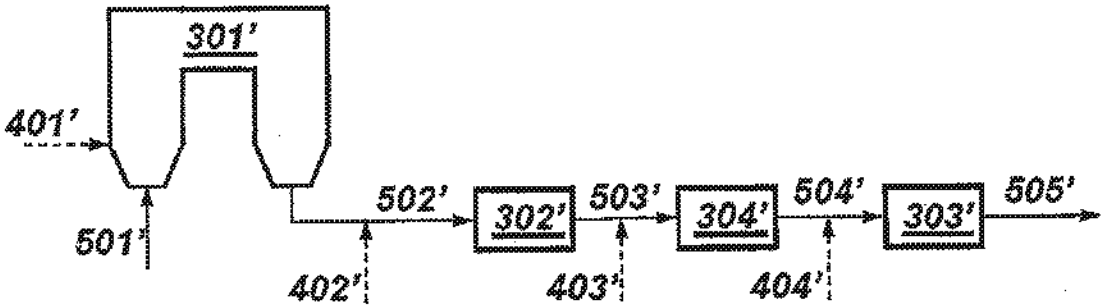


FIG. 5B

BHE et al. EXHIBIT 1023
Page 244

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 2006-0204418 A1 (CHIEN-CHUNG CHAO et al.) 14 September 2006 See the abstract, Paragraph [33] - Paragraph [101]	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)**
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(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.

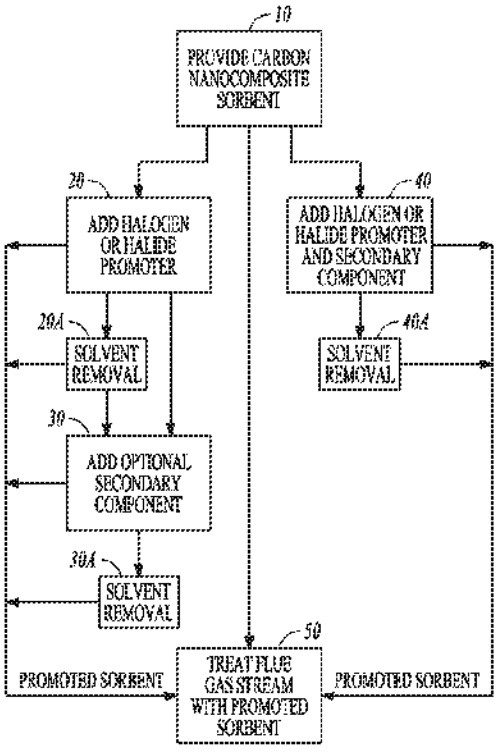


FIG. 1

WO 2013/162968 A2

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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

BHE et al. EXHIBIT 1023
Page 249

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

BHE et al. EXHIBIT 1023
Page 250

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

BHE et al. EXHIBIT 1023
Page 251

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

BHE et al. EXHIBIT 1023
Page 252

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

BHE et al. EXHIBIT 1023
Page 253

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

BHE et al. EXHIBIT 1023
Page 254

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

BHE et al. EXHIBIT 1023
Page 257

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

BHE et al. EXHIBIT 1023
Page 258

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

BHE et al. EXHIBIT 1023
Page 259

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.

BHE et al. EXHIBIT 1023
Page 260

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

BHE et al. EXHIBIT 1023
Page 261

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

BHE et al. EXHIBIT 1023
Page 262

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

BHE et al. EXHIBIT 1023
Page 263

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

BHE et al. EXHIBIT 1023
Page 264

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

BHE et al. EXHIBIT 1023
Page 266

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.,

BHE et al. EXHIBIT 1023
Page 267

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

BHE et al. EXHIBIT 1023
Page 268

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

BHE et al. EXHIBIT 1023
Page 269

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

BHE et al. EXHIBIT 1023
Page 270

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

BHE et al. EXHIBIT 1023
Page 271

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%,

BHE et al. EXHIBIT 1023
Page 272

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

BHE et al. EXHIBIT 1023
Page 274

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

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

BHE et al. EXHIBIT 1023
Page 276

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.

BHE et al. EXHIBIT 1023
Page 277

[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.

BHE et al. EXHIBIT 1023
Page 278

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

BHE et al. EXHIBIT 1023
Page 279

the art can be acceptable, as will be appreciated by those of ordinary skill in the art. For example, 169 can be a pump in the case that 120 is added as a liquid.

[00101] For clarity, single injection points 114, 116, and 119 are shown in FIG. 3A, although one of ordinary skill 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 113 or 115 (or 118, not shown) to provide signals representative of the optical density inside transport line 113, 115, or 118 as a function of time.

[00102] Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 can include 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 can exist, sequentially or in parallel, and that injection point 116 and 119 can be at a location upstream and/or downstream of 140 when parallel, sequential, or combinations thereof exist. Particulate separator 140 can produce at least a predominantly gaseous ("clean") stream 42 and a stream 141 including separated solid materials. A sorbent/ash separator 150 can separate stream 141 into a largely ash stream 152 and a largely sorbent stream 151. Alternatively, not shown, stream 141 can be disposed of as a waste stream or sent directly to the optional sorbent regenerator 160. Stream 151 can then be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

[00103] An optional aqueous scrubber 190 is provided after optional ESP 140. The aqueous scrubber 190 can be provided with ESP 140 or without ESP 140. Scrubber 190 can remove particulates from the gas stream, can remove pollutants such as SO_2 from the gas stream via chemical reaction with basic aqueous liquid, can remove pollutants such as mercury from the gas stream via reaction or absorption with activated carbon nanocomposite sorbent in the scrubber, or any suitable combination thereof. In addition to, or as an alternative to, the injection and promotion of carbon nanocomposite sorbent prior to unit 140, promoter 120 or promoter precursor can be provided to the aqueous scrubber 190. The promoter or promoter precursor can be injected into gas

BHE et al. EXHIBIT 1023
Page 280

stream 42, or can be provided directly into the scrubber (transport lines between 120/130 and 190 not shown). The promoter or promoter precursor can be provided before or into the scrubber 190 as a carbon nanocomposite sorbent coated or combined with the promoter or promoter precursor. Promotion of a coated or combined sorbent/precursor can occur in the scrubber 190, in the gas stream 42 prior to the scrubber, or in a heated carrier gas line (not shown) that brings the activated nanocomposite to 42 or 190. In addition to, or as an alternative to, the injection and promotion of carbon nanocomposite sorbent prior to unit 140, carbon nanocomposite can be provided to the aqueous scrubber 190. The carbon nanocomposite can be injected into gas stream 42, or can be provided directly into the scrubber (transport lines between 110 and 190 not shown). The aqueous solution in the scrubber can be regenerated or replaced in a batchwise or continuous process, to remove absorbed particulate, absorbed pollutant, or absorbed pollutant byproducts.

[00104] 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, 207, 208, and 209 are electrically connected via optional lines 227 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and can control the preparation and injection of promoted carbon sorbent into polluted flue gas stream 15.

[00105] In an example operation, a carbon nanocomposite sorbent and/or an optional promoter, and/or an optional alkali component, can be injected into polluted flue gas stream 15. After contacting the injected material with the polluted flue gas stream 15, the injected material reduces the mercury concentration, transforming polluted flue gas into reduced mercury flue gas stream 25. The injected material can be removed from the reduced mercury flue gas stream 25, by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. Alternatively or in addition, scrubber 190 can remove SO_2, pollutants such as mercury via promoted carbon nanocomposite, remove particulate, or any combination thereof. The reduced mercury "clean" flue gas

BHE et al. EXHIBIT 1023
Page 281

stream 42 and/or 35 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 can adjust flow controllers 201, 202, 203, 207, 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, 207, 208, 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.

[00106] Referring still to FIG. 3A, there are illustrated several embodiments for preparation and injection of carbon nanocomposite sorbents, promoted carbon sorbents, halogen and halide promoters, and/or alkali components. Stream 111 provides for introduction of carbon nanocomposite sorbent from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206. The halogen/halide can be combined and react with the carbon nanocomposite sorbent according to any of several provided methods. The halogen/halide (120 and/or 130) can be combined via transport line 121 (and/or 131) directly into transport line 115 (or 113), within which it contacts and reacts with the carbon nanocomposite sorbent (e.g., in reservoir 110) prior to injection point 116 (or 114). 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 (120 and/or 130) can be combined via flue gas stream 15 by transport line 121 (and/or 131) into transport line 115 and injection point 116 which it contacts and reacts with the carbon nanocomposite (e.g., from reservoir 110) in flue gas stream 15 after the carbon nanocomposite is transported in transport line 113 and injected at injection point 114. This option is another form of what is referred to herein as "in-flight" preparation of a promoted carbon nanocomposite sorbent in accordance with the invention. Further, the halogen/halide can be combined via transport line 121b with carbon nanocomposite sorbent prior to entering transport line 113 and/or 115. Still further, the halogen/halide can be contacted and react with the carbon nanocomposite sorbent by introduction via transport line 121c into reservoir 110. This option can be employed when, for example,

BHE et al. EXHIBIT 1023
Page 282

reservoir 110 includes an ebulliated or fluidized bed of carbon nanocomposite sorbent, through which halogen/halide flows in gaseous form or as a vapor. In other embodiments, the halogen/halide can be contacted with the carbon nanocomposite sorbent in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in FIG. 3A) can then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

[00107] Similarly, the optional secondary component can be contacted and react directly in transport line 115 (and/or 113) via transport line 131, or optionally as described above with respect to the halogen/halide, via transport lines 131b and 131c.

[00108] Similarly, the optional alkali component from reservoir 180 can either be added in transport line 113 and/or 115 directly, or can be injected separately by transport line 118, remaining separate and/or combining downstream in flue gas stream 15 for synergistic effects with carbon nanocomposite sorbent, promoted carbon, or optional secondary components. On-site variation of the amount of the optional alkali component relative to carbon nanocomposite sorbent, promoted carbon, or optional secondary components can be optimized for site-specific operating and flue gas conditions.

[00109] FIG. 3B shows a schematic flow diagram of mercury control system 300 including preparation of promoted carbon sorbents and flue gas mercury reduction in accordance with embodiments of the present invention. Carbon sorbent 310 can be injected through line 395 to location 396 or injected through line 390 to location 391. Promoted carbon sorbent 320 can be injected through line 395 to location 396 or injected through line 390 to location 391. Carbon sorbent 310 can be promoted in-flight, such as via injection of carbon sorbent 310 through line 390 and/or 395 to location 391 and/or 396 with halogen/halide promoter 340 through line 380 to location 385 or via injection of carbon sorbent 310 through line 390 and/or 395 to location 391 and/or 396 with halogen/halide promoter 340 through line 350 to location 355 and/or halogen/halide promoter 340 through line 360 to location 365 and/or halogen/halide promoter 340 through line 370 to location 375.

[00110] In addition to or as an alternative to use of promoted carbon nanocomposite prior to the optional ESP unit, the optional scrubber unit can be

BHE et al. EXHIBIT 1023
Page 283

used for removal of pollutants such as mercury via use of promoted carbon in the scrubber, removal of pollutants such as SO_2 via use of basic aqueous solution in the scrubber, removal of particulates in the scrubber, or any combination thereof. Injection of materials such as promoter or carbon nanocomposite sorbent to the scrubber can occur in the scrubber or between the ESP and the scrubber. Promoted sorbent 320 can be injected through line 397 into the scrubber. Carbon sorbent 310 can be promoted in-flight, such as via injection of carbon sorbent 310 through a heated carrier line (not shown) with promoter 340 to the scrubber. Halogen/halide promoter 340 can be added to the scrubber through line 381, while carbon sorbent 310 is added via line 397, and the sorbent can be promoted within the scrubber.

[00111] In some embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures can be provided. In some embodiments, the halogen/halide promoter and optional secondary component(s) can be sprayed in solution form into or on the carbon nanocomposite sorbent. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art can then be provided.

[00112] In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it can be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, can be passed through an ebulliated or fluidized bed of granular or fibrous carbon nanocomposite sorbent, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

[00113] In some embodiments, the secondary component(s) can include 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 embodiments, the promoted carbon sorbent can include from about 1 g to about 30 g halogen/halide per 100 g carbon nanocomposite sorbent. In some embodiments, the promoted carbon sorbent can include a secondary component in concentration of from about 1 wt% to about 15 wt% of the concentration of the halogen/halide component.

BHE et al. EXHIBIT 1023
Page 284

[00114] In still other embodiments, the promoted carbon nanocomposite sorbent can be applied to a substrate. In other embodiments, such prepared substrate(s) can be caused to contact a polluted flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates can be monolithic, rotating, moving, or exposed to the gas stream in any number of ways known to those skilled in the art. Substrates can include, for example, honeycomb structures, fabrics, filters, plates, and the like.

Examples

[00115] The present invention can be better understood by reference to the following examples which are offered by way of illustration. The present invention is not limited to the examples given herein.

Example 1. Mesoporous Activated Carbon (AC) Nanocomposites from Commercial Cane Molasses.

Example 1.1. NanoG-CM

[00116] High-surface-area montmorillonite (clay) obtained from Aldrich (200 g) was added rapidly to Brer Rabbit molasses (nonsulfurated) diluted with a smaller amount of water (200 g/140 mL) and stirred to make a thick paste.

[00117] As soon as all the clay was wetted with the molasses, the paste was dried overnight at 110°C to remove excess water. Alternatively, a smaller portion of the paste was heated for 1 min in a microwave. A smaller batch was dried more quickly (1 hour) in the oven at 110°C.

[00118] The dried solid was loaded in two batches in a cylindrical steel tube and heated to 700°C in a tube furnace with a flow of nitrogen through the bed. The effluent gas was bubbled through a water trap. Heating was continued for 1 hour. The tube was cooled slowly to ambient under nitrogen and emptied. The resulting black chunks of composite carbon were weighed and ground in a mortar and pestle. The product nanocomposite was separated into two sieve sizes, greater than 325 mesh and about 325 mesh. The about 325 mesh material was used for the Hg capture tests.

[00119] Yield of nanocomposite was 217 g.

BHE et al. EXHIBIT 1023
Page 285

Example 1.2. NanoG-CB.

[00120] Preparation was similar to NanoG-CM, except high-sodium bentonite was substituted for the montmorillonite. Yield was 10.1 g from 10.0 grams of bentonite.

Example 1.3. Impregnation of Promotion Agent

Example 1.3.1. Ammonium bromide.

[00121] An aqueous solution of ammonium bromide (7.3 g/35 mL) was added to 54 g of 325-mesh nanocomposite and stirred to form a paste. The paste was dried at 110°C and reground.

Example 1.3.2. Hydrogen bromide.

[00122] Aqueous HBr (0.1 N) was added to NanoG-CM (10 g) and the mixture stirred for 1 hr. The slurry was filtered and dried at 110°C.

Example 1.3.3. Bromine.

[00123] Bromine vapor (0.5 g) was transferred to a vial containing the powdered composite (10 g), where it was adsorbed.

Example 1.3.4. Sulfur.

[00124] Elemental sulfur (1 g) was dissolved in carbon disulfide (20 mL), and 10 g of NanoG-CM was added. After being stirred overnight, the carbon disulfide was removed.

Example 2. Mesoporous Activated Carbon Nanocomposites from American Crystal Sugar (ACS) Raffinate.

[00125] The previous versions of the NanoG-CM carbon composites were prepared using cane sugar molasses. Using the local ACS molasses would provide a more convenient source; e.g., a low-value raffinate remaining from sugar and betaine extraction is available in large amounts (approximately 170

BHE et al. EXHIBIT 1023
Page 286

tons). However, the amount of dissolved inorganic salts is much higher (>10%) than commercial cane molasses, and the sugar content is lower.

[00126] Nanocomposites were prepared using the ACS raffinate and two types of clay: a highly swelling, high-sodium bentonite and a low-swelling montmorillonite from Aldrich. Both were ground finely.

Example 2.1. NanoG-ACSB.

[00127] The bentonite was swelled by adding 10 g of dry bentonite to 80 g of water and grinding with a mortar and pestle. ACS raffinate (10 g) was added to the gelled mixture and mixed by grinding. After standing overnight to further disperse the sugar in the raffinate into the clay, the mixture was heated in a microwave at full power for 1 minute to develop macroporosity in the gel. The gel was dried overnight in a drying oven at 110°C.

[00128] The dried solid was loaded in two batches in a cylindrical steel tube and heated to 700°C in a tube furnace with a flow of nitrogen through the bed. The effluent gas was bubbled through a water trap. Heating was continued for 1 hr. The tube was cooled slowly to ambient under nitrogen and emptied. The resulting black chunks of composite carbon were weighed and ground in a mortar and pestle.

[00129] Yield of nanocomposite was 10.2 g.

Example 2.2. NanoG-2ACSB

[00130] Preparation was similar to NanoG-ACSB except the weight of raffinate added was doubled. Yield was 10.5 g.

Example 2.3. NanoG-2ACSM.

[00131] Preparation was similar to NanoG-CM, using 10g of Aldrich montmorillonite and 20 g of ACS raffinate was used and the amount doubled. Yield was 10.5 g.

BHE et al. EXHIBIT 1023
Page 287

Example 2.4. NanoG-2ACSB-Washed.

[00132] A sample of NanoG-2ACSB was stirred with water overnight, filtered, and then stirred with 0.1 N HBr for 2 hr. The slurry was filtered, and the composite was dried at 110°C.

Example 2.5. Impregnation of Promotion Agent.

Example 2.5.1. Ammonium bromide.

[00133] An aqueous solution of ammonium bromide (1.1 g/5 mL) was added to 10 g of nanocomposite and stirred to form a paste. The paste was dried at 110°C and reground.

Example 2.5.2. Bromine.

[00134] Bromine vapor (0.5 g) was transferred to a vial containing the powdered composite, where it was partially adsorbed (chemisorbed).

Example 3. Bench-Scale Hg Sorption Tests of NanoG Sorbents.

[00135] Bench-scale Hg sorption tests were conducted to evaluate the performance of the sorbents in a bed configuration for sorption of elemental Hg vapor in flue gas. These results are summarized in Table 1. While not as accurate at evaluating performance in an injection mode with very short contact time, the initial reactivity (as % Hg capture) and the initial slope gave a preliminary determination of reactivity in a short time scale. When the initial slope is flat, there are many active sites, and a higher reactivity has been found. A steep initial slope relates to fast breakthrough and corresponding lower reactivity.

[00136] The NanoG composite sorbents prepared from the cane molasses (NanoG-CM) gave excellent reactivities (98%-99% capture) at the start of the experiment and continued with high capture efficiency for 15 minutes (flat slope). On the other hand, the ACS raffinate gave lower reactivities and lower capacities (shorter 50% breakthrough times) compared with the composites prepared from cane sugar molasses. The amounts of carbon contained in the ACS composites were considerably less, owing to the lower sugar content, higher salt content and, perhaps, different burn-off rate. The composites prepared

BHE et al. EXHIBIT 1023
Page 288

with double the amount of molasses were less reactive than the lower dosage. These results could be explained by salt blockage in the pores of the composites from the ACS raffinate. The evolution of large amounts of H_2S when water was added to the sorbents is consistent with the formation of K_2S in the pores resulting from reduction of sulfate as well as the high potassium concentration. When the ACS raffinate sorbent was washed to dissolve out the salts, the reactivity and capacity improved considerably.

[00137] Table 1. Summary Results for Fixed-Bed Screening of NanoG Sorbents

Sorbent	Promotion Reagent	Initial Reactivity, % Hg Capture	Initial slope	50% Breakthrough, Time, hr
NanoG-CM	Br_2	98	Flat	0.45
NanoG-CM	NH_4Br	99	Flat	0.38
NanoG-CM	HBr	97	Moderate	0.29
NanoG-CM	S	92	Steep	0.06
NanoG-2ACSM	Br_2	67	Steep	0.02
NanoG-2ACSB	Br_2	95	Steep	0.16
NanoG-2ACSB	NH_4Br	90	Steep	0.29
NanoG-ACSB	NH_4Br	97	Moderate	0.32
NanoG-2ACSB-washed	Br_2	97	Moderate	0.53

[00138] Although sulfurization of ACs produces carbons with good reactivities for Hg, the addition of sulfur to the NanoG sorbent did not result in a good capacity. It is likely that the sulfur blocked the pores in the limited amount of carbon porosity available in these sorbents.

[00139] A comparison of HBr with Br_2 showed that Br_2 gave higher reactivity and capacity. A reason for this may be that carbenium-bromide ion pairs in these composite sorbents are less hydrated and more reactive in the sorbents produced by vapor deposition.

BHE et al. EXHIBIT 1023
Page 289

[00140] The ammonium bromide-promoted sorbents gave very good reactivities and capacities, consistent with decomposition of the ammonium bromide in the pores on heating forming ammonia and gaseous HBr. The HBr combines with carbon deposited on the proximate nanocarbon surfaces decorating the clay layers (sheets). Also, the ammonia is trapped inside the acidic clay layers of the composite where it is available for intercepting the SO_2 in the flue gas before it can oxidize on the carbon surface.

Example 4. Pilot-Scale Evaluation.

[00141] NanoG-CM was evaluated at the pilot scale during a Center for Air Toxic Metals® (CATM®)-sponsored run of the particulate test combustor (PTC). The coal for that evaluation was a subbituminous Montana Powder River Basin (PRB) (Absaloka), and comparisons were made to a commercially available untreated carbon.

[00142] Results from the PTC tests are summarized in FIG. 4 for the commercially available standard AC and two options with NanoG-CM. FIG. 4 shows PTC results for NanoG-CM testing on a total-injected-sorbent basis. The standard AC and the untreated NanoG-CM were tested with the moderate energy dissociation technology (MEDT) sorbent enhancement additive (SEA) option. As indicated in the figure, the results were better with the standard AC; however, the NanoG-CM did show potential for in-flight capture. More promising results were obtained with a treated sample of NanoG-CM. It was determined through a set of tests performed for MEDT SEA development that the pretreatment used with NanoG-CM was most effective at pre-air heater temperatures. Therefore, during evaluation of the treated NanoG-CM, it was injected into the ductwork at a point where the flue gas temperature was approximately 715°F.

[00143] FIG. 4 suggests that the NanoG-CM material shows potential as an in-flight mercury sorbent, but the total injected sorbent rates are higher than those with the standard AC. However, an alternate comparison is to evaluate the test results on a carbon component basis, since the underlying economic assumption for composite sorbents is that the AC component is perhaps an order of magnitude more expensive than the inorganic substrate. The results from FIG. 4 have been rescaled in FIG. 5 to depict the equivalent carbon-only injection rate

BHE et al. EXHIBIT 1023
Page 290

for the three options. FIG. 5 shows PTC results for NanoG-CM testing on a carbon-component basis. The standard AC results remain unchanged because they were considered 100% AC (mineral components of the carbon were not deducted), but the NanoG-CM data reflect much lower carbon-only injection rates since the average carbon content for NanoG-CM was only 8%.

[00144] The carbon-only results of FIG. 5 demonstrate at least one of the beneficial aspects of the nanocomposite sorbents: increased carbon utilization. Comparison of the standard AC and the NanoG-CM results in FIG. 5 suggests that the bulk of the standard AC's carbon content (e.g., the interior portion) goes unused and is not a factor in overall mercury capture. This reinforces a mechanistic understanding that predominantly the surface and near-surface sites are important for in-flight capture of mercury. Improved carbon utilization can have a beneficial effect on consumable sorbent cost, for example, if the base material cost advantage is not outweighed by added or more complicated production steps. Furthermore, improved carbon utilization can make it easier for utilities to meet carbon content restrictions in fly ash, for example, in fly ash destined for use in concrete.

[00145] Synergistic effects between the carbon layer and the interior substrate can be an advantage of the carbon nanocomposite sorbent. In one example, a synergistic effect could arise from a single particle including two sorbents: a conventional AC and an inorganic substrate that may be reactive toward acid gas components in flue gas. To support the potential benefits of a nanocomposite sorbent, an applied model for in-flight capture was used with results presented in FIG. 6, for composite sorbents with varying activated carbon surface coverage. FIG. 6 shows model results for in-flight mercury capture with a composite sorbent in a high-sulfur flue gas (3000 ppm SO_2, 15 ppm SO_3). The modeled flue gas was representative of a high-sulfur coal with significant amounts of SO_3 that limit mercury capture, as indicated by the 100% AC reference curve. An estimate of the synergistic benefit of the composite sorbent is shown by the 50% and 10% AC curves. Given the conservative assumptions that were used, benefits can exceed those shown by the model.

[00146] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use

BHE et al. EXHIBIT 1023
Page 291

of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

Additional Embodiments.

[00147] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance:

[00148] Embodiment 1 provides a method for separating a material from a gas that comprises the material, comprising providing or obtaining a carbon nanocomposite sorbent; contacting at least some of the material with the sorbent, to form a material-sorbent composition; and separating at least some of the material-sorbent composition from the material-containing gas, to give a separated gas.

[00149] Embodiment 2 provides the method of Embodiment 1, wherein the material is a pollutant.

[00150] Embodiment 3 provides the method of Embodiment 2, wherein the pollutant is mercury.

[00151] Embodiment 4 provides the method of any one of Embodiments 2-3, further comprising providing a promoter; and promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the promoter to form a promoted sorbent; wherein the sorbent that contacts at least some of the pollutant comprises the promoted sorbent.

[00152] Embodiment 5 provides the method of Embodiment 4, wherein the promoter is a halogen or halide promoter.

[00153] Embodiment 6 provides a method for reducing the pollutant content of a pollutant-containing gas, comprising providing or obtaining a carbon nanocomposite sorbent material; providing or obtaining a halogen or

halide promoter; 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; contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition; and separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas.

[00154] Embodiment 7 provides the method of Embodiment 6, wherein the pollutant is mercury.

[00155] Embodiment 8 provides the method of any one of Embodiments 6-7, wherein obtaining or providing the carbon nanocomposite sorbent comprises providing or obtaining a carbon precursor; providing or obtaining a substrate material; contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material; heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent.

[00156] Embodiment 9 provides the method of Embodiment 8, further comprising allowing the heated nanocomposite starting material to react with an acid or a base, to provide the carbon nanocomposite sorbent.

[00157] Embodiment 10 provides the method of any one of Embodiments 8-9, wherein the carbon precursor comprises a carbohydrate.

[00158] Embodiment 11 provides the method of any one of Embodiments 8-10, wherein the carbon precursor comprises brown sugar, barley sugar, caramel, cane sugar, corn syrup, starch, molasses, or a sugar waste product.

[00159] Embodiment 12 provides the method of any one of Embodiments 8-11, wherein the substrate material comprises diatomaceous earth, clay, zeolite, or mineral.

[00160] Embodiment 13 provides the method of any one of Embodiments 8-12, wherein the heating comprises heating to greater than about 100°C.

[00161] Embodiment 14 provides the method of any one of Embodiments 6-13, wherein the sorbent material comprises binding sites that bind with the pollutant in the pollutant-containing gas.

[00162] Embodiment 15 provides the method of any one of Embodiments 6-14, wherein the sorbent material comprises carbon that has been allowed to

BHE et al. EXHIBIT 1023
Page 293

react or become impregnated with halogens, hydrogen halides, and Group V and Group VI halides to form pollutant binding sites in the promoted sorbent.

[00163] Embodiment 16 provides the method of Embodiment 15, wherein the binding sites in the promoted AC bind to the pollutant in the pollutant-containing gas to form the pollutant-sorbent composition.

[00164] Embodiment 17 provides the method of any one of Embodiments 15-16, wherein the binding sites in the promoted AC react with the pollutant in the pollutant-containing gas to form the pollutant-sorbent composition.

[00165] Embodiment 18 provides the method of any one of Embodiments 15-17, wherein at least a portion of the binding sites of the AC react with oxidized pollutant in the pollutant-containing gas to form another pollutant-sorbent chemical composition.

[00166] Embodiment 19 provides the method of any one of Embodiments 6-18, wherein the step of separating particulates from the pollutant-containing gas comprises separating in a particulate separator comprising one or more ESPs.

[00167] Embodiment 20 provides the method of any one of Embodiments 7-19, wherein the mercury in the mercury-containing gas comprises elemental mercury.

[00168] Embodiment 21 provides the method of any one of Embodiments 7-20, wherein the mercury in the mercury-sorbent composition is oxidized mercury.

[00169] Embodiment 22 provides the method of any one of Embodiments 7-21, wherein the promoted sorbent combines with at least about 70 wt% of the mercury present in the mercury-containing gas.

[00170] Embodiment 23 provides the method of any one of Embodiments 6-22, wherein the halogen or halide promoter is in a form comprising a vapor form, a solid form, in a solvent, or a combination thereof.

[00171] Embodiment 24 provides the method of any one of Embodiments 6-23, wherein the halogen or halide promoter comprises at least one of a Group V halide and a Group VI halide.

[00172] Embodiment 25 provides the method of any one of Embodiments 6-24, wherein a promoter precursor on the sorbent or injected with the sorbent transforms into the halogen or halide promoter that reacts with the sorbent.

[00173] Embodiment 26 provides the method of any one of Embodiments 6-25, wherein the halogen or halide promoter is NH_4Br, NaBr, HBr, NaCl, $CaCl_2$, or HCl.

[00174] Embodiment 27 provides the method of any one of Embodiments 6-26, further comprising injecting an alkaline component into the pollutant-containing gas.

[00175] Embodiment 28 provides the method of Embodiment 27, wherein the alkaline component comprises an oxide, hydroxide, carbonate, or phosphate of an alkali or alkaline-earth element.

[00176] Embodiment 29 provides the method of any one of Embodiments 6-28, further comprising adding an additional halogen or halide promoter to the promoted sorbent.

[00177] Embodiment 30 provides the method of Embodiment 29, wherein the additional halogen or halide promoter comprises HI, HBr, HCl, a Group V element with halogen, or a Group VI element with halogen.

[00178] Embodiment 31 provides the method of any one of Embodiments 6-30, further comprising adding a stabilizing agent to the promoted containing sorbent.

[00179] Embodiment 32 provides the method of Embodiment 31, wherein the stabilizing agent comprises at least one of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, and P_2S_5.

[00180] Embodiment 33 provides the method of any one of Embodiments 6-32, wherein the step of promoting at least a portion of the sorbent material occurs at least partially before the contacting of the pollutant-containing gas with the promoted sorbent.

[00181] Embodiment 34 provides the method of any one of Embodiments 6-33, further comprising injecting the carbon nanocomposite sorbent at an injection rate and injecting separately at least one promoter at an injection rate into a gas stream whereby in-flight reaction produces the promoted sorbent, 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 about 100 grams of carbon nanocomposite sorbent material.

[00182] Embodiment 35 provides the method of Embodiment 34, wherein the gas stream is the pollutant-containing gas.

[00183] Embodiment 36 provides the method according to Embodiment 35, wherein the gas stream is a transport gas.

[00184] Embodiment 37 provides the method of any one of Embodiments 34-36, wherein the promoter injection rate and the sorbent injection rate into the gas are determined, at least in part, from a monitored pollutant content of the cleaned gas.

[00185] Embodiment 38 provides the method of any one of Embodiments 6-37, further comprising a step of regenerating the promoted sorbent from the pollutant-sorbent chemical composition.

[00186] Embodiment 39 provides the method of Embodiment 38, further comprising using the regenerated promoted sorbent to remove the pollutant from the pollutant-containing gas.

[00187] Embodiment 40 provides the method of any one of Embodiments 6-39, wherein at least one of the promoting, the contacting, and the separating, occurs in an aqueous scrubber.

[00188] Embodiment 41 provides the method of Embodiment 40, wherein the promoting occurs in the scrubber, wherein the scrubber comprises an aqueous slurry that comprises the promoter.

[00189] Embodiment 42 provides the method of any one of Embodiments 40-41, wherein the contacting occurs in the scrubber, wherein the scrubber comprises an aqueous slurry that comprises that activated carbon nanocomposite sorbent.

[00190] Embodiment 43 provides a method for reducing the mercury content of a mercury-containing gas, comprising providing or obtaining a carbon nanocomposite sorbent, the carbon nanocomposite sorbent made by steps comprising providing or obtaining a carbon precursor; providing or obtaining a substrate material; contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material; and heating the nanocomposite

starting material, provide the carbon nanocomposite sorbent; providing or obtaining a halogen or halide promoter; 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; contacting at least part of the promoted sorbent with the mercury, to form a mercury-sorbent composition; and separating at least some of the mercury-sorbent composition from the mercury-containing gas.

[00191] Embodiment 44 provides a method of making a carbon nanocomposite sorbent, comprising providing or obtaining a carbon precursor; providing or obtaining a substrate material; contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material; heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent.

[00192] Embodiment 45 provides the carbon nanocomposite sorbent made by the method of Embodiment 44.

[00193] Embodiment 46 provides a promoted carbon nanocomposite sorbent made by a method comprising promoting at least a portion of the sorbent material of Embodiment 45 by chemically reacting the portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent.

[00194] Embodiment 47 provides a mercury-sorbent composition made by contacting the carbon nanocomposite sorbent of any one of Embodiments 45-46 with a mercury-containing gas.

[00195] Embodiment 48 provides the carbon nanocomposite sorbent of any one of Embodiments 45-47 in contact with mercury or oxidized mercury.

[00196] Embodiment 49 provides a promoted carbon nanocomposite sorbent made by a method comprising promoting at least a portion of carbon nanocomposite sorbent material by chemically reacting the portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent.

[00197] Embodiment 50 provides the apparatus or method of any one or any combination of Embodiments 1-49 optionally configured such that all elements or options recited are available to use or select from.

BHE et al. EXHIBIT 1023
Page 297

CLAIMS

We claim:

1. A method for separating a material from a gas that comprises the material, the method comprising:

providing or obtaining a carbon nanocomposite sorbent;

contacting at least some of the material with the sorbent, to form a material-sorbent composition; and

separating at least some of the material-sorbent composition from the material-containing gas, to give a separated gas.

2. The method of claim 1, wherein the material is a pollutant.

3. The method of claim 2, wherein the pollutant is mercury.

4. The method of any one of claims 2-3, further comprising

providing a promoter; and

promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the promoter to form a promoted sorbent;

wherein the sorbent that contacts at least some of the pollutant comprises the promoted sorbent.

5. The method of claim 4, wherein the promoter is a halogen or halide promoter.

6. A method for reducing the pollutant content of a pollutant-containing gas, comprising:

providing or obtaining a carbon nanocomposite sorbent material;

providing or obtaining a halogen or halide promoter;

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;

contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition; and

separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas.

7. The method of claim 6, wherein the pollutant is mercury.

8. The method of any one of claims 6-7, wherein obtaining or providing the carbon nanocomposite sorbent comprises

providing or obtaining a carbon precursor;

providing or obtaining a substrate material;

contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material; and

heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent.

9. The method of claim 8, further comprising allowing the heated nanocomposite starting material to react with an acid or a base, to provide the carbon nanocomposite sorbent.

10. The method of any one of claims 8-9, wherein the carbon precursor comprises a carbohydrate.

11. The method of any one of claims 8-10, wherein the carbon precursor comprises brown sugar, barley sugar, caramel, cane sugar, corn syrup, starch, molasses, or a sugar waste product.

12. The method of any one of claims 8-11, wherein the substrate material comprises diatomaceous earth, clay, zeolite, or mineral.

13. The method of any one of claims 8-12, wherein the heating comprises heating to greater than about 100°C.

BHE et al. EXHIBIT 1023
Page 299

14. The method of any one of claims 6-13, wherein the sorbent material comprises binding sites that bind with the pollutant in the pollutant-containing gas.

15. The method of any one of claims 6-14, wherein the sorbent material comprises carbon that has been allowed to react or become impregnated with halogens, hydrogen halides, and Group V and Group VI halides to form pollutant binding sites in the promoted sorbent.

16. The method of claim 15, wherein the binding sites in the promoted AC bind to the pollutant in the pollutant-containing gas to form the pollutant-sorbent composition.

17. The method of any one of claims 15-16, wherein the binding sites in the promoted AC react with the pollutant in the pollutant-containing gas to form the pollutant-sorbent composition.

18. The method of any one of claims 15-17, wherein at least a portion of the binding sites of the AC react with oxidized pollutant in the pollutant-containing gas to form another pollutant-sorbent chemical composition.

19. The method of any one of claims 6-18, wherein the step of separating particulates from the pollutant-containing gas comprises separating in a particulate separator comprising one or more ESPs.

20. The method of any one of claims 7-19, wherein the mercury in the mercury-containing gas comprises elemental mercury.

21. The method of any one of claims 7-20, wherein the mercury in the mercury-sorbent composition is oxidized mercury.

BHE et al. EXHIBIT 1023
Page 300

22. The method of any one of claims 7-21, wherein the promoted sorbent combines with at least about 70 wt% of the mercury present in the mercury-containing gas.

23. The method of any one of claims 6-22, wherein the halogen or halide promoter is in a form comprising a vapor form, a solid form, in a solvent, or a combination thereof.

24. The method of any one of claims 6-23, wherein the halogen or halide promoter comprises at least one of a Group V halide and a Group VI halide.

25. The method of any one of claims 6-24, wherein a promoter precursor on the sorbent or injected with the sorbent transforms into the halogen or halide promoter that reacts with the sorbent.

26. The method of any one of claims 6-25, wherein the halogen or halide promoter is NH_4Br, NaBr, HBr, NaCl, $CaCl_2$, or HCl.

27. The method of any one of claims 6-26, further comprising injecting an alkaline component into the pollutant-containing gas.

28. The method of claim 27, wherein the alkaline component comprises at least one of an oxide, hydroxide, carbonate, and a phosphate of an alkali or alkaline-earth element.

29. The method of any one of claims 6-28, further comprising adding an additional halogen or halide promoter to the promoted sorbent.

30. The method of claim 29, wherein the additional halogen or halide promoter comprises at least one of HI, HBr, HCl, a Group V element with halogen, and a Group VI element with halogen.

BHE et al. EXHIBIT 1023
Page 301

31. The method of any one of claims 6-30, further comprising adding a stabilizing agent to the promoted containing sorbent.

32. The method of claim 31, wherein the stabilizing agent comprises at least one of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, and P_2S_5.

33. The method of any one of claims 6-32, wherein the step of promoting at least a portion of the sorbent material occurs at least partially before the contacting of the pollutant-containing gas with the promoted sorbent.

34. The method of any one of claims 6-33, further comprising injecting the carbon nanocomposite sorbent at an injection rate and injecting separately at least one promoter at an injection rate into a gas stream whereby in-flight reaction produces the promoted sorbent, 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 about 100 grams of carbon nanocomposite sorbent material.

35. The method of claim 34, wherein the gas stream is the pollutant-containing gas.

36. The method according to claim 35, wherein the gas stream is a transport gas.

37. The method of any one of claims 34-36, wherein the promoter injection rate and the sorbent injection rate into the gas are determined, at least in part, from a monitored pollutant content of the cleaned gas.

38. The method of any one of claims 6-37, further comprising a step of regenerating the promoted sorbent from the pollutant-sorbent chemical composition.

BHE et al. EXHIBIT 1023
Page 302

39. The method of claim 38, further comprising using the regenerated promoted sorbent to remove the pollutant from the pollutant-containing gas.

40. The method of any one of claims 6-39, wherein at least one of the promoting, the contacting, and the separating, occurs in an aqueous scrubber.

41. The method of claim 40, wherein the promoting occurs in the scrubber, wherein the scrubber comprises an aqueous slurry that comprises the promoter.

42. The method of any one of claims 40-41, wherein the contacting occurs in the scrubber, wherein the scrubber comprises an aqueous slurry that comprises that activated carbon nanocomposite sorbent.

43. A method for reducing the mercury content of a mercury-containing gas, the method comprising:

providing or obtaining a carbon nanocomposite sorbent, the carbon nanocomposite sorbent made by steps comprising

providing or obtaining a carbon precursor;

providing or obtaining a substrate material;

contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material; and

heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent;

providing or obtaining a halogen or halide promoter;

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;

contacting at least part of the promoted sorbent with the mercury, to form a mercury-sorbent composition; and

separating at least some of the mercury-sorbent composition from the mercury-containing gas.

BHE et al. EXHIBIT 1023
Page 303

44. A method of making a carbon nanocomposite sorbent, the method comprising:

providing or obtaining a carbon precursor;

providing or obtaining a substrate material;

contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material;

heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent.

45. The carbon nanocomposite sorbent made by the method of claim 44.

46. A promoted carbon nanocomposite sorbent made by a method comprising promoting at least a portion of the sorbent material of claim 45 by chemically reacting the portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent.

47. A mercury-sorbent composition made by contacting the carbon nanocomposite sorbent of any one of claims 45-46 with a mercury-containing gas.

48. The carbon nanocomposite sorbent of any one of claims 45-47 in contact with mercury or oxidized mercury.

49. A promoted carbon nanocomposite sorbent made by a method comprising promoting at least a portion of carbon nanocomposite sorbent material by chemically reacting the portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent.

BHE et al. EXHIBIT 1023
Page 304

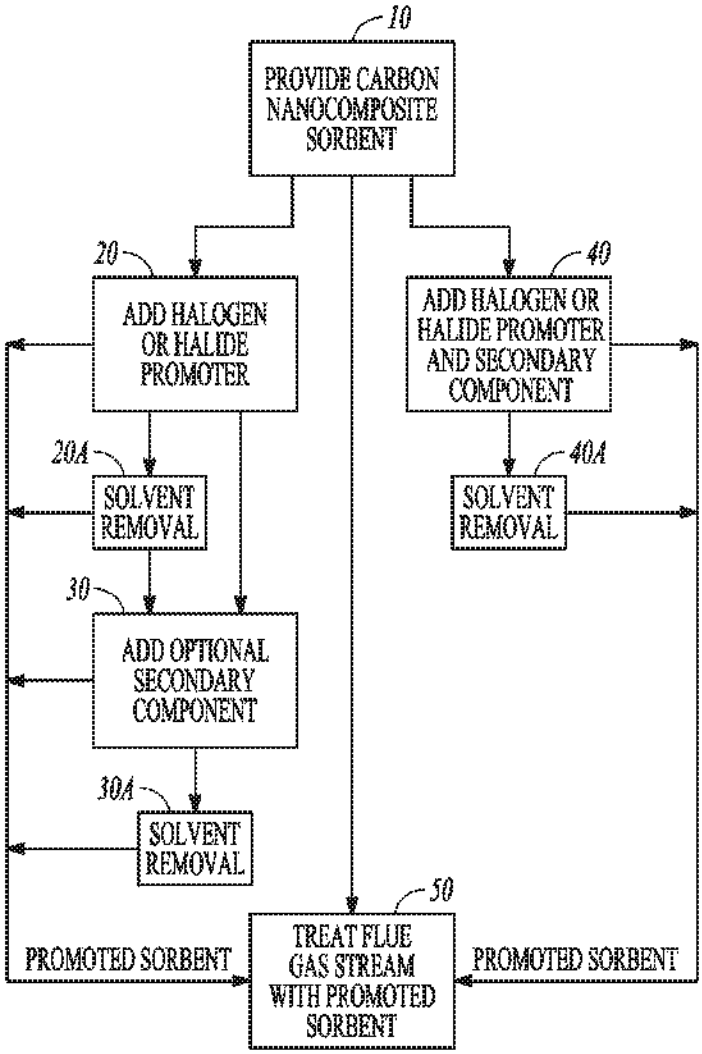

10
PROVIDE CARBON NANOCOMPOSITE SORBENT
20
ADD HALOGEN OR HALIDE PROMOTER
40
ADD HALOGEN OR HALIDE PROMOTER AND SECONDARY COMPONENT
20A
SOLVENT REMOVAL
40A
SOLVENT REMOVAL
30
ADD OPTIONAL SECONDARY COMPONENT
30A
SOLVENT REMOVAL
50
TREAT FLUE GAS STREAM WITH PROMOTED SORBENT
PROMOTED SORBENT
PROMOTED SORBENT

FIG. 1

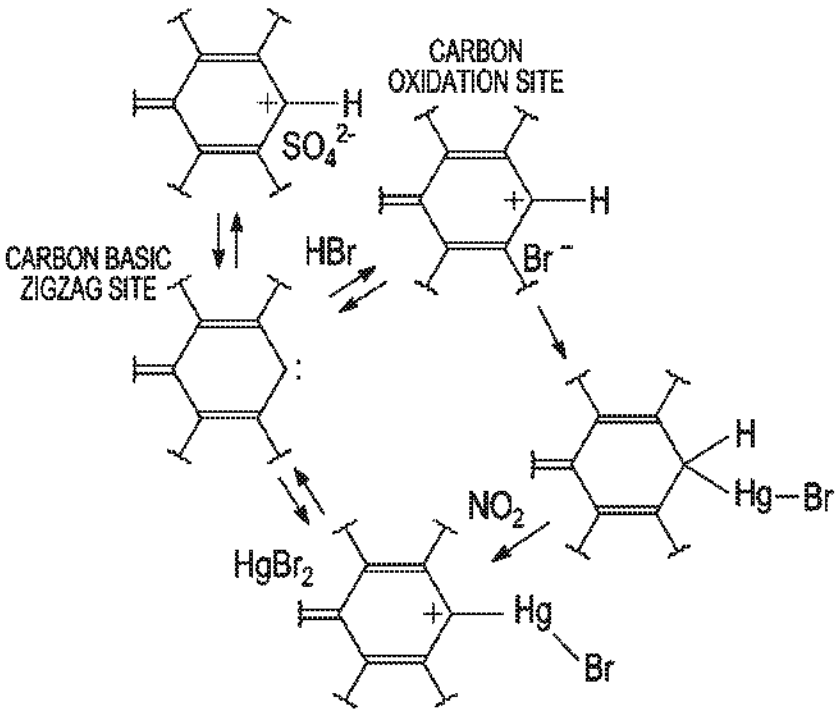

CARBON
OXIDATION SITE
H
SO_4^{2-}
H
CARBON BASIC
ZIGZAG SITE
HBr
Br^-
H
Hg—Br
NO_2
$HgBr_2$
Hg
Br

FIG. 2

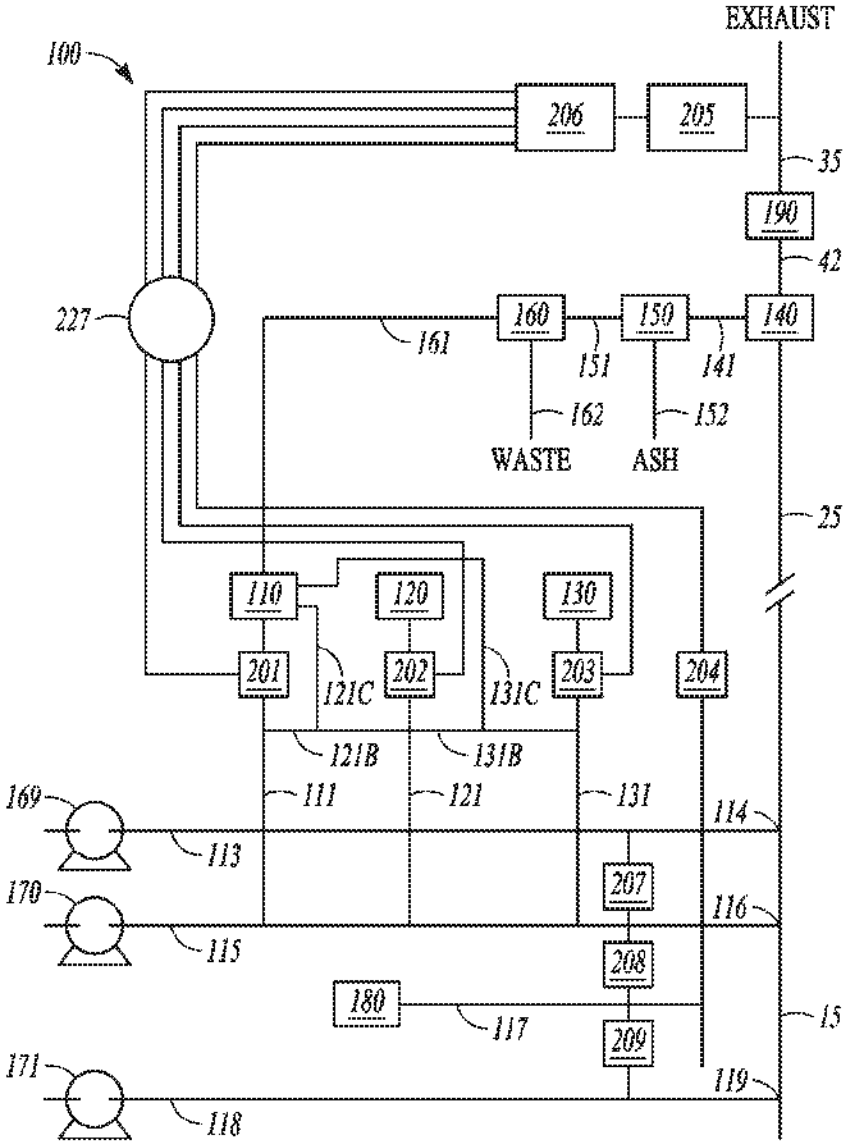

EXHAUST
100
206
205
35
190
42
227
160
150
140
161
151
141
162
152
WASTE
ASH
25
110
120
130
201
121C
202
131C
203
204
121B
131B
111
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113
207
116
170
115
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209
15
171
119
118

FIG. 3A

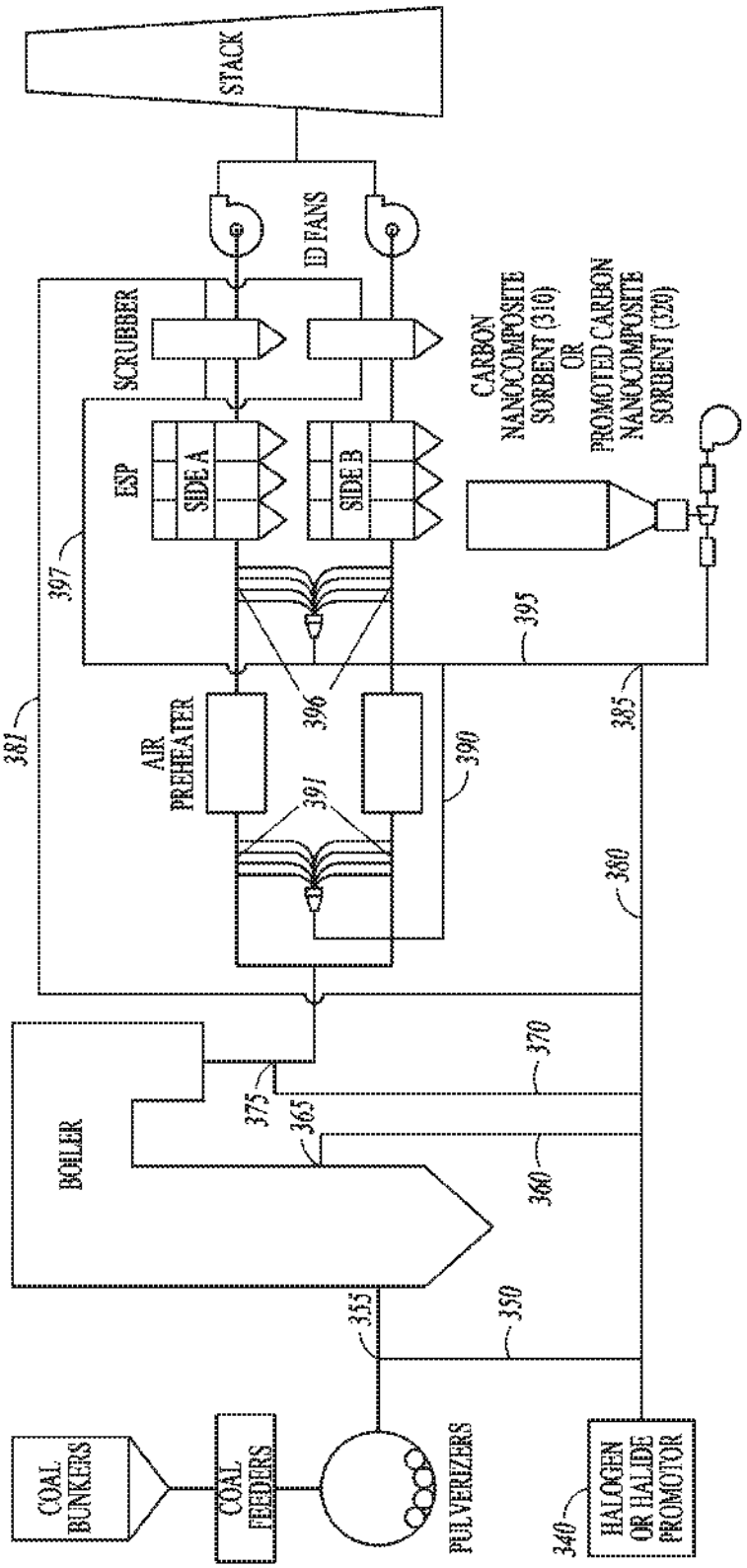

STACK
ID FANS
SCRUBBER
ESP
SIDE A
SIDE B
CARBON NANOCOMPOSITE SORBENT (310) OR PROMOTED CARBON NANOCOMPOSITE SORBENT (320)
397
395
396
381
385
AIR PREHEATER
391
390
360
370
375
365
BOILER
355
350
COAL BUNKERS
COAL FEEDERS
PULVERIZERS
340
HALOGEN OR HALIDE PROMOTOR

FIG. 3B

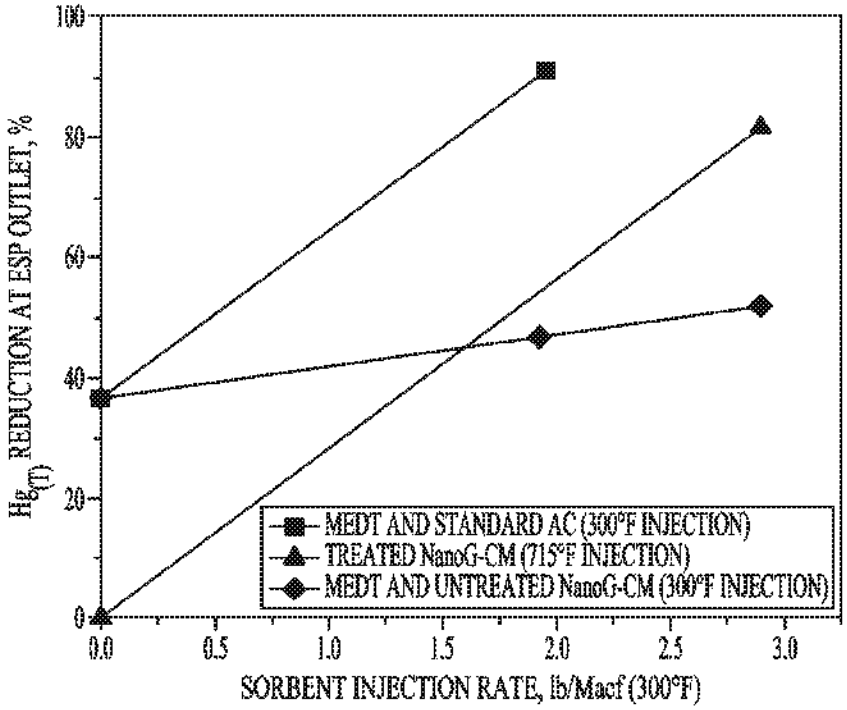

100
80
60
40
20
0
$Hg_{(T)}$ REDUCTION AT ESP OUTLET, %
0.0
0.5
1.0
1.5
2.0
2.5
3.0
SORBENT INJECTION RATE, lb/Macf (300°F)
MEDT AND STANDARD AC (300°F INJECTION)
TREATED NanoG-CM (715°F INJECTION)
MEDT AND UNTREATED NanoG-CM (300°F INJECTION)

FIG. 4

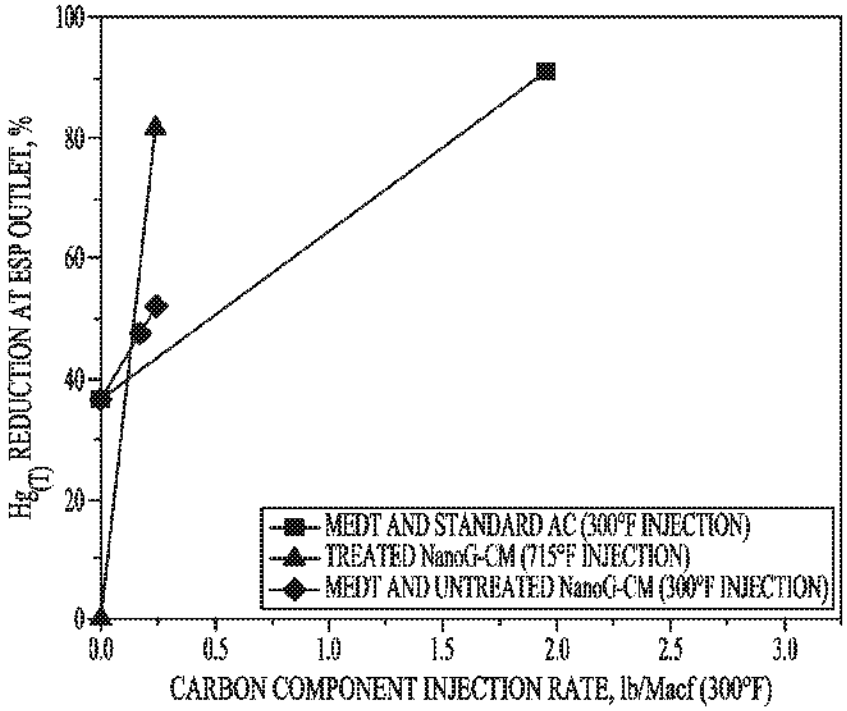

100
80
60
40
20
0
$Hg_{(T)}$ REDUCTION AT ESP OUTLET, %
0.0
0.5
1.0
1.5
2.0
2.5
3.0
CARBON COMPONENT INJECTION RATE, lb/Macf (300°F)
MEDT AND STANDARD AC (300°F INJECTION)
TREATED NanoG-CM (715°F INJECTION)
MEDT AND UNTREATED NanoG-CM (300°F INJECTION)

FIG. 5

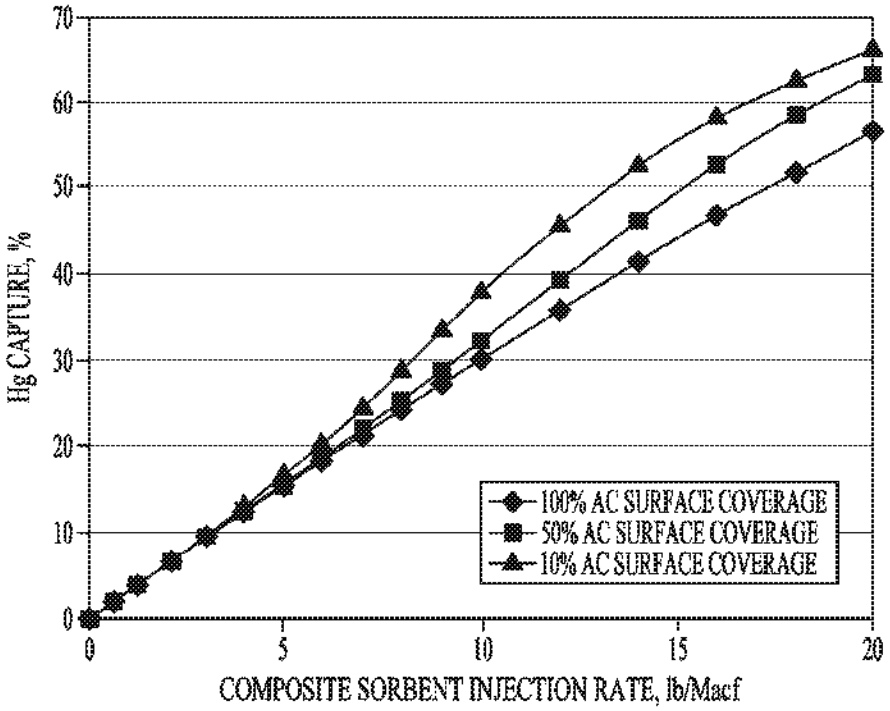

70
60
50
40
30
20
10
0
Hg CAPTURE, %
0
5
10
15
20
COMPOSITE SORBENT INJECTION RATE, lb/Macf
100% AC SURFACE COVERAGE
50% AC SURFACE COVERAGE
10% AC SURFACE COVERAGE

FIG. 6

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[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.

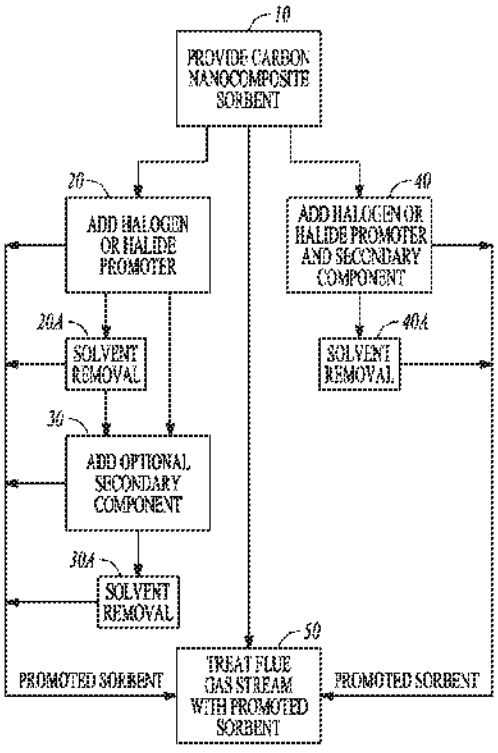


FIG. 1

WO 2013/162968 A3

NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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B01J20/20
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J B01D

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/168018 A1 (MOHAMADALIZADEH ALI [IR] ET AL) 14 July 2011 (2011-07-14) paragraph [0029] paragraph [0062]; example 2 -----	1,2,44, 45,48
X	US 2009/136401 A1 (YANG XIAOLIN DAVID [US] ET AL) 28 May 2009 (2009-05-28) paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2 paragraph [0048] - paragraph [0050]; table 3 ----- -/--	1-5,45, 48

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 July 2013	29/11/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Klemps, Christian

4

Form PCT/ISA/210 (second sheet) (April 2005)

BHE et al. EXHIBIT 1023
Page 313

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 2004/076570 A1 (JIA CHARLES Q [CA]) 22 April 2004 (2004-04-22) paragraph [0084] - paragraph [0086]; example 1 paragraph [0087] - paragraph [0092]; example 2 paragraph [0095] - paragraph [0099]; example 5	1-3,44, 45,48
X	A. BAKANDRITSOS ET AL: "High Surface Area Montmorillonite-Carbon Composites and Derived Carbons", CHEMISTRY OF MATERIALS, vol. 16, no. 8, 16 March 2004 (2004-03-16) , pages 1551-1559, XP055072551, ISSN: 0897-4756, DOI: 10.1021/cm0350030 Section: "Sample Preparation"; page 1552, right-hand column; figure 1	44,45,48
X	US 2008/090951 A1 (MAO DONGSHENG [US] ET AL) 17 April 2008 (2008-04-17) paragraph [0015]; figure 1	44,45,48

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/036964

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

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 fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-5, 44, 45, 48

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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5, 44, 45, 48

related to a method for separating a material from a gas that comprises the material, the method comprising providing or obtaining a carbon nanocomposite sorbent, contacting at least some of the material with the sorbent, to form a material-sorbent composition, and separating at least some of the material-sorbent composition from the material-containing gas, to give a separated gas; further to a method of making a such carbon nanocomposite sorbent; further to a such carbon nanocomposite

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2. claims: 6-42, 46, 49

related to a method for reducing the pollutant content of a pollutant-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent material, providing or obtaining a halogen or halide promotor, 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, contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition, and separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas; further to a promoted corbon nanocomposite sorbent made by reacting a portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent

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3. claims: 43, 47

related to a method for reducing the mercury content of a mercury-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent, the carbon nanocomposite sorbent made by steps comprising providing or obtaining a carbon precursor, providing or obtaining a substrate material, contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material, and heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent, providing or obtaining a halogen or halide promoter, 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, contacting at least part of the promoted sorbent with the mercury, to form a mercury-sorbent composition, and separating at least some of the mercury-sorbent composition from the mercury-containing gas; further to a mercury-sorbent composition made by

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

contacting a carbon nanocomposite sorbent with a mercury-containing gas

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/036964

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011168018 A1	14-07-2011	NONE	
US 2009136401 A1	28-05-2009	US 2009136401 A1	28-05-2009
		US 2012292564 A1	22-11-2012
US 2004076570 A1	22-04-2004	AU 2003278010 A1	04-05-2004
		CA 2408858 A1	18-04-2004
		US 2004076570 A1	22-04-2004
		WO 2004035176 A1	29-04-2004
US 2008090951 A1	17-04-2008	NONE	

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Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME

(57) Abstract: The present invention relates to activated carbon sorbents including nitrogen. In various embodiments, the present invention provides an activated carbon sorbent including a halogen- or halide-promoted activated carbon, the activated carbon sorbent particles including nitrogen in a surface layer of the sorbent particles. In various embodiments, the present invention provides a method of reducing the pollutant content in a pollutant-containing gas using the activated carbon sorbent. In various embodiments, the activated carbon sorbent can remove mercury from a mercury-containing gas that includes sulfur(VI) such as SO3 more efficiently than other sorbents

WO 2014/137907 A2

ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 61/773,549, filed March 6, 2013, the disclosure of which is incorporated herein in its entirety by reference.

BACKGROUND OF THE INVENTION

[0002] 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 mercury 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 sorbents such as activated carbon, which can then be removed by particulate separation 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 larger amounts are used.

[0003] Inhibition of mercury capture from gas streams by active carbon sorbents can occur when sulfur(VI) (e.g. SO_3, H_2SO_4) is present in the gas stream, with increasing inhibition at higher concentrations. Mercury capture above sulfur(VI) concentrations of 3 ppm by mole is limited. Many utilities desire to operate SO_3 injection systems at a minimum of about 5-6 ppm to improve ash collectability. However, a sulfur(VI) concentration of about 6 ppm can diminish elemental mercury capture by about 25%-50% or more. With this reduction, it becomes difficult, if not impossible, to economically achieve desired mercury levels. The scientific understanding of why a severe inhibition of mercury sorption exists when sulfur(VI) concentrations increase by such a small amount is limited.

SUMMARY OF THE INVENTION

[0004] In various embodiments, the present invention provides an activated carbon sorbent. The activated sorbent includes a halogen- or halide-promoted carbon. The activated carbon includes activated carbon sorbent particles including nitrogen. The concentration of nitrogen in a surface layer of the sorbent particles is at least one of 1) higher than the concentration of nitrogen in a core of the sorbent particles and 2) higher than the concentration of nitrogen in the carbon material from which the sorbent particles are derived.

[0005] In various embodiments, the present invention provides a method of making an activated carbon sorbent. The method includes contacting a carbonaceous material and a nitrogenous material, to provide an unpromoted carbon sorbent comprising nitrogen. The method also includes promoting at least a portion of the unpromoted sorbent by contacting the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen, wherein the concentration of nitrogen in the sorbent particles is higher than the concentration of nitrogen in the carbonaceous material.

[0006] In various embodiments, the present invention provides an activated carbon sorbent for use in mercury removal from a mercury-containing gas. The activated carbon sorbent includes a halogen- or halide-promoted inorganic activated carbon particles including nitrogen in a surface layer of the sorbent particles. The nitrogen atoms are at sufficient concentration in the surface layer of the activated carbon sorbent particles to at least one of a) decrease neutralization by HSO_3^{1-} or SO_3^{2-} of carbocations in the activated carbon sorbent, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions, and b) at least partially block carbocations in the activated carbon from forming ionic bonds with HSO_3^{1-} or SO_3^{2-}, as compared to a corresponding activated carbon sorbent including less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

[0007] In various embodiments, the present invention provides a method of reducing the pollutant content in a pollutant-containing gas. The method

BHE et al. EXHIBIT 1023
Page 321

includes obtaining or providing an activated carbon sorbent including activated carbon sorbent particles including nitrogen in a surface layer of the sorbent particles. The method includes contacting a pollutant-containing gas with the activated carbon sorbent. The contacting forms a pollutant-sorbent composition. The method also includes separating at least some of the pollutant-sorbent composition from the pollutant-containing gas. The separating gives a separated gas.

[0008] In various embodiments, the present invention provides a method for reducing the mercury content of a mercury-containing gas. The method includes obtaining or providing a carbon precursor. The carbon precursor includes nitrogen. The method includes obtaining or providing a substrate material. The method includes contacting the carbon precursor and the substrate material. The contacting provides an inorganic matrix-supported sorbent starting material. The method includes heating the inorganic matrix-supported sorbent starting material. The heating provides an unpromoted sorbent. The method includes promoting at least a portion of the unpromoted sorbent by contacting (e.g., chemically reacting) the portion of the unpromoted sorbent with a promoter to form a promoted inorganic matrix-supported activated carbon sorbent. The activated carbon sorbent includes activated carbon sorbent particles including nitrogen in a surface layer of the sorbent particles. The method includes contacting the mercury-containing gas with the activated carbon sorbent. The contacting forms a mercury-sorbent composition. The method also includes separating at least some of the mercury-sorbent composition from the mercury-containing gas. The separating gives a separated gas. The concentration of sulfur(VI) in the mercury-containing gas is about 3 – 1000 ppm by mole. A first quantity of the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate. The first adsorption rate is higher than a mercury absorption rate of the first quantity of a corresponding activated carbon sorbent including at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support.

BHE et al. EXHIBIT 1023
Page 322

[0009] In various embodiments, the present invention provides a method of making an activated carbon sorbent. The method includes obtaining or providing an unpromoted carbon sorbent including nitrogen. The method includes promoting at least a portion of the unpromoted sorbent by contacting (e.g., chemically reacting) the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent including activated carbon sorbent particles including nitrogen in a surface layer of the sorbent particles.

[0010] Various embodiments of the present invention provide certain advantages over other activated carbon sorbents and methods of using the same, at least some of which are unexpected. In some embodiments, the activated carbon sorbent can separate a material (e.g., a pollutant) from a gas that includes that material more efficiently than other methods. In various embodiments, mercury removal efficiencies of the activated carbon exceed or match that of conventional methods with added benefits such as reduced costs. The method and materials of various embodiments of the present invention can operate more efficiently than other methods of mercury removal. In some embodiments, 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.

[0011] For example, in some embodiments, a given mass of the nitrogen-containing activated carbon sorbent can absorb mercury from a mercury-containing gas stream including sulfur(VI) (e.g., SO_3, H_2SO_4, or the like), such as greater than about 3 ppm sulfur(VI), such as about 3-200 ppm sulfur (VI), 3-1000 ppm sulfur(VI), or about 3-10 ppm sulfur(VI), at a higher rate than the same mass of a corresponding activated carbon sorbent including less or no nitrogen, such as a lower concentration of nitrogen or no nitrogen in a corresponding particle surface layer. In some embodiments, carbocations in the activated carbon sorbent are neutralized less by ions derived from SO_3, such as SO_3^{2-} or HSO_3^{1-}, than other activated carbon sorbents, such as other activated carbon sorbents including less or substantially no nitrogen in a corresponding

BHE et al. EXHIBIT 1023
Page 323

particle surface layer. In some embodiments, carbocations in the activated carbon sorbent are at least partially blocked from ions derived from SO_3, such as SO_3^{2-} or HSO_3^{1-}, more than in other activated carbon sorbents, such as in other activated carbon sorbents including less or substantially no nitrogen in a corresponding particle surface layer.

[0012] In some embodiments, the sorbent can be regenerated and reused, reducing disposal of spent sorbents and decreasing the cost of mercury removal. In some embodiments, preparation or promotion of the activated carbon sorbent can advantageously occur on site. On site preparation and promotion can have advantages including, for example: reduction or elimination of equipment costs and operating costs of a separate preparation facility or location, reduction or elimination of transportation costs, fresher and more reactive sorbent, reduction of handling, on-site tailoring of composition (such as when changing fuels or reducing loads).

[0013] In some embodiments, counter to traditional teachings that inorganic components can hinder sorption of pollutants on activated carbon, an inorganic matrix support in the sorbent can enhance the sorption of pollutant in the activated carbon, such as on a proximate and oxidatively reactive carbon graphene layer. In various embodiments, an inorganic matrix support can stabilize the development of cationic sites on the proximate graphene carbon structures which can oxidize pollutants such as mercury. In embodiments that include an inorganic matrix-supported nanocomposite that is promoted via a 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 can form a complex with basic character that can react with SO_2 or SO_3 in the pollutant-containing gas and can prevent their interference with the sorption of pollutants such as mercury in or near active sites on the activated carbon.

[0014] Clays are usually difficult to filter or separate from an aqueous medium. In some embodiments that include clay as an inorganic matrix support, the clay is advantageously stabilized to dispersion in an aqueous medium, and can be easily separated from an aqueous medium by filtration.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Reference will now be made in detail to certain embodiments of the disclosed subject matter. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0016] 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 range of "about 0.1% to about 5%" or "about 0.1% to 5%" should be interpreted to include not just about 0.1% to about 5%, but also the individual values (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. The statement "about X to Y" has the same meaning as "about X to about Y," unless indicated otherwise. Likewise, the statement "about X, Y, or about Z" has the same meaning as "about X, about Y, or about Z," unless indicated otherwise.

[0017] 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.

[0018] 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. 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

[0019] The term "about" as used herein 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.

[0020] The term "substantially" as used herein 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.

[0021] The term "number-average molecular weight" as used herein refers to the ordinary arithmetic mean of the molecular weight of individual molecules in a sample. It is defined as the total weight of all molecules in a sample divided by the total number of molecules in the sample. Experimentally, the number average molecular weight (M_n) is determined by analyzing a sample divided into molecular weight fractions of species i having n_i molecules of molecular weight M_i through the formula $M_n = \Sigma M_i n_i / \Sigma n_i$. The number average molecular weight can be measured by a variety of well-known methods including gel permeation chromatography, spectroscopic end group analysis and osmometry.

[0022] The term "weight-average molecular weight" as used herein refers (M_w), which is equal to $\Sigma M_i^2 n_i / \Sigma M_i n_i$, where n_i is the number of molecules of molecular weight M_i. In various examples, the weight average molecular weight can be determined using light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.

BHE et al. EXHIBIT 1023
Page 326

[0023] 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.

[0024] 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.

[0025] The term "room temperature" as used herein refers to a temperature of about 15 °C to 28 °C.

[0026] 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

[0027] In various embodiments, the present invention provides an activated carbon sorbent and associated method for reduction of mercury content for use in combustion systems that have inherently high levels of sulfur(VI) (e.g. as SO_3, or related compounds that can be derived therefrom such as H_2SO_4 or other sulfates) in the flue gas and for use in plants that use SO_3 injection for ash conditioning for improved ash collection. The method can obtain high mercury capture rates in a high sulfur(VI)-content flue gas by, in some examples, overcoming the kinetic and equilibrium effects that can inhibit mercury capture in high SO_3 or high-sulfate (e.g. high sulfur(VI)) systems. The activated carbon sorbent includes activated carbon sorbent particles. The concentration of nitrogen in a surface layer of the sorbent particles can be higher than the concentration of nitrogen in a core of the sorbent particles. In some examples, the activated carbon sorbent can be promoted.

[0028] In various embodiments, the activated carbon sorbent and associated method can be effective for removal of elemental mercury vapor in an air or flue gas stream at moderate temperatures (e.g., about 25-330°C, or about

BHE et al. EXHIBIT 1023
Page 327

50-500 °C). In some examples, the activated carbon is not impregnated with sulfur or metal halides, which can be unstable at higher temperatures.

[0029] In some embodiments, the removal process does not involve adsorption of the elemental mercury like that occurring at low temperatures, but can involve the catalyzed reaction of mercury with an oxidant to form an organomercury compound that includes the mercury bound to the activated carbon surface, wherein the mercury can be released via, e.g., reaction with acid, to provide a mercury (II) species with low vapor pressures such as mercury sulfate, mercury bromide, or mercury chloride. The ionic mercury(II) form can be an oxide or salt of an optional acid used in the process (such as sulfate from sulfuric acid), which can have lower volatility. The activated carbon can exhibit a high rate of oxidative catalytic activity due to, for example, numerous active catalytic sites and, at the same time, possess a large surface area for generation of the organomercury compound and thus rapidly generate the converted mercury(II) salt.

Activated carbon sorbent including nitrogen.

[0030] In various embodiments, the present invention provides an activated carbon sorbent. The activated carbon sorbent can include halogen- or halide-promoted activated carbon particles; in other embodiments, the activated carbon sorbent is not promoted. In some examples, the activated carbon can have an inorganic matrix-support.

[0031] The activated carbon sorbent can include activated carbon sorbent particles. The concentration of nitrogen in a surface layer of the sorbent particles can be at least one of 1) higher than the concentration of nitrogen in a core of the sorbent particles and 2) higher than the concentration of nitrogen in the activated carbon material from which the activated carbon sorbent particle was derived. The surface layer of each particle can independently be continuous (e.g., unbroken, with minimal or no gaps) or non-continuous. The surface layer can be at the outer surface of the particle. The surface layer of each particle can independently have any suitable thickness. The surface layer can have a variable thickness, or can have a substantially consistent thickness. In some embodiments, the surface layer can have a thickness of about 0.000,001% to

about 99.99% of the radius of the particle, 0.001% to 99%, 0.001% to about 50%, 1% to about 50%, 0.1% to 25%, or about 25% to 50% of the radius of the particle. If the particle is non-spherical the radius can be estimated as about one-half of the largest dimension of the particle.

[0032] In some embodiments, each activated carbon particle can independently include about 1.001 times higher nitrogen concentration in the surface layer than in the core or less, or about 1.01, 1.1, 1.2, 1.4, 1.6, 1.8, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 50, 100, or about 1000 times higher nitrogen concentration in the surface layer than in the core. In some embodiments, the concentration of nitrogen in the surface layer can be about 0.000,001 wt% or less, or about 0.001 wt%, 0.01 wt%, 0.1 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, or about 90 wt% or more nitrogen. In some examples, the concentration of nitrogen in the surface layer can be about 0.001 wt% - 99 wt% nitrogen, 5 wt% - 80 wt%, or about 5-60 wt%. In various embodiments, the concentration of nitrogen in the core can be about 0 wt%, 0.000,001 wt%, or about 0.001 wt%, 0.01 wt%, 0.1 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 50 wt%, or 90 wt% or more. In some examples, the concentration of nitrogen in the core can be about 0.001 wt% - 99 wt% nitrogen, 0.1 wt% - 20 wt%or about 1 wt% - 6 wt%.

[0033] The activated carbon sorbent can be in any suitable form. For example, the activated carbon can be granular, or fine particles. The activated carbon can have any suitable shape, such as spherical or irregular. The activated carbon can have an average diameter of about 0.1 nm or less, or about 1 nm, 10 nm, 100 nm, 1 μm, 10 μm, 100 μm, 1 mm, or about 10 mm or more. In some examples, the activated carbon has a diameter of about 0.01 μm or less, or about 0.1 μm, 1 μm, 2 μm, 3 μm, 4 μm, 5 μm, 10 μm, 20 μm, 30 μm, 40 μm, 50 μm, 60 μm, 70 μm, 80 μm, 90 μm, 100 μm, 1000 μm or more. In some examples, the diameter of the particle is about 0.1-1000 μm, or 1-100 μm, or about 1-30 μm. If a particle is non-spherical, the diameter can be estimated as the longest dimension of the particle. The absorption capacity of the activated carbon sorbent including mercury can be about 0.000,1 mg mercury per gram of sorbent or less, or about 0.001 mg/g, 0.01, 0.1, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45,

BHE et al. EXHIBIT 1023
Page 329

50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 150, 200, 300, 400, 500, 750, or about 1 g mercury per gram of sorbent or more.

[0034] In some embodiments, at least some of the carbon in the activated carbon is in the graphene form of carbon. The graphene form of carbon can, in some embodiments, include higher concentrations of locations suitable as active sites. In some examples, certain parts of graphene carbon can have the highest concentrations of locations suitable as active sites: 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 activated carbon sorbent 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.

[0035] In some embodiments, the nitrogen is substantially homogenously distributed throughout the activated carbon particles. In some embodiments, the nitrogen is substantially homogenously distributed in the core of the activated carbon sorbent particles; in other embodiments, the nitrogen can have any suitable distribution in the core. In some embodiments, the nitrogen is substantially homogenously distributed in the surface layer of the activated carbon sorbent particles. In some embodiments, the nitrogen in the surface layer is not homogeneously distributed; e.g., the nitrogen can have a gradient with the highest concentration at the outside of the surface layer and a lower concentration at an inside of the surface layer.

[0036] The nitrogen can be in any suitable form within the activated carbon. In some examples, the nitrogen can be a nitrogen atom bound to one or more hydrogen atoms or one or more other atoms that are, for example, carbon-containing groups that are part of the activated carbon framework (e.g. the activated carbon backbone or appendages thereof), or to an organic group. In some examples, for example, the nitrogen can be neutral or can bear a positive charge (e.g. ammonium) or a negative charge. The nitrogen can have any suitable oxidation state, for example zero or one. The nitrogen can be bound to 4, 3, 2, 1, or zero hydrogen atoms. The nitrogen can be bound to one or more

activated carbon frameworks at zero, 1, 2, 3, or 4 locations. In some embodiments, the nitrogen can include one or two double bonds or one triple bond to the carbon framework of the activated carbon or to other functional groups, such that the nitrogen is bound to 1, 2, or 3 carbon atoms.

[0037] The nitrogen in the activated carbon can be derived from any nitrogen containing compound, such as a nitrogen-containing organic or inorganic compound, such as by pyrolysis or carbonization. In some examples, the nitrogen is derived from or part of any nitrogen-containing heterocycle, or from any other nitrogen-containing compound. For example, the nitrogen can be derived from indole, quinoxaline, carbazole, isoquinoline, piperazine, quinolone, quinoxaline, diazabicyclooctane, polyacrylonitrile, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, vinylpyrrolidone-acrylic acid copolymer, vinylpyrrolidone-maleic acid copolymer, polyethylenimine, an amino acid (e.g., alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, or valine), analine, nitrobenzene, hydroxylamine, urea, hydrazine, sulfamic acid, nitriles, carbamates, isocyanates, urethanes, or a combination thereof. In some examples, the nitrogen in the activated carbon can be derived from or part of a nitrogen-containing inorganic compound, such as ammonia, ammonium bromide, ammonium chloride, nitric acid, nitrous acid, nitrogen dioxide, compounds including NO_3, compounds including NO_2, and the like.

[0038] In various embodiments, the nitrogen-containing activated carbon sorbent can absorb pollutants such as mercury at a higher rate in a given concentration of sulfur(VI) than other sorbents. In some examples, a first quantity of the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate in a gas composition including mercury wherein the concentration of sulfur(VI) in the gas composition is about 3 - 2000 ppm by mole, where the first adsorption rate is higher than a mercury absorption rate of the first quantity of a corresponding activated carbon sorbent including at least one of a) less (e.g., lower concentration) or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support.

BHE et al. EXHIBIT 1023
Page 331

[0039] The mechanism of operation of the activated carbon sorbent is not intended to be limited to any particular theory of operation as advanced herein. In some embodiments, the nitrogen in the surface layer at least partially decreases neutralization by SO_3 (or ions or other materials derived from SO_3 such as HSO_3^{1-} or SO_3^{2-}) of carbocations in the activated carbon sorbent, as compared to a corresponding activated carbon sorbent including less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions. In some examples, the nitrogen in the surface layer at least partially blocks carbocations in the activated carbon from forming ionic bonds with SO_3 (or ions or other materials derived from SO_3 such as HSO_3^{1-} or SO_3^{2-}), as compared to a corresponding activated carbon sorbent including less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

[0040] In various active carbon sorbents, two issues can occur during pollutant capture such as mercury capture: 1) getting high oxidation reactivity at a carbon edge site (kinetic effect) and 2) preventing/avoiding the loss of oxidized mercury from the carbon-bound states as a result of displacement by sulfate (equilibrium effect). Elemental mercury in the gas phase can be oxidized at the carbon edge surface (cationic zigzag sites) and can be bound covalently as an organomercury halide. The cationic sites can be formed by addition of acids or halogens (X_2) to the carbon edge structure, which can result in a carbenium-halide ion pair. The oxidation can be assisted by the negative halide ion stabilizing the developing positive charge on the mercury atom as it adds to the carbenium atom. The oxidation can occur more readily if the oxidation potential (charge) of the carbenium ion or stability thereof is higher, which can be influenced or determined by the adjacent charges present in the carbon framework structure and nearby surroundings. Additional cationic functionality in the structure can raise the oxidation potential (increases positive charge) at the reactive site, or can increase the stability of a positive charge at the reactive site. Negative groups (such as ions derived from SO_3, e.g., SO_3^{2-} and SO_2^{1-}, can stabilize and lower the overall charge and available carbenium ions and thereby reduce the reactivity for oxidation of the mercury and availability for capture of mercury.

BHE et al. EXHIBIT 1023
Page 332

[0041] The longer-term equilibrium effect can be less important for capture over a short contact time, such as inflight capture by electrostatic precipitators (ESPs). However, in some situations the equilibrium displacement problem can be more important, e.g., baghouse collection or SO_3 injection or formation in a selective catalytic reduction (SCR) unit. Since sulfate concentrations can increase with time of exposure on the carbon surface, their effect in displacing mercury halides into the gas phase (desorption and breakthrough) can be important in long exposure times. When SO_3 related compounds and ions such as sulfuric acid, sulfate, or related ions, are initially present or form quickly on a wet surface, e.g., with SO_3 injection, the equilibrium displacement effect can also become important in systems with a short contact time.

[0042] In various embodiments, the nitrogen in the surface layer can stabilize or increase positive charge in the carbon structure which can overcome depletion of charge by sulfate and the carbon edge can be promoted with a halogen/halide. In some embodiments, the collection of cationic centers in the carbon edge structures (normally present in a halogenated (e.g. brominated) carbon and useful for rapid mercury oxidation) can be impaired by interference of bisulfate ions and other related ions formed from SO_3 reaction at the carbon surface. These anions can neutralize the positive charge of the carbenium ions and lower the overall oxidation potential of the remaining reactive sites that have a shared charge. Additional cationic centers can be generated within the carbon structure by introducing nitrogen atoms during the activated carbon formation, helping to counter this effect and offset some of the charge that can used by ionic or other interactions with, e.g., SO_3 or ions derived from SO_3. Atoms such as nitrogen can be added in the polycyclic structure to form increased cations or to stabilize existing cations.

[0043] In some embodiments, the nitrogen in the surface layer of the activated carbon sorbent particles increases the cationic charge in the sorbent because the nitrogen protects the cation centers from SO_3 and ions or compounds derived from SO_3. The nitrogen atoms can form or be part of a charged cage or other protective blocking structure around a carbon edge structure to prevent access by SO_3 and ions or compounds derived from SO_3 such as anionic sulfate

groups but allow diffusion of mercury atoms into the nanostructure to reach active centers for oxidation or sorbtion.

[0044] In some embodiments, an inorganic matrix support such as clay can help to block active cationic centers from access by SO_3 and ions or compounds derived from SO_3 or can help to stabilize or increase the cationic charge in the active carbon sorbent.

[0045] In some embodiments, addition of acid or acidic materials to the activated carbon improves the performance. In various embodiments, acid or acidic materials can be added prior to the use of the carbon by impregnating an acidic solution into the carbon, or can be added as a solution or gas to the sorbent bed during use. The modified carbon can be impregnated with an acidic material, such as about 1 wt% or less or about 2 wt%, 3, 4, 5, 6, 7, 8, 9, 10, 15, or about 20 wt% or more or acidic material, such as HBr, HCl, H_2SO_4, and the like.

Method of reducing pollutant content in a pollutant-containing gas.

[0046] In various embodiments, the present invention provides a method of using the activated carbon sorbent. The method can be any suitable method. For example, some embodiments provide a method of reducing the pollutant content in a pollutant-containing gas. In some examples, the pollutant-containing gas can include at least some oxygen. The method can include obtaining or providing an activated carbon sorbent including activated carbon sorbent particles including nitrogen in a surface layer or the sorbet particles. In some embodiments, the concentration of nitrogen in a surface layer of the sorbent particles can be higher than the concentration of nitrogen in a core of the sorbent particles. The activated carbon sorbent can be any activated carbon sorbent including nitrogen described herein. In some examples, the activated carbon sorbent including nitrogen can be a promoted activated carbon sorbent including nitrogen. In some examples, the activated carbon sorbent including nitrogen can be an inorganic matrix-supported or nanocomposite activated carbon sorbent including nitrogen. In some examples, the activated carbon sorbent can be both promoted and an inorganic matrix-supported or nanocomposite activated carbon sorbent including nitrogen. In some

embodiments, the activated carbon sorbent can be promoted but include no inorganic matrix support. In some embodiments, the activated carbon sorbent can be neither promoted nor inorganic matrix-supported. The activated carbon sorbent can include binding sites that can bind with at least one of the pollutant in the pollutant-containing gas and an oxidized species of the pollutant, to form the pollutant-sorbent composition. At least a portion of the binding sites in the activated carbon sorbent can react with at least one of the pollutant and an oxidized species of the pollutant, to form the pollutant-sorbent composition.

[0047] The method of reducing the pollutant content in a pollutant-containing gas can include contacting a pollutant-containing gas with the activated carbon sorbent. The contacting forms a pollutant-sorbent composition. The contacting can be any suitable contacting. In some embodiments, contacting the pollutant-containing gas with the activated carbon sorbent can include adding or injecting the activated carbon sorbent into the pollutant containing gas. 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.

[0048] In some embodiments, during the contacting of the pollutant-containing gas with the activated carbon sorbent, the activated carbon sorbent can be in any suitable configuration such that it contacts the pollutant-containing gas. For example, during the contacting, the activated carbon sorbent can be at least one of in a fixed structure such as a fixed bed, in a moving structure such as a moving bed, in a scrubber, in a filter (e.g., a fixed filter or a travelling/moving filter) or suspended in the pollutant-containing gas.

[0049] The pollutant-sorbent composition can be any suitable composition including the pollutant or an oxidized or otherwise chemically transformed form of the pollutant and the activated carbon sorbent. In some embodiments, 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 organomercury compound including the carbon framework

of the activated carbon bound to mercury, which can be released as a mercury (II) compound upon reaction with a suitable acid to generate the salt thereof. In some embodiments, the mercury-sorbent composition can include at least one of elemental mercury, organomercury compound, and Hg(II) compounds.

[0050] 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 after separating the pollutant-sorbent composition from the pollutant-containing gas, the separated gas has about 1% or less, 3%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.9%, 99.99%, or about 99.999% or more of the mercury that was originally present in the pollutant-containing gas. 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 or another step. In some examples, elemental or transformed mercury that has been released from the mercury-sorbent composition can contact activated carbon sorbent to form a mercury-sorbent composition, to be removed later via the separation step.

[0051] The method of reducing the pollutant content in a pollutant-containing gas can include separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give separated gas. In some embodiments, separating at least some of the pollutant-sorbent composition from the pollutant containing gas includes separating in a particulate separator. The particulate separator can be any suitable particulate separator, such as an

BHE et al. EXHIBIT 1023
Page 336

electrostatic precipitator (ESP), a baghouse, a wet scrubber, a filter, cyclone, fabric separator, or any combination thereof. 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. 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.

[0052] 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%, 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, or in the form of a transformed mercury, such as an organomercury compound including the mercury bound to the carbon framework of the activated carbon or as Hg(II) complexed with a suitable counterion.

[0053] In some embodiments, at least one of the contacting and the separating occurs in an aqueous scrubber. The aqueous scrubber can be any suitable aqueous scrubber. For example, the scrubber can include an aqueous slurry that includes the activated carbon sorbent.

[0054] In some embodiments, the method removes about 1% or less, or about 2%, 3, 4, 5, 10, 20, 30, 40, 50, 60, 70, 80, 85, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.5, 99.9, 99.99, 99.999, or about 99.9999% or more of the mercury present in the mercury-containing gas (e.g. the final concentration of mercury divided by the initial concentration of mercury). In some embodiments, the activated carbon sorbent combines with about 50-100 wt% of the mercury present in the mercury-containing gas, or about 60-90 wt%, 60-80 wt%, 70-80 wt%, 80-90 wt%, 90-100 wt%, or about 95-100 wt% or the mercury present in the mercury-containing gas.

[0055] In some embodiments, the concentration of sulfur(VI) in the mercury-containing gas (e.g. from SO_3, H_2SO_4, and the like) is greater than about 3 ppm (by mole) and a first quantity of the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate, wherein the first adsorption rate is higher than a mercury absorption rate under substantially similar conditions of the first quantity of a corresponding activated carbon sorbent including at least one of a) less or substantially no nitrogen in a corresponding surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support. In some embodiments, the concentration of SO_3 in the pollutant-containing gas at or near the location wherein the pollutant-containing gas contacts the sorbent is about 1 ppm to about 100,000 ppm, 2-10,000 ppm, 3 ppm-1000 ppm, 3-100 ppm, 3-50 ppm, 3-10 ppm, or about 3-6 ppm or more, or the concentration of sulfur(VI) in the pollutant-containing gas (e.g. from SO_3, H_2SO_4, and the like) at or near the location wherein the pollutant-containing gas contacts the sorbent is about 1 ppm to about 100,000 ppm, 2-10,000 ppm, 3 ppm-1000 ppm, 3-100 ppm, 3-50 ppm, 3-10 ppm, or about 3-6 ppm or more, wherein ppm designates parts per million by mole. The concentration can be an instantaneous concentration, or an average concentration over time. The nitrogen in the surface layer of the activated carbon sorbent particles can decrease neutralization of carbocations in the activated carbon by at least one of SO_3^{2-} and HSO_3^{1-}, as compared to a corresponding activated carbon sorbent including less or substantially no nitrogen in a corresponding surface layer under substantially similar conditions. The nitrogen in the surface layer of the activated carbon sorbent particles can at least partially block carbocations in the activated carbon from at least one of SO_3^{2-} and HSO_3^{1-}, as compared to a corresponding activated carbon sorbent including less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

[0056] In some embodiments, the method of reducing the pollutant content in a pollutant-containing gas includes at least one of during and prior to the contacting adding or injecting an alkaline component into the pollutant-containing gas. The alkaline component can be any suitable alkaline component, such as an oxide, hydroxide, carbonate, or phosphate of an alkali element, an

BHE et al. EXHIBIT 1023
Page 338

alkali or alkaline-earth element, and a compound or material including the same. In various examples, the addition of an alkaline component separately or with the carbon sorbent can result in improved mercury capture. 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, Se, 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.

[0057] In some embodiments, the activated carbon includes a stabilizing agent. In some examples, the stabilizing agent can include at least one of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, or mixtures thereof. The stabilizing agent can be added before or after promotion.

[0058] In various embodiments, the rate of mercury removal can decrease gradually with increasing temperature and with increased loading of mercury, at least partially due to the increase in the rate of a reverse reaction. In some examples, the highest rates can occur at about 100 to 150 °C, 50-200 °C, or about 50-250 °C. In some examples, at 400°C, the reverse reaction can be highly favored thermodynamically. In some examples, the activated carbon can be regenerated by washing with water to remove sulfuric acid thereon, such as described in U.S. Patent No. 8,173,566.

[0059] In some embodiments, the method of reducing the pollutant content in a pollutant-containing gas can include regenerating the pollutant-sorbent composition to give a regenerated activated carbon sorbent. The regeneration can be any suitable regeneration that allows the regenerated activated carbon sorbent to be reused for removing pollutant from the pollutant-containing gas. The method can include using the regenerated activated carbon sorbent to remove the pollutant from the pollutant-containing gas.

Method of making activated carbon including nitrogen.

[0060] In some embodiments, the activated carbon including activated carbon particles including nitrogen is commercially acquired. In other embodiments, the activated carbon including nitrogen is synthesized. For

example, the method of reducing the pollutant content in a pollutant-containing gas can include making an activated carbon including nitrogen.

[0061] For example, in the method of reducing the pollutant content in a pollutant-containing gas, obtaining or providing the activated carbon sorbent can include obtaining or providing a carbon precursor including nitrogen. The method can also include processing (e.g., heating) the carbon precursor, to provide the activated carbon sorbent. The processing can include any suitable processing. In methods that include heating the carbon precursor, the method can include any other suitable optional step in addition to the heating, such as washing, chemical treatment, or vibration. In some embodiments, the carbon precursor includes a carbonaceous material including carbon and a nitrogenous material including nitrogen. The heating can include heating to about 100 °C to 15,000 °C, 200 °C to 10,000 °C, 300 °C to 9000 °C, or about 400 °C to 8000 °C.

[0062] The carbonaceous material can be any suitable carbonaceous material. For example, the carbonaceous material can be an organic compound. In some examples, the carbonaceous material includes at least one of brown sugar, barley sugar, caramel, cane sugar, corn syrup, starch, molasses, molasses raffinate (sugar waste product), glucans, galactans, xylans, and a sugar waste product. In some examples, the carbonaceous material includes powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, or 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. The nitrogen can be derived from or part of can be any suitable nitrogenous material. For example, the nitrogenous material can be a nitrogen-containing organic compound, such as a nitrogen-containing heterocycle. In some examples, the nitrogenous material includes indole, quinoxaline, carbazole, isoquinoline, piperazine, quinolone, quinoxaline, diazabicyclooctane, polyacrylonitrile, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, vinylpyrrolidone-acrylic acid copolymer, vinylpyrrolidone-maleic acid copolymer, polyethylenimine, an amino acid (e.g., alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, or valine),

BHE et al. EXHIBIT 1023
Page 340

aniline, nitrobenzene, hydroxylamine, urea, hydrazine, sulfamic acid, nitriles, carbamates, isocyanates, urethanes, or a combination thereof. The nitrogenous material can be any suitable ammonium salt, such as an ammonium salt derived from an aliphatic nitrogen-containing compound, an aromatic amine-containing compound, or a heterocyclic nitrogen-containing compound; in embodiments wherein the nitrogenous material is a halide salt, the activated carbon including nitrogen perform equivalently to an promoted material and a promotion step can be skipped or reduced. In some examples, the nitrogenous material can be at least one of ammonia, ammonium bromide, ammonium chloride, nitric acid, nitrous acid, nitrogen dioxide, compounds including NO_3, compounds including NO_2, and the like.

[0063] In one example, the activated carbon including activated carbon sorbent particles including nitrogen can be prepared by surface modification of any kind of activated carbon or char by applying a nitrogen-containing polymer coating or impregnation to the existing carbon or lower temperature char and recarbonizing the impregnated carbon. The coating or impregnation can include a polymer or copolymer containing a nitrogen heterocycle such as a polymerized vinylpyrollidone. In one example of this type of carbon, poly(vinylpyrrolidone), poly(vinylpyrrolidone-co-maleic acid) or poly(vinylpyrrolidone-covinyl acetate) is used to coat the carbon surface. Upon heating or recarbonization, the impregnated mixture can form a nitrogen-containing activated carbon surface layer on the particles. The nitrogen-concentration in the surface layer of the nitrogen-containing activated carbon can be higher than the nitrogen concentration of the material prior to the surface modification or impregnation with nitrogen.

[0064] In one example, the activated carbon including nitrogen can be prepared by surface modification of an oxidized char by treatment of the char with a suitable nitrogenous compound, such as ammonia or urea, followed by activation of the nitrogen-impregnated material.

[0065] In one example, the activated carbon including nitrogen can be prepared by impregnation of nitrogen containing compounds into a char followed by carbonization and activation of the impregnated char by convention methods. One example carbon of this type is the combination of amines or

BHE et al. EXHIBIT 1023
Page 341

amino acids with carbohydrates, which combination undergoes the Maillard condensation reaction on heating to form carbon surface containing nitrogen heterocyclics.

[0066] In one example, the activated carbon including nitrogen can be prepared by impregnation of a nitrogen containing compound into a coal, lignite, or leonardite, followed by carbonization and activation.

Promoted activated carbon sorbent including nitrogen.

[0067] In some embodiments, the activated carbon including activated carbon sorbent particles including nitrogen includes a promoted activated carbon sorbent including nitrogen. The activated carbon sorbent including nitrogen used in the method of reducing the pollutant content in a pollutant-containing gas can be a promoted activated carbon sorbent, and can include nitrogen. The method can include promoting an unpromoted activated carbon sorbent, or the promoted sorbent can be commercially acquired.

[0068] For example, the method of reducing the pollutant content in a pollutant-containing gas can include obtaining or providing an unpromoted carbon sorbent. The unpromoted carbon sorbent can be any suitable unpromoted sorbent including nitrogen, and can be synthesized or commercially acquired. The method can include obtaining or providing a promoter. The method can include promoting at least a portion of the unpromoted sorbent by contacting (e.g., chemically reacting) the portion of the unpromoted sorbent with the promoter to form the activated carbon sorbent.

[0069] The promoter can be any suitable promoter, such that a promoted sorbent is formed that is effective for the removal of pollutants such as mercury from a pollutant-containing gas. For example, the promoter can include a halogen or halide promotor. The halogen or halide can be fluorine or fluoride, chlorine or chloride, bromine or bromide, or iodine or iodide. In some examples, the promotor can include at least one of a halogen, a Group V halide, a Group VI halide, a hydrogen halide, an ammonium halide, an alkali earth metal halide, and an alkaline earth metal halide. Thus, the activated carbon in some embodiments can be at least one of halogen-promoted, Group V halide-promoted, Group VI halide-promoted, hydrogen halide-promoted, ammonium halide-promoted, alkali

BHE et al. EXHIBIT 1023
Page 342

earth metal halide-promoted, and alkaline earth metal halide-promoted. The promoter can include at least one of HI, IBr, ICl NH_4Br, NaBr, $CaBr_2$, HBr, NaCl, $CaCl_2$, and HCl. In some examples, the promoter is NH_4Br, and can be injected into a warm zone in a duct, for example separately or with the activated carbon sorbent. In some examples, any suitable halogen- or halide-containing material, such as NaCl, $CaCl_2$, NaBr, or $CaBr_2$ can be injected with the coal during the combustion process, which can activate the carbon. In various embodiments, the halogen- or halide-containing material can transform into an activate promotor such as active bromide or chloride compounds like HCl, HBr, xCl, or xBr. In some examples, the promoter is in a form including at least one of a vapor form, in a solvent, as a liquid, as a solid, and a combination thereof. In some embodiments, the promoting can occur in an aqueous scrubber, wherein the scrubber includes an aqueous slurry that includes the promotor.

[0070] The promoting of the sorbent material can occur before addition or injection into a gas stream, during addition or injection into a gas stream, after addition or 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 a solid such as a salt, or other substance (e.g., acid) dissolved in liquid (e.g., water), for example, hydrobromic acid. 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 activated carbon 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.

BHE et al. EXHIBIT 1023
Page 343

[0071] In some embodiments, a promoter precursor transforms into the halogen or halide promoter that reacts with the activated carbon sorbent to give the activated carbon material. The promoter precursor can be any suitable precursor that can transform into the halogen or halide promoter. In some embodiments, the promoter precursor can be at least one of on the unpromoted sorbent and added or injected with the unpromoted sorbent. 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 added or injected in the flue gas separately from the activated carbon sorbent or with the activated carbon sorbent (e.g., can be applied to the sorbent pre-injection, added or injected simultaneously at the same location, or added or injected simultaneously at different locations). In some examples, NaCl, $CaCl_2$, NaBr, or $CaBr_2$ can be added with uncombusted material such as uncombusted coal.

Inorganic matrix-support or nanocomposites.

[0072] In some embodiments, the activated carbon including activated carbon particles including nitrogen includes an inorganic matrix-support or is a nanocomposite. The activated carbon including nitrogen used in the method of reducing the pollutant content in a pollutant-containing gas can include an inorganic matrix-support or can be a nanocomposite. The method can include adding an inorganic matrix-support to the activated carbon or making a nanocomposite using unsupported activated carbon including nitrogen, or the method can include commercially acquiring the matrix-supported or nanocomposite activated carbon. In various embodiments, the inorganic matrix

BHE et al. EXHIBIT 1023
Page 344

support includes at least one of diatomaceous earth, a clay, a zeolite, or a mineral.

[0073] For example, the method of reducing the pollutant content in a pollutant-containing gas can include obtaining or providing a substrate material. The substrate material can be any suitable substrate. For example, the substrate can be at least one of diatomaceous earth, a clay, a zeolite, or a mineral. The method can include contacting the carbon precursor and the substrate material, to provide a sorbent starting material. 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 or supported sorbent is formed. The contacting can be performed such that the carbon precursor 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.

[0074] 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.

[0075] 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.

[0076] The method can include processing (e.g., heating, vibrating, sonicating, microwaving, or otherwise adding energy to) the sorbent starting material, to provide the activated carbon sorbent. The contacted composition of the carbon precursor and the substrate can then be processed (e.g., heated, vibrated, sonicated, microwaved, or other suitable addition of energy) to form the carbon nanocomposite or inorganic matrix-supported sorbent. The processing can take place at any suitable temperature, such that the sorbent is sufficiently formed, for example heating to 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 or higher. The processing 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 substantially excludes oxygen, e.g., that allows heated inert gas air to flow around the mixture being heated. In one example, the heating occurs in a furnace having an inert gas environment therein. The processing can be accelerated, or lengthened, depending on the apparatus and the nanocomposite or supported material.

[0077] In some embodiments, heating the sorbent starting material can provide a second sorbent starting material. The method can further include reacting the second sorbent starting material with an acidic or basic material, to provide the activated carbon sorbent. The acidic or basic material can be any suitable acidic or basic material, such as HBr, HCl, H_2SO_4, KOH, NaOH, and the like. In some embodiments, treatment with an acidic or basic material can prepare the activated carbon for treatment with a promotor or can prepare the

BHE et al. EXHIBIT 1023
Page 346

material such that sufficient reactivity or absorption with mercury or another pollutant is obtained.

Method of making an active carbon sorbent including nitrogen.

[0078] In various embodiments, the present invention provides a method of making an activated carbon sorbent including activated carbon sorbent particles including nitrogen. Embodiments of the present invention can include any activated carbon sorbent including nitrogen made by the method. The method includes obtaining or providing unpromoted sorbent including nitrogen. The unpromoted sorbent including nitrogen can be any suitable activated carbon sorbent including nitrogen, such as any activated carbon sorbent including nitrogen described herein. The unpromoted sorbent including nitrogen can be acquired commercially or can be synthesized. The method can include promoting at least a portion of the unpromoted sorbent. The promoting can include contacting (e.g., chemically reacting) the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent including activated carbon sorbent particles including nitrogen.

[0079] In some examples, the unpromoted sorbent including nitrogen can include an inorganic matrix support or can be a nanocomposite. For example, the method of making an activated carbon sorbent including nitrogen can include obtaining or providing a carbon precursor including nitrogen. The method can include obtaining or providing a substrate material. The method can include contacting the carbon precursor and the substrate material to provide a sorbent starting material. The method can also include heating the sorbent starting material to provide the unpromoted carbon sorbent including nitrogen. The unpromoted sorbent including nitrogen can include activated carbon sorbent particles including nitrogen.

[0080] In some embodiments, the method of making an activated carbon sorbent including nitrogen can include synthesizing the carbon precursor including nitrogen from carbonaceous and nitrogenous materials. For example, the method can include obtaining or providing a carbonaceous material including carbon and a nitrogenous material including nitrogen. The method can include suitably contacting and processing the carbonaceous material and the

nitrogenous material, wherein processing can including at least one of heating, microwaving, sonication, vibration, and the like, to provide the carbon precursor including nitrogen.

Examples

[0081] The present invention can be better understood by reference to the following examples which are offered by way of illustration. The present invention is not limited to the examples given herein.

Example 1. Impregnation of nitrogen precursors into a char followed by carbonization and activation of the impregnated char.

Example 1a. Carbon precursor.

[0082] A carbon (20 X 60 mesh) prepared by steam activation of a lignite char was stirred with an aqueous solution of dextrose and ethanolamine in ratio of 1 part of carbon to 0.016 parts of ethanolamine and 0.034 parts of dextrose. The water solvent was removed by rotovaporation and the impregnated carbon was air-dried. The dried material was reactivated at 750°C for 2 hours under nitrogen stream.

Example 1b. Char precursor.

[0083] A char (20 X 60 mesh)prepared by heating a lignite at 400°C was stirred with an aqueous solution of dextrose and ethanolamine in ratio of 1 part of carbon to 0.016 parts of ethanolamine and 0.034 parts of dextrose. The water solvent was removed by rotovaporation and the impregnated carbon was air-dried. The dried material was activated at 750°C for 2 hours under nitrogen stream.

Example 1c. Wood charcoal precursor.

[0084] A carbon (20 X 60 mesh) prepared by steam activation of a wood char was stirred with an aqueous solution of dextrose and ethanolamine in ratio of 1 part of carbon to 0.016 parts of ethanolamine and 0.034 parts of dextrose. The water solvent was removed by rotovaporation and the impregnated carbon

BHE et al. EXHIBIT 1023
Page 348

was air-dried. The dried material was reactivated at 750°C for 2 hours under nitrogen stream.

Example 1d. Wood charcoal – alanine.

[0085] A carbon (20 X 60 mesh)prepared by steam activation of a wood char was stirred with an aqueous solution of dextrose and alanine in ratio of 1 part of carbon to 0.016 parts of ethanolamine and 0.034 parts of alanine. The water solvent was removed by rotovaporation and the impregnated carbon was air-dried. The dried material was reactivated at 750°C for 2 hours under nitrogen stream.

Example 2. Tube reactor testing.

[0086] The molecular sieve carbons obtained as described in Examples 1a-d were impregnated with 5 wt% of sulfuric acid. The impregnated carbon was then dried in an oven at 110°C. The carbon (0.100 g) was packed into a 3 mm diameter pyrex tube and held in place by glass wool plugs at both ends. A constriction in the pyrex tube at exit end prevented the plug from blowing out. The reactor tube was heated in a GC oven at 150°C ± 0.50 as a constant temperature device. The mercury vapor was contained in an air flow of 100 cm^3/min through the reactor tube at a concentration of 429-447 micrograms/m^3, determined with a continuous mercury vapor monitor.

[0087] The mercury source was a temperature-calibrated permeation tube. The permeation tube was heated in a double-jacketed glass condenser with a circulating hot silicone oil system. The concentration in the effluent air stream from the reactor tube was monitored with a continuous cold-vapor UV mercury vapor monitor (EPM). Blank runs were conducted before each carbon test to determine the mercury concentration. The instrument was zeroed with an air stream passed through a large iodized carbon filter. This apparatus thus gave the percent of mercury not removed by the carbon bed (the concentration of mercury in the outlet divided by the concentration of mercury in the inlet, times 100). For the nitrogenous molecular sieve carbons (examples 1-4) only 1% of the mercury vapor was not removed by the carbon bed over a period of several hours.

BHE et al. EXHIBIT 1023
Page 349

Example 3. Filter bed testing.

[0088] The sorbent carbon pretreated as in Example 1e was ground to about 200 mesh and introduced into a tube where it could be drawn by reduced pressure onto a teflon or quartz filter held in a stainless steel holder. The carbon-impregnated filter and holder were then placed in the oven under air flow and tested as described in Example 2.

Examples 4. Impregnation of nitrogen-containing polymers into an activated carbon or char followed by carbonization and activation of the impregnated material.

Example 4a. Vinylpyrrolidone-acrylic acid copolymer.

[0089] A carbon prepared by steam activation of a lignite was stirred with an aqueous solution of poly(vinylpyrrolidone-co-acrylic acid) for 30 min. The amount of the polymer was selected to provide loadings of 1 % to 30% by weight. The solvent was evaporated by rotovaping at 50°C and further dried in an oven at 110°C. The impregnated carbon was reactivated by heating at 750°C for 2 hours in a stream of nitrogen. Approximately 40% of the polymer weight was converted to surface coating and 60% was volatilized.

Example 4b. Vinylpyrrolidone-vinyl acetate copolymer.

[0090] An activated carbon was impregnated with poly(vinylpyrrolidone-co-vinyl acetate) dissolved in dichloromethane. The solvent was evaporated and the impregnated carbon died in an oven at 110°C. The impregnated carbon was then activated by heating at 750°C for 2 hours in a nitrogen stream.

Example 4c. Poly(vinylpyrrolidone).

[0091] An activated carbon was impregnated with one of poly(vinylpyrrolidone) and the copolymers described in Examples 4a-b and activated as described in Example 4a.

Example 4d. Poly(vinylpyrrolidone).

[0092] A KOH-activated lignite was impregnated with one of polyvinylpyrrolidone and and the copolymers described in Examples 4a-4b and activated as described in Example 4a.

Example 4e. Wood-derived charcoal.

[0093] Wood-derived charcoal was impregnated with one of poly(vinylpyrrolidone) and the copolymers described in Examples 4a-4b and activated as described in Example 4a.

Example 4f. Carbonization of a lignite. (hypothetical example)

[0094] Chars are produced by carbonization of a lignite, impregnated by one of poly(vinylpyrrolidone) and the copolymers described in Examples 4a-4b, and activated as described in Example 4a. As an alternative, steam activation can be used.

Example 4g. Steam activation.

[0095] Examples 4a-4c were carried out using steam activation of the carbon material impregnated with nitrogen-containing polymers to generate effective sorbents.

Example 5. Impregnation of nitrogen precursors into a coal, lignite, or leonardite, followed by carbonization and activation of the impregnated material.

Example 5a. 1,4-Diazabicyclo[2.2.2]octane (DABCO).

[0096] Lignite (as received) was stirred with an aqueous solution of DABCO in a ratio of 1 part of coal to 0.02 parts of DABCO. The water solvent was removed by filtration, and the impregnated coal was air-dried. The dried material was carbonized at 400°C and activated at 750°C for 2 hours under a nitrogen stream.

BHE et al. EXHIBIT 1023
Page 351

Example 5b. Sulfamic acid.

[0097] Lignite (as received) was stirred with an aqueous solution of sulfamic acid in a ratio of 1 part of coal to 0.02 parts of sulfamic acid. The water solvent was removed by filtration, and the impregnated coal was air-dried. The dried material was carbonized and activated at 750°C for 2 hours under a nitrogen stream.

Example 5c. Carbonized lignite.

[0098] Lignite was carbonized at 400°C for 30 minutes, and the resulting char was treated by stirring with sulfamic acid solution as described in Example 5b. The treated char was then activated as described in Example 5b.

Example 5d. Steam activation.

[0099] Steam activation of the DABCO or sulfamic acid-impregnated chars was also effective in producing mercury sorbent carbons.

Example 6. Preparation of Nitrogen-Containing Pitches.

[00100] Nitrogen-containing pitches were prepared using a procedure reported by Mochida et al. (Mochida, I.; An, K.H.; Korai, Y. *Carbon* **1995**, *33*, 1069). Preparations are summarized in Table 1. As an example, a mixture of isoquinoline (26 g, 0.2 mole), anhydrous aluminum(III) chloride (13.3 g, 0.25 mole), and nitrobenzene (7.68 g, 0.06 mole) was placed in a two-necked flask equipped with a reflux condenser and a nitrogen inlet tube. The mixture was refluxed at 280°C for 4 hours. The residue was extracted with 0.1 N hydrochloric acid and filtered. The residue was washed with 0.1 N hydrochloric acid. The residue was further extracted with methanol to remove any monomer. The methanol-insoluble pitch was dried in vacuo. The yield of the pitch was 49%. A portion of the nitrogen-containing pitches were carbonized using Procedure A or B in a nitrogen stream, as described in Example 7.

[00101] Table 1. Preparation of nitrogen-containing pitches. * indicates reactions carried out in 300-mL Parr reactor. ** indicates ethylenediamine.

Substrate (g, mole)	Catalyst	Cocatalyst (g, mole)	Temperature (°C)	Time	Yield (g,	Soluble (%)

BHE et al. EXHIBIT 1023
Page 352

	(g, mole)			(hr)	%)	
Indole (10 , 0.77)	None	None	253*	4	9.6 (96%)	Methano l (100)
Quinoxaline (26, 0.2)	$AlCl_3$ (13.3, 0.1)	Nitrobenzen e (7.68, 0.06)	225*	4	13.5 (52%)	EDA**
Carbazole (16.7, 0.1)	$AlCl_3$ (27.7, 0.2)	Nitrobenzen e (3.6, 0.03)	25	12	59.1 (92%)	EDA**
Isoquinolin e (26, 0.2)	$AlCl_3$ (13.3, 0.1)	Nitrobenzen e (7.68, 0.06)	280	4	6.5 (25%)	EDA**

[00102] Several modifications of the method were utilized for the quinoline polymerization. In addition to the flask method, a Parr reactor was used for the reaction, and temperatures and reaction times were varied. The yields are reported in Table 2. In this procedure, 64.5 g of quinoline and 33.25 g of aluminum(III) chloride were placed in a 300-mL Parr autoclave. The reactor was sealed under nitrogen and heated at 280°C for 4 hours. The hard black mass was extracted with 0.1 N hydrochloric acid followed by extraction with methanol and drying in vacuo. In order to determine the solubility of the polymer, a 10-g portion of this black mass was extracted with 100 mL of ethanol. Extraction data showed that 27 wt% of the product dissolved in ethanol.

[00103] Table 2. Preparation of nitrogen-containing pitches. * indicates reactions carried out in 300-mL Parr reactor. ** indicates 10 g of pitch was extracted with ethanol.

Quinoline (g)	$AlCl_3$ (g)	Temp. (°C)	Time (hr)	Yield (g, %)	Ethanol-S (g)	Ethanol-I (g)
64.5	33.25	280	12	57.7 (89%)	-	-
64.5*	33.25	175	12	0 (0%)	-	-
64.5*	33.25	280	12	59.1 (92%)	-	-
64.5*	33.25	280	4	56.8 (88%)	7.3** (73%)	2.7 (27%)

BHE et al. EXHIBIT 1023
Page 353

Example 7. Preparation of Nitrogen-Impregnated Carbon.

[00104] Impregnations and recarbonizations were performed to investigate the effects of precursor concentration, activation procedure, and sorbent particle size on mercury sorption. The precursor base carbon, granular activated carbon (Calgon F400 or Gascoyne AC, 20 x 60) was impregnated with various nitrogen-containing polymers and pitches using an incipient wetness method, described below. For the fine-particle sorbent tests in flue gas compositions, the Calgon carbon was ground to about a 400 mesh size prior to impregnation. The nitrogen polymers such as vinylpyrrolidone polymers and copolymers are commercially available. The urea, alanine-dextrose, piperazine-dextrose, and polyethylenimine-dextrose compositions were prepared similarly.

[00105] In a typical procedure for the incipient wetness method, the desired amount of polymer or pitch dissolved in an appropriate solvent was added to the carbon slowly with thorough mixing. The paste was dried to remove solvent. The dried product was packed in a stainless steel tube and activated in a gentle flow of nitrogen using procedure A or procedure B.

[00106] Procedure A included: Heated from 25°C to 400°C at 10°C/min; held at 400°C for 30 min; heated from 400° to 750°C at 20°C/min; and held at 750°C for 4 hr.

[00107] Procedure B included: Heat from 25°C to 225°C at 15°C/min; heated from 225°C 270°C at 1 °C/min; held at 270°C for 1 hr; cooled to room temperature; heated up to 750°C at 15°C/min; and held at 750°C for 4 hr.

Example 8. Preparation of nitrogen-containing carbons from insoluble fractions.

[00108] Insoluble fractions of pitches described in Table 1 were converted into nitrogen-containing carbons by heating in a gentle flow of nitrogen using Procedure B as described above. The resulting carbons were porous glassy materials, similar to cokes.

Example 9. Preliminary screening of sorbents made using the nitrogen containing materials of examples 6-7 for mercury capture.

Example 9a. Simulation of the Sulfuric Acid Accumulation.

BHE et al. EXHIBIT 1023
Page 354

[00109] Capture of SO_3 and subsequent sulfuric acid formation on the surface of the nitrogen containing carbons in the hot flue gas stream was simulated by adding 5 wt% sulfuric acid by the incipient wetness method. The acid-impregnated carbons were dried at 110 °C.

Example 9b. Packed-Bed Tests.

[00110] Packed-bed tests in airflow were conducted on the granular carbon products to evaluate the effects of surface modification. The mercury sorption was tested in a flow-through tubular reactor system equipped with continuous in-line mercury analysis of the effluent from the bed to determine mercury removal rates as a function of time. Integration of breakthrough volumes allows determination of mercury sorption per unit mass carbon (mg/g). Air with an elemental mercury concentration of 56 or 81 $\mu g/m^3$ was passed through the heated (150°C) reactor. To obtain this concentration, the mercury source was placed in a double-jacketed glass condenser and heated to the desired temperature by pumping hot oil through the condenser.

[00111] A glass tube with constriction and glass wool plug was used as the reactor for the mercury sorption tests. A gas chromatography (GC) oven was used as a constant temperature (150°C) chamber for the reactor. Before the actual test, a blank test was run. The glass tube was attached to the source and the mercury analyzer by Teflon tubes. Mercury vapors diluted with air (2000-4000 cm^3/min or 4-8 scfh measured at the detector end) were passed through the tube. The mercury analyzer (Environmental and Process Monitoring [EPM] continuous vapor monitor) was interfaced to a Hydra and personal computer (PC) to record the data. For the packed-bed tests, impregnated activated carbons (20 x 60-mesh size) were used. In an actual test, about 0.2-0.6 g of sorbent was packed in the glass tube and held by glass wool plugs on both ends. The tests were conducted with a source temperature of 150°C, an oven temperature of 150°C, and an airflow= 4 or 8 scfh (4000 cm^3/min). Numerous tests were performed at 4000 cm^3/min (8 scfh) with carbons prepared by impregnation of various nitrogen compounds, polymers, and pitches into a base Calgon carbon (Tables 3 and 4). These conditions gave partial breakthroughs for the sorbents and allowed comparisons of their kinetic activities.

BHE et al. EXHIBIT 1023
Page 355

[00112] Table 3. Sorbent testing of surface-treated carbons for mercury removal at 8 scfh. Airflow = 4000 cm^3/min (8 scfh), over temperature = 150 °C. mercury concentration = 81 $\mu g/m^3$. * indicates that the activated carbon was prepared in Example 4a.

BHE et al. EXHIBIT 1023
Page 356

Carbon source	Recarbonization method	H_2SO_4 Impregnation	% Hg removed (time, min)		
			Initial	50%	End of test
Blank		-	0 (0)	<1	-
Calgon		5%	87 (0)	50 (171)	38 (304)
Calgon/urea	A	5%	95 (0)	50 (305)	49 (306)
EERC*/urea	A	5%	100 (0)	50 (575)	38 (1221)
Calgon/2% sulfamic acid	A	5%	92 (0)	50 (226)	39 (1303)
Calgon/5% PVP	A	5%	94 (0)	50 (2217)	42 (2574)
Calgon/10% PVP	A	5%	88 (0)	50 (150)	55 (253)
Calgon/10% PVP	A	5%	90 (0)	50 (300)	65 (1098)
Calgon/5% PVP	A	5%	98 (0)	50 (3315)	43 (4010)
Calgon/2% PVP	A	5%	79 (0)	50 (312)	49 (320)
Calgon/10% PVP	A	5%	85 (0)	50 (424)	30 (1114)
Calgon/5% vinylpyrrolidone-vinyl acetate copolymer	A	5%	90 (0)	50 (84)	39 (180)
Calgon/5% vinylpyrrolidone-acrylic acid copolymer	A	5%	90 (0)	50 (76)	29 (362)
Calgon/5% vinylpyrrolidone-acrylic acid copolymer	A	5%	98 (0)	50 (223)	50 (223)
Calgon/polyethylenimine	A	5%	88 (0)	50 (373)	22 (1147)
Calgon/dextrose+polyethylenimine	A	5%	88 (0)	50 (51)	35 (350)
Calgon/dextrose+alanine	A	5%	88 (0)	50 (76)	53 (216)
Calgon/dextrose+piperazine	A	5%	65 (0)	50 (35)	25 (942)

[00113] Table 4. Sorbent testing of nitrogenous pitch-impregnated carbons for mercury capture. Recarbonization procedure B was used for all samples. Sorbent = 0.20 g, particle size = 20 X 50 mesh, airflow = 8 scfh (4000 mL/min), source temperature = 150 °C, oven temperature = 150 °C. * indicates pitch obtained from heating quinolone and aluminum(III) chloride in Parr reactor

BHE et al. EXHIBIT 1023
Page 357

was dissolved in ethanol and impregnated on Calgon carbon. ** indicates pitch obtained from refluxing of quinolone with aluminum(III) chloride was dissolved in EDA and impregnated on Calgon carbon.

File name	Sorbent (g)	H_2SO_4 (wt%)	Mercury Concentration ($\mu g/m^3$)	% Hg removed (time, min)		
				Initial	50%	Final
RKS32	None	-	81	-	50 <1	-
RKS35	Calgon/5 wt% quinolone *	5%	-	89 (0)	50 (306)	49 (308)
RKS23	Calgon/5 wt% quinolone *	5%	-	91 (0)	50 (204)	46 (292)
RKS37	Calgon/5 wt% quinoxaline	5%	-	90 (0)	50 (632)	25 (1300)
RKS31	Calgon/5 wt% isoquinoline	5%	-	90 (0)	54 (584)	34 (1214)
RKS75	Calgon/5 wt% indole	5%	-	98 (0)	50 (1403)	49 (1473)

Example 9c. Test Results.

[00114] Carbons prepared by impregnation of urea or sulfamic acid into the Calgon base carbon and recarbonization gave initial capture rates of 95% or 92%, respectively. These results are significantly better than those observed with the unmodified Calgon carbon. Testing the urea carbon at lower temperature (75°C) gave 100% initial capture. Carbons prepared by impregnation of a nitrogen-containing polymer were highly active in these tests. The sorbent prepared by impregnation of 5 wt% PVP and activated using procedure A (fast heating rate) demonstrated superior activity. The initial removal was 94%, and the decrease to 50% removal required 2217 min. Thus this sorbent retains its high activity far longer than the urea carbon. The sorbent prepared using 10% PVP (also Procedure A) was less active (initially 88% removal, decreasing to 50% at 150 min.

[00115] Using procedure B (slower heating rate) gave more active sorbent at the 10% PVP concentration level. Another set of carbons was prepared with different concentrations using Procedure B. Again, the impregnation with 5%

BHE et al. EXHIBIT 1023
Page 358

concentration of PVP resulted in high activity (initially 98% removal, decreasing to 50% at 3315 mm). The 10% PVP was again less active, and the 2% PVP concentration was the least active.

[00116] The carbons prepared from the copolymers of PVP were also prepared and evaluated. The copolymer with vinyl acetate (PVPcoVA) impregnated at 5% concentration (Procedure A) gave a sorbent with relatively low activity. The poly(vinylpyrrolidone-co-acrylic acid) (PVPc0AA) at 5% also gave a low activity sorbent. Using Procedure B for activation improved the activity slightly.

[00117] Another type of N-polymer-impregnated carbon was prepared using polyethylenimine. This polymer precursor contains nitrogen in the polymer backbone, in constrast to the PVP where the nitrogen is attached to the carbon chain backbone. The activity was similar to that of the 10% PVP polymers.

[00118] Several carbons were prepared by impregnating mixtures of dextrose and amines. None of these exhibited high activities in these tests. Previous tests showed that the dextrose + alanine-impregnated carbon (Procedure B) was fairly active. Since Procedure A was used in the present study, decreases in activity might be related to the fast heating rate used. It may be quite beneficial to perform the reaction slowly in preparing sorbents from these precursors.

[00119] The sorbents prepared by impregnation of the nitrogenous pitches prepared by polymerization of various heterocyclics were all fairly active (Table 4), but significant differences in activity were observed. The N-carbon prepared from impregnation of quinoxaline pitch was 2-3 times more active than the quinoline-derived N-carbon. The activity of the isoquinoline-derived carbon was also very high. The high activity of the indole-derived carbon was also of great interest. It is an important lead since indoles are more readily available than the quinoxaline precursors.

[00120] Testing was also conducted on the carbonized pitches prepared from the insoluble fractions of the nitrogenous pitches. The activities of the carbonized pitches were very poor. Initial breakthrough was substantial, with percent removals of 21% to 54%, possibly related to the the glassy nature of the

BHE et al. EXHIBIT 1023
Page 359

carbonized pitches. Although the surface areas were not determined, they may be very low, since the materials did not resemble activated carbons but, rather, cokes.

[00121] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

Additional Embodiments.

[00122] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance:

[00123] Embodiment 1 provides a method of reducing the pollutant content in a pollutant-containing gas, the method comprising: obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles; contacting a pollutant-containing gas with the activated carbon sorbent, to form a pollutant-sorbent composition; and separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give a separated gas.

[00124] Embodiment 2 provides the method of Embodiment 1, wherein the pollutant comprises mercury, and the pollutant-containing gas is a mercury-containing gas.

[00125] Embodiment 3 provides the method of any one of Embodiments 1-2, wherein the concentration of nitrogen in the surface layer of the sorbent

BHE et al. EXHIBIT 1023
Page 360

particles is higher than the concentration of nitrogen in a core of the sorbent particles.

[00126] Embodiment 4 provides the method of any one of Embodiments 2-3, wherein the activated carbon sorbent combines with at least about 70 wt% of the mercury present in the mercury-containing gas.

[00127] Embodiment 5 provides the method of any one of Embodiments 2-4, wherein the mercury-containing gas further comprises a concentration of sulfur(VI) and the concentration of sulfur(VI) in the mercury-containing gas is greater than about 3 ppm by mole and the activated carbon sorbent forms a mercury-sorbent composition at a higher absorption rate relative to a corresponding activated carbon sorbent comprising at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, wherein the activated carbon sorbent comprising the activated carbon sorbent particles is halide- or halogen-promoted, and c) less or substantially no inorganic matrix support, wherein the activated carbon sorbent comprising the activated sorbent particles is inorganic matrix-supported.

[00128] Embodiment 6 provides the method of any one of Embodiments 1-5, wherein the pollutant-containing gas further comprises a concentration of sulfur(VI) and the concentration of sulfur(VI) in the pollutant-containing gas is about 3 ppm - 2000 ppm.

[00129] Embodiment 7 provides the method of any one of Embodiments 1-6, wherein the nitrogen is substantially homogenously distributed in the core of the activated carbon sorbent particles.

[00130] Embodiment 8 provides the method of any one of Embodiments 1-7, wherein the nitrogen in the surface layer decreases neutralization of carbocations in the activated carbon by at least one of SO_3^{2-} and HSO_3^{1-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer.

[00131] Embodiment 9 provides the method of any one of Embodiments 1-8, wherein the nitrogen in the surface layer at least partially blocks carbocations in the activated carbon from at least one of SO_3^{2-} and HSO_3^{1-}, as

BHE et al. EXHIBIT 1023
Page 361

compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer.

[00132] Embodiment 10 provides the method of any one of Embodiments 1-9, further comprising: obtaining or providing an unpromoted carbon sorbent; obtaining or providing a promoter; and promoting at least a portion of the unpromoted sorbent by contacting the portion of the unpromoted sorbent with the promoter to form the activated carbon sorbent.

[00133] Embodiment 11 provides the method of Embodiment 10, wherein the promoter comprises a halogen or halide promoter.

[00134] Embodiment 12 provides the method of any one of Embodiments 10-11, wherein the promoter comprises at least one of a halogen, a Group V halide, a Group VI halide, a hydrogen halide, an ammonium halide, an alkali earth metal halide, and an alkaline earth metal halide.

[00135] Embodiment 13 provides the method of any one of Embodiments 10-12, wherein the promoter comprises at least one of HI, IBr, ICl NH_4Br, NaBr, $CaBr_2$, HBr, NaCl, $CaCl_2$, and HCl.

[00136] Embodiment 14 provides the method of any one of Embodiments 10-13, wherein the promoter is in a form comprising at least one of a vapor form, in a solvent, as a liquid, as a solid, and a combination thereof.

[00137] Embodiment 15 provides the method of any one of Embodiments 10-14, wherein the promoting occurs in an aqueous scrubber, wherein the scrubber comprises an aqueous slurry that comprises the promotor.

[00138] Embodiment 16 provides the method of any one of Embodiments 1-15, wherein contacting the pollutant-containing gas with the activated carbon sorbent comprises adding the activated carbon sorbent into the pollutant-containing gas.

[00139] Embodiment 17 provides the method of any one of Embodiments 1-16, wherein the activated carbon sorbent is at least one of in a fixed bed, in a moving bed, in a scrubber, in a filter, or suspended in the pollutant-containing gas.

[00140] Embodiment 18 provides the method of any one of Embodiments 1-17, wherein the core of the activated carbon sorbent particles comprise about 0 wt% - about 99 wt% nitrogen.

[00141] Embodiment 19 provides the method of any one of Embodiments 1-18, wherein the core of the activated carbon sorbent particles comprise about 1 wt% - about 6 wt% nitrogen.

[00142] Embodiment 20 provides the method of any one of Embodiments 1-19, wherein the surface layer of the activated carbon sorbent particles comprises about 0.001 wt% - about 99 wt% nitrogen.

[00143] Embodiment 21 provides the method of any one of Embodiments 1-20, wherein the surface layer of the activated carbon sorbent particles comprises about 5 wt% - about 80 wt% nitrogen.

[00144] Embodiment 22 provides the method of any one of Embodiments 1-21, wherein the surface layer of the activated carbon sorbent comprises a layer at the surface of the particle having a thickness of about 0.001% to about 99% of the radius of the particles.

[00145] Embodiment 23 provides the method of any one of Embodiments 1-22, wherein the surface layer of the activated carbon sorbent particles comprises a layer at the surface of the particles having a thickness of about 0.001% to about 50% of the radius of the particles.

[00146] Embodiment 24 provides the method of any one of Embodiments 1-23, wherein the activated carbon sorbent particles have an average diameter of about 0.1 μm to about 1000 μm.

[00147] Embodiment 25 provides the method of any one of Embodiments 1-24, wherein the surface layer of the sorbent particles is a continuous surface layer.

[00148] Embodiment 26 provides the method of any one of Embodiments 1-25, wherein obtaining or providing the activated carbon sorbent comprises: obtaining or providing a carbon precursor comprising nitrogen; and processing the carbon precursor with at least one of heating, microwaving, and irradiating, to provide the activated carbon sorbent.

[00149] Embodiment 27 provides the method of Embodiment 26, wherein the carbon precursor comprises a carbonaceous material comprising carbon and a nitrogenous material comprising nitrogen.

[00150] Embodiment 28 provides the method of Embodiment 27, wherein the carbonaceous material comprises at least one of brown sugar, barley sugar,

caramel, cane sugar, corn syrup, starch, molasses, a glucan, a galactan, a xylan, and a sugar waste product.

[00151] Embodiment 29 provides the method of any one of Embodiments 27-28, wherein the nitrogenous material comprises a nitrogen-containing organic or inorganic compound.

[00152] Embodiment 30 provides the method of any one of Embodiments 27-29, wherein the nitrogenous material comprises a nitrogen heterocycle, a nitrogen-containing polymer or copolymer, a nitrile, a carbamate, an amino acid, nitrobenzene, hydroxylamine, urea, hydrazine, sulfamic acid, or a combination thereof.

[00153] Embodiment 31 provides the method of any one of Embodiments 26-30, further comprising: obtaining or providing a substrate material; contacting the carbon precursor and the substrate material, to provide a sorbent starting material; and processing the sorbent starting material with at least one of heating, microwaving, and irradiating, to provide the activated carbon sorbent.

[00154] Embodiment 32 provides the method of Embodiment 31, wherein heating the sorbent starting material provides a second sorbent starting material, further comprising reacting the second sorbent starting material with an acidic or basic material, to provide the activated carbon sorbent.

[00155] Embodiment 33 provides the method of any one of Embodiments 31-32, wherein the substrate comprises at least one of diatomaceous earth, a clay, a zeolite, or a mineral.

[00156] Embodiment 34 provides the method of any one of Embodiments 31-33, wherein heating the sorbent starting material comprises heating to about 100 °C – about 1200 °C.

[00157] Embodiment 35 provides the method of any one of Embodiments 31-34 wherein the activated carbon sorbent comprises a carbon nanocomposite sorbent.

[00158] Embodiment 36 provides the method of any one of Embodiments 1-35, wherein the activated carbon sorbent comprises one or more binding sites.

[00159] Embodiment 37 provides the method of Embodiment 36, wherein at least a portion of the binding sites in the activated carbon sorbent react with at

least one of the pollutant and the oxidized species of the pollutant, to form the pollutant-sorbent composition.

[00160] Embodiment 38 provides the method of any one of Embodiments 1-37, wherein the separating at least some of the pollutant-sorbent composition from the pollutant containing gas comprises separating in a particulate separator.

[00161] Embodiment 39 provides the method of Embodiment 38, wherein the particulate separator comprises an electrostatic precipitator (ESP), a baghouse, a wet scrubber, a filter, cyclone, fabric separator, or any combination thereof.

[00162] Embodiment 40 provides the method of any one of Embodiments 10-39, wherein a promoter precursor transforms into the halogen or halide promoter which then reacts with the activated carbon sorbent to give the activated carbon material.

[00163] Embodiment 41 provides the method of Embodiment 40, wherein the promoter precursor is at least one of on the unpromoted sorbent and added with the unpromoted sorbent.

[00164] Embodiment 42 provides the method of any one of Embodiments 1-41, further comprising at least one of during and prior to the contacting adding an alkaline component into the pollutant-containing gas.

[00165] Embodiment 43 provides the method of Embodiment 42, wherein the alkaline component comprises at least one of an oxide, hydroxide, carbonate, or phosphate of an alkali element, an alkali or alkaline-earth element, and a compound or material including the same.

[00166] Embodiment 44 provides the method of any one of Embodiments 1-43, wherein the activated carbon sorbent comprises a stabilizing agent comprising at least one of S, Se, or mixtures thereof.

[00167] Embodiment 45 provides the method of any one of Embodiments 1-44, wherein the activated carbon sorbent comprises a stabilizing agent comprising at least one of H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, or mixtures thereof.

[00168] Embodiment 46 provides the method of any one of Embodiments 1-45, further comprising regenerating the pollutant-sorbent composition to give a regenerated activated carbon sorbent.

BHE et al. EXHIBIT 1023
Page 365

[00169] Embodiment 47 provides the method of any one of Embodiments 1-46, wherein the activated carbon sorbent is a generated activated carbon sorbent

[00170] Embodiment 48 provides the method of any one of Embodiments 1-47, wherein at least one of the contacting and the separating occurs in an aqueous scrubber.

[00171] Embodiment 49 provides the method of Embodiment 48, wherein the scrubber comprises an aqueous slurry that comprises the activated carbon sorbent.

[00172] Embodiment 50 provides a method for reducing the mercury content of a mercury-containing gas, the method comprising: obtaining or providing a carbon precursor comprising nitrogen; obtaining or providing a substrate material; contacting the carbon precursor and the substrate material, to provide an inorganic matrix-supported sorbent starting material; heating the inorganic matrix-supported sorbent starting material, to provide an unpromoted sorbent; promoting at least a portion of the unpromoted sorbent by chemically reacting the portion of the unpromoted sorbent with a promoter to form a promoted inorganic matrix-supported activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles; contacting a mercury-containing gas with the activated carbon sorbent, to form a mercury-sorbent composition; and separating at least some of the mercury-sorbent composition from the mercury-containing gas, to give a separated gas; wherein the mercury-containing gas has a concentration of sulfur(VI) of about 3 - 2000 ppm by mole and a first quantity the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate, wherein the first adsorption rate is higher than a mercury absorption rate of the first quantity of a corresponding activated carbon sorbent comprising at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support.

[00173] Embodiment 51 provides a method of making an activated carbon sorbent, comprising: obtaining or providing an unpromoted carbon sorbent comprising nitrogen; promoting at least a portion of the unpromoted sorbent by

contacting the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen, wherein the concentration of nitrogen in a surface layer of the sorbent particles is higher than the concentration of nitrogen in a core of the sorbent particles.

[00174] Embodiment 52 provides the method of Embodiment 51, further comprising: obtaining or providing a carbon precursor comprising nitrogen; obtaining or providing a substrate material; contacting the carbon precursor and the substrate material, to provide a sorbent starting material; and processing the sorbent starting material, to provide the unpromoted carbon sorbent comprising nitrogen.

[00175] Embodiment 53 provides the method of Embodiment 52, wherein obtaining or providing the carbon precursor comprising nitrogen comprises: obtaining or providing a carbonaceous material comprising carbon and a nitrogenous material comprising nitrogen; and contacting and heating the carbonaceous material and the nitrogenous material, to provide the carbon precursor comprising nitrogen.

[00176] Embodiment 54 provides a method of making an activated carbon sorbent, comprising: contacting a carbonaceous material and a nitrogenous material, to provide an unpromoted carbon sorbent comprising nitrogen; promoting at least a portion of the unpromoted sorbent by contacting the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen, wherein the concentration of nitrogen in the sorbent particles is higher than the concentration of nitrogen in the carbonaceous material.

[00177] Embodiment 55 provides an activated carbon sorbent made by the method of any one of Embodiments 51-54.

[00178] Embodiment 56 provides an activated carbon sorbent, comprising: a halogen- or halide-promoted activated carbon, the activated carbon comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles.

[00179] Embodiment 57 provides the activated carbon sorbent of Embodiment 56, wherein the concentration of nitrogen in the surface layer of the

BHE et al. EXHIBIT 1023
Page 367

sorbent particles is higher than the concentration of nitrogen in a core of the sorbent particles.

[00180] Embodiment 58 provides the activated carbon sorbent of any one of Embodiments 56-57, wherein the activated carbon sorbent particles have an average diameter of about 0.1 μm to about 1000 μm.

[00181] Embodiment 59 provides the activated carbon sorbent of any one of Embodiments 56-58, wherein the activated carbon is at least one of halogen-promoted, Group V halide-promoted, Group VI halide-promoted, hydrogen halide-promoted, ammonium halide-promoted, alkali earth metal halide-promoted, and alkaline earth metal halide-promoted.

[00182] Embodiment 60 provides the activated carbon sorbent of any one of Embodiments 56-59, wherein the activated carbon sorbent is inorganic matrix-supported, the inorganic matrix support comprising at least one of diatomaceous earth, a clay, a zeolite, or a mineral.

[00183] Embodiment 61 provides the activated carbon sorbent of any one of Embodiments 56-60, wherein the nitrogen is substantially homogenously distributed in the core of the activated carbon sorbent particles.

[00184] Embodiment 62 provides the activated carbon sorbent of any one of Embodiments 56-61, wherein the nitrogen in the surface layer of the particles at least partially decreases neutralization by HSO_3^{1-} or SO_3^{2-} of carbocations in the activated carbon sorbent, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

[00185] Embodiment 63 provides the activated carbon sorbent of any one of Embodiments 56-62, wherein the nitrogen in the surface layer of the particles at least partially blocks carbocations in the activated carbon from forming ionic bonds with HSO_3^{1-} or SO_3^{2-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

[00186] Embodiment 64 provides the activated carbon sorbent of any one of Embodiments 56-63, wherein a first quantity of the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate in a gas composition comprising mercury wherein the concentration of sulfur(VI) in the

gas composition is about 3 - 2000 ppm by mole, and wherein the first adsorption rate is higher than a mercury absorption rate of the first quantity of a corresponding activated carbon sorbent comprising at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support, wherein the activated carbon sorbent is inorganic-matrix supported.

[00187] Embodiment 65 provides the activated carbon sorbent of any one of Embodiments 56-64, wherein the nitrogen is derived from a nitrogen-containing organic or inorganic compound.

[00188] Embodiment 66 provides the activated carbon sorbent of any one of Embodiments 56-65, wherein the nitrogen is derived from indole, quinoxaline, carbazole, isoquinoline, nitrobenzene, urea, sulfamic acid, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, vinylpyrrolidone-acrylic acid copolymer, vinylpyrrolidone-maleic acid copolymer, polyethylenimine, alanine, piperazine, quinolone, quinoxaline, diazabicyclooctane, an amino acid, an ammonium salt, or a combination thereof.

[00189] Embodiment 67 provides an activated carbon sorbent for use in mercury removal from a mercury-containing gas, the sorbent comprising: a halogen- or halide-promoted activated carbon comprising activated carbon particles, the particles comprising nitrogen in a surface layer, the nitrogen in the surface layer at sufficient concentration to at least one of a) decrease neutralization by HSO_3^{1-} or SO_3^{2-} of carbocations in the activated carbon sorbent, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions, and b) at least partially block carbocations in the activated carbon from forming ionic bonds with HSO_3^{1-} or SO_3^{2-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

[00190] Embodiment 68 provides the apparatus or method of any one or any combination of Embodiments 1-67 optionally configured such that all elements or options recited are available to use or select from.

BHE et al. EXHIBIT 1023
Page 369

CLAIMS

What is claimed is:

1. A method of reducing the pollutant content in a pollutant-containing gas, the method comprising:

obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles;

contacting a pollutant-containing gas with the activated carbon sorbent, to form a pollutant-sorbent composition; and

separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give a separated gas.

2. The method of claim 1, wherein the pollutant comprises mercury, and the pollutant-containing gas is a mercury-containing gas.

3. The method of any one of claims 1-2, wherein the concentration of nitrogen in the surface layer of the sorbent particles is higher than the concentration of nitrogen in a core of the sorbent particles.

4. The method of any one of claims 2-3, wherein the activated carbon sorbent combines with at least about 70 wt% of the mercury present in the mercury-containing gas.

5. The method of any one of claims 2-4, wherein the mercury-containing gas further comprises a concentration of sulfur(VI) and the concentration of sulfur(VI) in the mercury-containing gas is greater than about 3 ppm by mole and the activated carbon sorbent forms a mercury-sorbent composition at a higher absorption rate relative to a corresponding activated carbon sorbent comprising at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, wherein the activated carbon sorbent comprising the activated carbon sorbent particles is halide- or halogen-promoted, and c) less or substantially no inorganic

BHE et al. EXHIBIT 1023
Page 370

matrix support, wherein the activated carbon sorbent comprising the activated sorbent particles is inorganic matrix-supported.

6. The method of any one of claims 1-5, wherein the pollutant-containing gas further comprises a concentration of sulfur(VI) and the concentration of sulfur(VI) in the pollutant-containing gas is about 3 ppm - 2000 ppm.

7. The method of any one of claims 1-6, wherein the nitrogen is substantially homogenously distributed in the core of the activated carbon sorbent particles.

8. The method of any one of claims 1-7, wherein the nitrogen in the surface layer decreases neutralization of carbocations in the activated carbon by at least one of SO_3^{2-} and HSO_3^{1-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer.

9. The method of any one of claims 1-8, wherein the nitrogen in the surface layer at least partially blocks carbocations in the activated carbon from at least one of SO_3^{2-} and HSO_3^{1-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer.

10. The method of any one of claims 1-9, further comprising: obtaining or providing an unpromoted carbon sorbent; obtaining or providing a promoter; and promoting at least a portion of the unpromoted sorbent by contacting the portion of the unpromoted sorbent with the promoter to form the activated carbon sorbent.

11. The method of claim 10, wherein the promoter comprises a halogen or halide promoter.

BHE et al. EXHIBIT 1023
Page 371

12. The method of any one of claims 10-11, wherein the promoter comprises at least one of a halogen, a Group V halide, a Group VI halide, a hydrogen halide, an ammonium halide, an alkali earth metal halide, and an alkaline earth metal halide.

13. The method of any one of claims 10-12, wherein the promoter comprises at least one of HI, IBr, ICl NH_4Br, NaBr, $CaBr_2$, HBr, NaCl, $CaCl_2$, and HCl.

14. The method of any one of claims 10-13, wherein the promoter is in a form comprising at least one of a vapor form, in a solvent, as a liquid, as a solid, and a combination thereof.

15. The method of any one of claims 10-14, wherein the promoting occurs in an aqueous scrubber, wherein the scrubber comprises an aqueous slurry that comprises the promotor.

16. The method of any one of claims 1-15, wherein contacting the pollutant-containing gas with the activated carbon sorbent comprises adding the activated carbon sorbent into the pollutant-containing gas.

17. The method of any one of claims 1-16, wherein the activated carbon sorbent is at least one of in a fixed bed, in a moving bed, in a scrubber, in a filter, or suspended in the pollutant-containing gas.

18. The method of any one of claims 1-17, wherein the core of the activated carbon sorbent particles comprise about 0 wt% - about 99 wt% nitrogen.

19. The method of any one of claims 1-18, wherein the core of the activated carbon sorbent particles comprise about 1 wt% - about 6 wt% nitrogen.

20. The method of any one of claims 1-19, wherein the surface layer of the activated carbon sorbent particles comprises about 0.001 wt% - about 99 wt% nitrogen.

BHE et al. EXHIBIT 1023
Page 372

21. The method of any one of claims 1-20, wherein the surface layer of the activated carbon sorbent particles comprises about 5 wt% - about 80 wt% nitrogen.

22. The method of any one of claims 1-21, wherein the surface layer of the activated carbon sorbent comprises a layer at the surface of the particle having a thickness of about 0.001% to about 99% of the radius of the particles.

23. The method of any one of claims 1-22, wherein the surface layer of the activated carbon sorbent particles comprises a layer at the surface of the particles having a thickness of about 0.001% to about 50% of the radius of the particles.

24. The method of any one of claims 1-23, wherein the activated carbon sorbent particles have an average diameter of about 0.1 μm to about 1000 μm.

25. The method of any one of claims 1-24, wherein the surface layer of the sorbent particles is a continuous surface layer.

26. The method of any one of claims 1-25, wherein obtaining or providing the activated carbon sorbent comprises:

obtaining or providing a carbon precursor comprising nitrogen; and

processing the carbon precursor with at least one of heating, microwaving, and irradiating, to provide the activated carbon sorbent.

27. The method of claim 26, wherein the carbon precursor comprises a carbonaceous material comprising carbon and a nitrogenous material comprising nitrogen.

28. The method of claim 27, wherein the carbonaceous material comprises at least one of brown sugar, barley sugar, caramel, cane sugar, corn syrup, starch, molasses, a glucan, a galactan, a xylan, and a sugar waste product.

29. The method of any one of claims 27-28, wherein the nitrogenous material comprises a nitrogen-containing organic or inorganic compound.

30. The method of any one of claims 27-29, wherein the nitrogenous material comprises a nitrogen heterocycle, a nitrogen-containing polymer or copolymer, a nitrile, a carbamate, an amino acid, nitrobenzene, hydroxylamine, urea, hydrazine, sulfamic acid, or a combination thereof.

31. The method of any one of claims 26-30, further comprising:

obtaining or providing a substrate material;

contacting the carbon precursor and the substrate material, to provide a sorbent starting material; and

processing the sorbent starting material with at least one of heating, microwaving, and irradiating, to provide the activated carbon sorbent.

32. The method of claim 31, wherein heating the sorbent starting material provides a second sorbent starting material, further comprising reacting the second sorbent starting material with an acidic or basic material, to provide the activated carbon sorbent.

33. The method of any one of claims 31-32, wherein the substrate comprises at least one of diatomaceous earth, a clay, a zeolite, or a mineral.

34. The method of any one of claims 31-33, wherein heating the sorbent starting material comprises heating to about 100 °C – about 1200 °C.

35. The method of any one of claims 31-34 wherein the activated carbon sorbent comprises a carbon nanocomposite sorbent.

36. The method of any one of claims 1-35, wherein the activated carbon sorbent comprises one or more binding sites.

BHE et al. EXHIBIT 1023
Page 374

37. The method of claim 36, wherein at least a portion of the binding sites in the activated carbon sorbent react with at least one of the pollutant and the oxidized species of the pollutant, to form the pollutant-sorbent composition.

38. The method of any one of claims 1-37, wherein the separating at least some of the pollutant-sorbent composition from the pollutant containing gas comprises separating in a particulate separator.

39. The method of claim 38, wherein the particulate separator comprises an electrostatic precipitator (ESP), a baghouse, a wet scrubber, a filter, cyclone, fabric separator, or any combination thereof.

40. The method of any one of claims 10-39, wherein a promoter precursor transforms into the halogen or halide promoter which then reacts with the activated carbon sorbent to give the activated carbon material.

41. The method of claim 40, wherein the promoter precursor is at least one of on the unpromoted sorbent and added with the unpromoted sorbent.

42. The method of any one of claims 1-41, further comprising at least one of during and prior to the contacting adding an alkaline component into the pollutant-containing gas.

43. The method of claim 42, wherein the alkaline component comprises at least one of an oxide, hydroxide, carbonate, or phosphate of an alkali element, an alkali or alkaline-earth element, and a compound or material including the same.

44. The method of any one of claims 1-43, wherein the activated carbon sorbent comprises a stabilizing agent comprising at least one of S, Se, or mixtures thereof.

BHE et al. EXHIBIT 1023
Page 375

45. The method of any one of claims 1-44, wherein the activated carbon sorbent comprises a stabilizing agent comprising at least one of H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, or mixtures thereof.

46. The method of any one of claims 1-45, further comprising regenerating the pollutant-sorbent composition to give a regenerated activated carbon sorbent.

47. The method of any one of claims 1-46, wherein the activated carbon sorbent is a regenerated activated carbon sorbent.

48. The method of any one of claims 1-47, wherein at least one of the contacting and the separating occurs in an aqueous scrubber.

49. The method of claim 48, wherein the scrubber comprises an aqueous slurry that comprises the activated carbon sorbent.

50. A method for reducing the mercury content of a mercury-containing gas, the method comprising:

obtaining or providing a carbon precursor comprising nitrogen;

obtaining or providing a substrate material;

contacting the carbon precursor and the substrate material, to provide an inorganic matrix-supported sorbent starting material;

heating the inorganic matrix-supported sorbent starting material, to provide an unpromoted sorbent;

promoting at least a portion of the unpromoted sorbent by chemically reacting the portion of the unpromoted sorbent with a promoter to form a promoted inorganic matrix-supported activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles;

contacting a mercury-containing gas with the activated carbon sorbent, to form a mercury-sorbent composition; and separating at least some of the mercury-sorbent composition from the mercury-containing gas, to give a separated gas;

wherein the mercury-containing gas has a concentration of sulfur(VI) of about 3 - 2000 ppm by mole and a first quantity the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate, wherein the first adsorption rate is higher than a mercury absorption rate of the first quantity of a corresponding activated carbon sorbent comprising at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support.

51. A method of making an activated carbon sorbent, comprising:

obtaining or providing an unpromoted carbon sorbent comprising nitrogen;

promoting at least a portion of the unpromoted sorbent by contacting the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen, wherein the concentration of nitrogen in a surface layer of the sorbent particles is higher than the concentration of nitrogen in a core of the sorbent particles.

52. The method of claim 51, further comprising:

obtaining or providing a carbon precursor comprising nitrogen;

obtaining or providing a substrate material; contacting the carbon precursor and the substrate material, to provide a sorbent starting material; and

processing the sorbent starting material, to provide the unpromoted carbon sorbent comprising nitrogen.

53. The method of claim 52, wherein obtaining or providing the carbon precursor comprising nitrogen comprises:

obtaining or providing a carbonaceous material comprising carbon and a nitrogenous material comprising nitrogen; and

contacting and heating the carbonaceous material and the nitrogenous material, to provide the carbon precursor comprising nitrogen.

BHE et al. EXHIBIT 1023
Page 377

54. A method of making an activated carbon sorbent, comprising:

contacting a carbonaceous material and a nitrogenous material, to provide an unpromoted carbon sorbent comprising nitrogen; and

promoting at least a portion of the unpromoted sorbent by contacting the portion of the unpromoted sorbent with a promoter to form an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen, wherein the concentration of nitrogen in the sorbent particles is higher than the concentration of nitrogen in the carbonaceous material.

55. An activated carbon sorbent made by the method of any one of claims 51-54.

56. An activated carbon sorbent, comprising: a halogen- or halide-promoted activated carbon, the activated carbon comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles.

57. The activated carbon sorbent of claim 56, wherein the concentration of nitrogen in the surface layer of the sorbent particles is higher than the concentration of nitrogen in a core of the sorbent particles.

58. The activated carbon sorbent of any one of claims 56-57, wherein the activated carbon sorbent particles have an average diameter of about 0.1 μm to about 1000 μm.

59. The activated carbon sorbent of any one of claims 56-58, wherein the activated carbon is at least one of halogen-promoted, Group V halide-promoted, Group VI halide-promoted, hydrogen halide-promoted, ammonium halide-promoted, alkali earth metal halide-promoted, and alkaline earth metal halide-promoted.

BHE et al. EXHIBIT 1023
Page 378

60. The activated carbon sorbent of any one of claims 56-59, wherein the activated carbon sorbent is inorganic matrix-supported, the inorganic matrix support comprising at least one of diatomaceous earth, a clay, a zeolite, or a mineral.

61. The activated carbon sorbent of any one of claims 56-60, wherein the nitrogen is substantially homogenously distributed in the core of the activated carbon sorbent particles.

62. The activated carbon sorbent of any one of claims 56-61, wherein the nitrogen in the surface layer of the particles at least partially decreases neutralization by HSO_3^{1-} or SO_3^{2-} of carbocations in the activated carbon sorbent, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

63. The activated carbon sorbent of any one of claims 56-62, wherein the nitrogen in the surface layer of the particles at least partially blocks carbocations in the activated carbon from forming ionic bonds with HSO_3^{1-} or SO_3^{2-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

64. The activated carbon sorbent of any one of claims 56-63, wherein a first quantity of the activated carbon sorbent forms a mercury-sorbent composition at a first mercury adsorption rate in a gas composition comprising mercury wherein the concentration of sulfur(VI) in the gas composition is about 3 - 2000 ppm by mole, and wherein the first adsorption rate is higher than a mercury absorption rate of the first quantity of a corresponding activated carbon sorbent comprising at least one of a) less or substantially no nitrogen in a corresponding particle surface layer, b) less or substantially no halide- or halogen-promotion, and c) less or substantially no inorganic matrix support, wherein the activated carbon sorbent is inorganic-matrix supported.

BHE et al. EXHIBIT 1023
Page 379

65. The activated carbon sorbent of any one of claims 56-64, wherein the nitrogen is derived from a nitrogen-containing organic or inorganic compound.

66. The activated carbon sorbent of any one of claims 56-65, wherein the nitrogen is derived from indole, quinoxaline, carbazole, isoquinoline, nitrobenzene, urea, sulfamic acid, polyvinylpyrrolidone, vinylpyrrolidone-vinyl acetate copolymer, vinylpyrrolidone-acrylic acid copolymer, vinylpyrrolidone-maleic acid copolymer, polyethylenimine, alanine, piperazine, quinolone, quinoxaline, diazabicyclooctane, an amino acid, an ammonium salt, or a combination thereof.

67. An activated carbon sorbent for use in mercury removal from a mercury-containing gas, the sorbent comprising:

a halogen- or halide-promoted activated carbon comprising activated carbon particles, the particles comprising nitrogen in a surface layer, the nitrogen in the surface layer at sufficient concentration to at least one of a) decrease neutralization by HSO_3^{1-} or SO_3^{2-} of carbocations in the activated carbon sorbent, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions, and b) at least partially block carbocations in the activated carbon from forming ionic bonds with HSO_3^{1-} or SO_3^{2-}, as compared to a corresponding activated carbon sorbent comprising less or substantially no nitrogen in a corresponding particle surface layer under substantially similar conditions.

Electronic Acknowledgement Receipt

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Application Number:	15951970
International Application Number:	
Confirmation Number:	6410
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
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Time Stamp:	15:54:29
Application Type:	Utility under 35 USC 111(a)

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Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
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	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
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	Transmittal Letter	5	6
	Miscellaneous Incoming Letter	2	4
	Miscellaneous Incoming Letter	1	1

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New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PATENT APPLICATION FEE DETERMINATION RECORD

Substitute for Form PTO-875

Application or Docket Number: 15/951,970

APPLICATION AS FILED - PART I

FOR	(Column 1) NUMBER FILED	(Column 2) NUMBER EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	300
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	660
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	760
TOTAL CLAIMS (37 CFR 1.16(i))	20 minus 20 =	*			OR	x 100 =	0.00
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 minus 3 =	*				x 460 =	0.00
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						0.00
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							0.00
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	1720

APPLICATION AS AMENDED - PART II

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	SMALL ENTITY RATE($)	SMALL ENTITY ADDITIONAL FEE($)	OR	OTHER THAN SMALL ENTITY RATE($)	OTHER THAN SMALL ENTITY ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1) CLAIMS REMAINING AFTER AMENDMENT		(Column 2) HIGHEST NUMBER PREVIOUSLY PAID FOR	(Column 3) PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
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APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
15/951,970	04/12/2018	Edwin S. Olson	4820.001US8

CONFIRMATION NO. 6410

21186
SCHWEGMAN LUNDBERG & WOESSNER, P.A.
P.O. BOX 2938
MINNEAPOLIS, MN 55402

INFORMAL NOTICE

OC000000099418175

Date Mailed: 05/10/2018

INFORMATIONAL NOTICE TO APPLICANT

Applicant is notified that the above-identified application contains the deficiencies noted below. No period for reply is set forth in this notice for correction of these deficiencies. However, if a deficiency relates to the inventor's oath or declaration, the applicant must file an oath or declaration in compliance with 37 CFR 1.63, or a substitute statement in compliance with 37 CFR 1.64, executed by or with respect to each actual inventor no later than the expiration of the time period set in the "Notice of Allowability" to avoid abandonment. See 37 CFR 1.53(f).

The item(s) indicated below are also required and should be submitted with any reply to this notice to avoid further processing delays.

- A properly executed inventor's oath or declaration has not been received for the following inventor(s):
  Edwin S. Olson
  Michael J. Holmes
  John H. Pavlish

Questions about the contents of this notice and the requirements it sets forth should be directed to the Office of Data Management, Application Assistance Unit, at **(571) 272-4000** or **(571) 272-4200** or **1-888-786-0101**.

/sabubeker/

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APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/951,970	04/12/2018	1736	1880	4820.001US8	20	2

CONFIRMATION NO. 6410

21186
SCHWEGMAN LUNDBERG & WOESSNER, P.A.
P.O. BOX 2938
MINNEAPOLIS, MN 55402

FILING RECEIPT

OC000000099418174

Date Mailed: 05/10/2018

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)

Edwin S. Olson, Grand Forks, ND;
Michael J. Holmes, Thompson, ND;
John H. Pavlish, East Grand Forks, MN;

Applicant(s)

Midwest Energy Emissions Corp, Residence Not Provided;

Power of Attorney: None

Domestic Priority data as claimed by applicant

This application is a CON of 14/712,558 05/14/2015
which is a CON of 14/318,270 06/27/2014 PAT 9757689
which is a CON of 13/966,768 08/14/2013 PAT 8821819
which is a CON of 13/427,665 03/22/2012 PAT 8512655
which is a CON of 12/419,219 04/06/2009 PAT 8168147
which is a CON of 12/201,595 08/29/2008 ABN
which is a DIV of 11/209,163 08/22/2005 PAT 7435286
which claims benefit of 60/605,640 08/30/2004

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: Yes

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Projected Publication Date: 08/16/2018
Non-Publication Request: No
Early Publication Request: No
Title

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

Preliminary Class

423

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific

countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

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technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s): Edwin S. Olson et al.
Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
Attorney Docket No.: 4820.001US8
Customer No.: 21186

PATENT APPLICATION TRANSMITTAL

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

We are transmitting herewith the following attached items and information (as indicated with an "X"):

X **CONTINUATION under 37 CFR 1.53(b) of prior Patent Application No. 11/209,163 comprising:**
- X Application Data Sheet (8 pgs).
- X Specification (61 pgs, including claims numbered 1 through 20 and a 1 page Abstract).
- X Formal Drawing(s) (11 sheets).
- X **Authorization to charge Deposit Account 19-0743 in the amount of $1,880.00**

The filing fee has been calculated below as follows:

	No. Filed	No. Extra	Rate	Fee
TOTAL CLAIMS	20- 20	0	x $100.00 =	$0.00
INDEPENDENT CLAIMS	2 - 3	0	x $460.00 =	$0.00
[]MULTIPLE DEPENDENT CLAIMS PRESENTED				$0.00
BASIC FEE				$300.00
SEARCH FEE				$660.00
EXAMINATION FEE				$760.00
DECLARATION LATE FILING FEE				$160.00
	No. of pages (75% for e-filing)	Extra sets of 50 pages	Rate	
APPLICATION SIZE FEE	(54 - 100) / 50	0	$400.00	$0.00
TOTAL				$1,880.00

Please charge any additional required fees or credit overpayment to Deposit Account No. 19-0743. If applicable, any papers or fees supplied herewith are considered to be timely filed pursuant to 37 C.F.R. § 1.7(a), the response period falling on a Federal Holiday, Saturday or Sunday being extended to the next succeeding business day.

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
Customer Number: 21186

By: /Ryan J. Connell/
Ryan J. Connell
Reg. No. 74,611

Date of Deposit: April 12, 2018
This paper or fee is being filed on the date indicated above using the USPTO's electronic filing system EFS-Web, and is addressed to The Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ **Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)**

Inventor Information:

Inventor 1: Edwin S. Olson

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Edwin	S.	Olson	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	Grand Forks	State/Province	ND	Country of Residence	United States of America

Mailing Address of Inventor:

Address 1	223 Circle Hills Drive		
Address 2			
City	Grand Forks	State/Province	ND
Postal Code	58201	Country	United States of America

Inventor 2: Michael J. Holmes

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Michael	J.	Holmes	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	Thompson	State/Province	ND	Country of Residence	United States of America

Mailing Address of Inventor:

Address 1	614 6th Avenue Northeast		
Address 2			
City	Thompson	State/Province	ND
Postal Code	58278	Country	United States of America

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

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Inventor 3: John H. Pavlish

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	John	H.	Pavlish	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	East Grand Forks	State/Province	MN	Country of Residence	United States of America

Mailing Address of Inventor:

Address 1	42204 210th Street SW		
Address 2			
City	East Grand Forks	State/Province	MN
Postal Code	56721	Country	United States of America

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ An Address is being provided for the correspondence Information of this application.

Customer Number	21186
Email Address	request@slwip.com

Application Information:

Title of the Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY		
Attorney Docket Number	4820.001US8	Small Entity Status Claimed ☐	
Application Type	Non-Provisional		
Subject Matter	Utility		
Suggested Class (if any)		Sub Class (if any)	
Suggested Technology Center (if any)			
Total Number of Drawing Sheets (if any)	11	Suggested Figure for Publication (if any)	

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

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This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). **Do not** complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country Publication

Publication Information:

☐ **Request Early Publication (Fee required at time of Request 37 CFR 1.219)**

☐ **Request Not to Publish. I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application has not and will not be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.**

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32). Entereither Customer Number or complete the Representative Name section below. If bothsections are completed the Customer Number will be used for the Representative Information during processing.

Please Select One:	☒ Customer	☐ US Patent Practitioner	☐ Limited Recognition (37 CFR 11.9)
Customer Number	21186		

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

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Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78(a)(2) or CFR 1.78(a)(4), and need not otherwise be made part of the specification.

Prior Application Status	Pending		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
This Application	continuation of	14/712,558	2015-05-14
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
14/712,558	continuation of	14/318,270	2014-06-27
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
14/318,270	continuation of	13/966,768	2013-08-14
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
13/966,768	continuation of	13/427,665	2012-03-22
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
13/427,665	continuation of	12/419,219	2009-04-06
Prior Application Status	Abandoned		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
12/419,219	continuation of	12/201,595	2008-08-29
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
12/201,595	division of	11/209,163	2005-08-22
Prior Application Status	Expired		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
11/209,163	Claims benefit of provisional	60/605,640	2004-08-30

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)i the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the POX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Application Number	Country	Parent Filing Date (YYYY-MM-DD)	Access Code (if applicable)

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

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This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant must opt-out of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is ONLY reviewed and processed with the INITIAL filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby grants the USPTO authority to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ **A. Applicant DOES NOT authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.**

☐ **B. Applicant DOES NOT authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.**

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

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This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant: Midwest Energy Emissions Corp

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

☒ Assignee	☐ Legal Representative under 35 U.S.C. 117	☐ Joint Inventor
☐ Person to whom the inventor is obligated to assign	☐ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

☐ Deceased	☐ Legally incapacitated

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here: ☒

Organization Name: Midwest Energy Emissions Corp

Prefix	Given Name	Middle Name	Family Name	Suffix

Mailing Address Information:

Address 1	670 D Enterprise Dr		
Address 2			
City	Lewis Center	City	Lewis Center
Country	United States of America	Country	United States of America
Phone Number			
Email Address			

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US8
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
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Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	Given Name	Middle Name	Family Name	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		State/Province	
Country		Postal Code	
Phone Number		Fax Number	
Email Address			

Signature:

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is **a juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Ryan J. Connell/			Date (YYYY-MM-DD)	4/12/18
First Name	Ryan	Last Name	Connell	Registration Number	74,611

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-14**

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. Patent Application Serial No. 14/318,270, filed June 27, 2014, which is a continuation of U.S. Patent Application Serial No. 13/966,768, filed August 14, 2013, issued as U.S. Patent No. 8,821,819, which is a continuation of U.S. Patent Application Serial No. 13/427,665, filed March 22, 2012, issued as U.S. Patent No. 8,512,655, which is a continuation of U.S. Patent Application Serial No. 12/419,219, filed April 06, 2009, issued as U.S. Patent No. 8,168,147, which is a continuation of U.S. Patent Application Serial No. 12/201,595, filed August 29, 2008, which is a division of U.S. Patent Application Serial No. 11/209,163, filed August 22, 2005, issued as U.S. Patent No. 7,435,286, which application claims the benefit under 35 U.S.C. § 119 (e) of U.S. Provisional Patent Application No. 60/605,640 filed Aug. 30, 2004, the disclosure of which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with United States Government support under Grant Numbers R 827649-01 and CR 830929-01 awarded by the United States Environmental Protection Agency and under Contract Number DE-FC26-98FT40320 awarded by the United States Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

1. 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.

2. 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

BHE et al. EXHIBIT 1023
Page 407

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,

BHE et al. EXHIBIT 1023
Page 408

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, 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

BHE et al. EXHIBIT 1023
Page 409

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 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

BHE et al. EXHIBIT 1023
Page 410

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 in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increase, 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.

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.

BHE et al. EXHIBIT 1023
Page 411

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-containing sorbent particles are regenerated to remove some or substantially all of the mercury. In

BHE et al. EXHIBIT 1023
Page 412

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.

FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 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.

BHE et al. EXHIBIT 1023
Page 413

FIG. 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.

FIG. 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.

FIG. 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

FIG. 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

FIG. 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

FIG. 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

FIG. 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility.

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

BHE et al. EXHIBIT 1023
Page 414

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 FIG. 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 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 FIG. 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

BHE et al. EXHIBIT 1023
Page 415

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 FIG. 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 FIG. 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.

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,

BHE et al. EXHIBIT 1023
Page 416

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 FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 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

BHE et al. EXHIBIT 1023
Page 417

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 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 FIG. 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 FIG. 3 as compressors or blowers, any source

BHE et al. EXHIBIT 1023
Page 418

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 FIG. 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 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

BHE et al. EXHIBIT 1023
Page 419

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 FIG. 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 121*b* with base activated carbon prior to entering transport line 115. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line 121*c* 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

BHE et al. EXHIBIT 1023
Page 420

solvent removal (not shown in FIG. 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 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 131*b* and 131*c*.

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

BHE et al. EXHIBIT 1023
Page 421

component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

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.

BHE et al. EXHIBIT 1023
Page 422

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 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. 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

BHE et al. EXHIBIT 1023
Page 423

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).

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

BHE et al. EXHIBIT 1023
Page 424

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 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.

BHE et al. EXHIBIT 1023
Page 425

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 conjunction 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

BHE et al. EXHIBIT 1023
Page 426

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 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,

BHE et al. EXHIBIT 1023
Page 427

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, Tex. (USA), although others are suitable, as will be recognized by those skilled in the 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 and passed out of the generator. The outlet from the gaseous bromine generator is connected via a 1/4 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 so that the excess of nitrogen is released after the bromine is transferred 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

BHE et al. EXHIBIT 1023
Page 428

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 in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach Fla. 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

BHE et al. EXHIBIT 1023
Page 429

flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to FIG. 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. FIG. 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).

FIG. 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

BHE et al. EXHIBIT 1023
Page 430

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 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

BHE et al. EXHIBIT 1023
Page 431

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 ¼ 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 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

BHE et al. EXHIBIT 1023
Page 432

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.

BHE et al. EXHIBIT 1023
Page 433

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 FIG. 6. As can be observed in FIG. 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 FIG. 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 FIG. 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)

BHE et al. EXHIBIT 1023
Page 434

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 on the sorbent particle/ash separation system used. Note that in FIG. 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

BHE et al. EXHIBIT 1023
Page 435

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, Fla., 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 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

BHE et al. EXHIBIT 1023
Page 436

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

BHE et al. EXHIBIT 1023
Page 437

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 inert sand is shown in FIG. 8, and the breakthrough curve for the mixture with CaO is shown in FIG. 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 FIG. 10. As shown in FIG. 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.

BHE et al. EXHIBIT 1023
Page 438

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 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

BHE et al. EXHIBIT 1023
Page 439

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 (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.

BHE et al. EXHIBIT 1023
Page 440

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.

	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 thereof can be made by one skilled in the art without

BHE et al. EXHIBIT 1023
Page 441

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.

PROVISIONAL APPLICATION

A reactive sorbent material is described for capture of mercury in a vapor stream. The vapor stream includes flue gas from coal combustion or incineration, synthesis gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories. The sorbent is especially suited to, but not limited to, use in low-chlorine flue or exhaust gases where the mercury is mainly elemental. The sorbent comprises a bromide-modified carbon form containing a reactive compound produced by the reaction of bromine with the carbon. Other additional promoting substances can be added in smaller amounts to increase the reactivity with and

BHE et al. EXHIBIT 1023
Page 442

sorption of elemental mercury. This combination results in a carbon bromide structure in the carbon lattice that can oxidize the mercury to a species that is strongly bonded to the carbon structure and, therefore, easily retained on the sorbent at higher temperatures in the presence of flue gas constituents. In some examples, the sorbent consists of a fine or coarse powdered material for injection into the gas stream or a granular or fibrous material for use in a fixed or moving bed. In some examples, the sorbent does not require in situ activation (an induction period) in a flue gas stream as do conventional activated carbon sorbents. Other additives of base chemistry (Ca, Na, and others) may be added to flue gas as a sorbent mixture, or co-injected to selectively sorb acid gases or other flue gas constituents to keep available reactive sites for mercury oxidation and subsequent capture. The sorbent can be regenerated by washing off contaminating components derived from flue gas that poison the spent sorbent. Novel methods for introduction of the sorbent dispersion into the mercury contaminated gas stream are described.

Following is an outline of examples of the invention. The invention may also take on various other examples or embodiments, as a person skilled in the art would understand.

1. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by applying a solution of molecular bromine in an organic solvent to the carbon, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. The solution may also contain an additional promoting substance in small amounts. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30g per 100g of activated carbon, depending on the proportions used.

1A. (Dependent)

Same as 1, carbon is powdered activated carbon.

Carbon is granular activated carbon.

Carbon is very fine carbon black.

Carbon is very fine carbon fiber.

BHE et al. EXHIBIT 1023
Page 443

Carbon is aerogel carbon film.

Carbon is char recovered from pyrolysis process.

Carbon is powdered activated carbon of size distribution larger than fly ash size distribution, so that it can be physically separated from the ash and regenerated for reuse.

Carbon is regenerated from previous usage cycle and recycled.

Other desired types of carbon may also be used.

1B. (Dependent)

Same as 1, Solvent is chlorinated hydrocarbon such as dichloromethane.

Same as 1, Solvent is hydrocarbon solvent such as petroleum ether or ligroin or pentane or hexane or toluene or benzene.

Same as 1, Solvent is water.

Same as 1, Solvent is carbon disulfide.

Same as 1, Solvent is a waste solvent.

Same as 1, Solvent is an ether.

Same as 1, Solvent is recycled from previous batch.

Same as 1, Solvent is supercritical solvent such as CO_2.

Other desired types of Solvents may also be used.

1C. (Dependent)

Same as 1, solution of bromine is applied by stirring the carbon in the bromine solution.

Same as 1, solution of bromine is applied by spraying a solution of molecular bromine in an organic solvent, followed by removal of solvent from the pores by drying the carbon in air or nitrogen.

The bromine may also be applied using other desired techniques.

1D. (Dependent)

Same as 1, removal of solvent is by filtration, centrifugation, settling, and decantation and drying in vacuum, air, or other gas.

BHE et al. EXHIBIT 1023
Page 444

Same as 1, when sprayed or minimal volume, removal of solvent is by drying in air, vacuum, or other gas.

The solvent may also be removed using other desired techniques.

1E. (Dependent)

Same as 1, additional substance is iodine, at 1%-10% of the bromine concentration added.

Same as 1, additional substance is hydrohalide (HI, HBr, HCl), etc:, 1%-10 % of bromine.

Same as 1, additional substance is a compound comprised of a Group V or VI element or combination of Group V or VI with Group VII element, such as SCl_2, 1-10 wt % of bromine.

2. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by contacting the carbon with a gas containing molecular bromine. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100g of activated carbon, depending on the proportions used.

Contacting is by passing the Br_2 gas through a bed of the carbon.

Bed is ebullated or fluidized.

Bed is moving bed of granules or fibers.

Contacting is by admitting Br_2 gas to a duct through which the carbon is transported from a reservoir to the flue gas duct via an air-driven entrainment method, thus promoting the activity of the carbon in-flight.

Same additives as 1E, except these are added in the gas phase, and added in-flight as in 2 above.

3. A modified activated carbon sorbent was prepared by reacting the carbon with hydrogen bromide (HBr) by stirring the carbon in a solution of HBr in an organic solvent or in water, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon

BHE et al. EXHIBIT 1023
Page 445

in air or nitrogen. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms. Same solutions and treatment as 1B,1C, 1D.

Same additives as 1E, added into the solution phase or later in the gas phase, and added in-flight as in 2 above.

4. An activated carbon sorbent was prepared by impregnating hydrogen bromide by passing a gas composition containing hydrogen bromide diluted with nitrogen or air through a fluidized bed or ebullated bed of the carbon. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms.

Contacting options are similar to 2.

5. Sequential treatment of activated carbon with bromine or HBr, followed by another mercury stabilizing reagent to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H_2S, SO_2, H_2Se, Se, SeO_2, CS_2, P_2S_5.

6. Sequential treatment of activated carbon with mercury stabilizing reagent, followed by bromine or HBr to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H_2S, SO_2, H_2Se, Se, SeO_2, CS_2, P_2S_5.

7. Treatment of a carbon with a Group V or VI element combined with Group VII element, such as PBr_3 or SCl_2. In one example, the amount of Group V or VI halide is 1-30 wt % of the carbon. The compound is added in vapor phase or in solution (solvent is hydrocarbon, chlorinated hydrocarbon, or other solvent as described in 1B, but not water, since the compound is destroyed in water solution).

BHE et al. EXHIBIT 1023
Page 446

8. The process for preparing the bromine-containing activated carbon sorbent as described in Examples 1-6 and coupled with the injection of the bromine-containing fine-particle sorbent into the contaminated gas stream and subsequent removal of the fine particles of sorbent from the gas stream in a collection device, such as bag filtration of electrostatic precipitator (ESP).

9. The process of using additives (1-8) in conjunction with sorbents to capture acid gases and other flue gas constituents that block oxidation reactions or consume sorbent sites that would otherwise capture mercury. The additive is a compound comprised of Group I or II elements, such as Ca, Na, and others. These additives of base chemistry may be added to flue gas as a sorbent mixture or co-injected to selectively sorb acid gases or other gas constituents that compete for mercury reactive/sorption sites, thereby improving the effectiveness of activated carbon to capture mercury. In addition, the base additives can augment the treated activated carbon by helping to capture oxidized mercury forms in the flue gas, such as mercuric chloride, or that are produced on the carbon sorbent, such as mercuric bromide, but are released to the gas phase as the sorbent becomes saturated or capacity limited.

10. The process of preparing a larger-than-normal (>40 μm) sorbent particle size, promoting with the halogen treatment as described in 1-8, using the treated sorbent for capture of mercury by injecting in the flue gas, and finally separating and recovering the sorbent from the ash particles. The larger sorbent size thus will allow easy mechanical/physical separation so that sorbent can be regenerated, recycled, and reused, and the ash can be sold as a low-carbon cementatious byproduct for concrete. The separation can be effected by various methods, such as density (gravity), floatation, or sieving methods.

11. The process for preparing the bromine-containing activated carbon sorbent as described in Example 1-10, coupled with the direct injection of the slurry of the

BHE et al. EXHIBIT 1023
Page 447

prepared fine-particle sorbent in the solvent or aqueous phase, so that the aerosol particles of the slurry achieve a high degree of dispersion in the gas stream and evaporation of the solvent in the hot gas occurs rapidly. The amount of slurry added is flow-controlled, and the concentration of particles in the slurry is monitored by optical density measurements prior to injection. Collection of particles is performed.

12. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, coupled where the fine-particle dispersion of brominated sorbent in the gas stream at the top of the ebullated bed is led to the flue gas or offgas duct where the said dispersion is contacted with mercury-contaminated flue gas or offgas stream. The amount of aerosol dispersion added is controlled by the gas flow to the ebullated bed, and the concentration of particles in the dispersion can be monitored by optical density measurements prior to injection. Collection of particles is performed by the existing particulate-collection equipment.

13. The process for preparing the bromine-containing activated carbon sorbent bed, coupled with contacting the bed with the mercury-contaminated flue gas or offgas.

14. The process for preparing the bromine-containing activated carbonBsorbent, as described in Examples 2 and 4, or untreated activated carbon, coated on a substrate or as activated carbon material. This material is placed in a moving system that geometrically allows for control of rate of exposure, sorption, and exchange of material in a continuous or semicontinuous manner.

15. In the sorbent and mercury removal process outlined in paragraphs above, the bromine reagents promote metal oxidation activity by creating cationic or radical character on the carbon edge structure that attracts mercury atoms and extracts electrons from said mercury atoms, resulting in oxidized mercury, which is more easily captured on a sorbent. A similar mechanism applies to oxidation and capture of reduced arsenic and other pollutant species.

BHE et al. EXHIBIT 1023
Page 448

The invention relates to the process for the removal of mercury and other pollutant species from gas streams generated during the burning of fossil fuels, such as in a coal-fired utility or synthesis gas from gasification facilities. This removal process would utilize a sorbent and/or a combination of additives to remove pollutants from the gas stream, which are at the same time interacting with other gas components that result in poisoning or deactivating the sorbent and reducing its capacity or reaction rates with the targeted pollutant species. The present invention provides a cost-effective way to capture the pollutants by utilizing exceptionally active carbon sorbents and promoting mercury sorbent surface reactions, containing a bromide form of the carbon, that capture mercury with high kinetic chemisorption (oxidation) activity, so that capture can occur during contact times of seconds or less. The sorbent does not require in situ activation (induction period) in the gas stream to achieve high activity as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants and the sorption capacity can be regenerated, recycled, and reused.

Burning fossil fuels generates a flue gas that contains mercury (and other trace elements) that was in the coal, plus 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. While control of other elements and/or flue gas pollutants may apply, the discussion provided is focused on mercury. Initially, mercury is released in the elemental form during combustion/gasification, but downstream of the boiler, in the ducts and stack of the combustion system, part of the elemental mercury is oxidized. The amount oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the coal, but a typical concentration of mercury in the stream of combustion gas is about 5 parts per billion (ppb). A pound of mercury or more per day may be emitted in some utilities.

Discussion of Sorbent Technologies

BHE et al. EXHIBIT 1023
Page 449

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 (for example, see U.S. Patent 6,214,304), and basic silicate or oxide sorbents (for example, see the Ghorishi reference (Ghorishi,B.; Gullet, B.K. Waste Manage Res. 1993, 16, 582). and Lancia references). When particle injection is employed, the mercury chemisorbed to the sorbent particle is removed from the gas stream in a bag house or ESP and collected along with ash particulates (for example, see U.S. Patents 4,889,698, 4,956,162, 5,672,323, 5,827,352, 6,027,551, and 5,505,766). 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 approximately 60% was attained with a baghouse to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon, since 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 exposure to the flue gas for about 20 minutes does the seasoned sorbent become effective and provide capture of 60% of the mercury in the gas. Consequently, these sorbents must be used in large amounts (high sorbent-to-mercury ratios) to effectively capture the mercury. These sorbents can be relatively expensive and cannot be easily separated from the ash, regenerated and reused. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash for use in various applications.

Use of Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have not previously been effective. Halogen is defined as a member of the very active

BHE et al. EXHIBIT 1023
Page 450

elements comprising Group VII-A of the periodic table. In the molecular elemental halogen form, including F_2, Cl_2, Br_2, and I_2, the reaction with elemental mercury is not fast enough to result in the formation of oxidized mercury in a coal combustion flue gas with conventional ash control technology. The atomic elemental halogen form, which includes F atom, Cl atom, Br atom, and I atom, is about a million times more reactive to mercury, but the concentrations of these forms are extremely low, and also, therefore, cannot result in oxidation of mercury in a utility flue gas.

A halide is a compound formed from reaction of a halogen with another element or radical. In general, the halide compounds are normally very much less reactive than the molecular halogens, having expended their high chemical potential in forming the low energy halide. The halide is considered a reduced form and cannot therefore oxidize anything by itself. It is for this reason that it is not obvious that a halide-halogen treated activated carbon would be effective at oxidizing elemental mercury and provide effective capture of elemental mercury. In fact, for tests with salts, analytical data show the addition of bromine to an activated carbon or carbon black or soot does form a compound by reacting with the unsaturated groups on the carbon. By applying x-ray photoelectron spectroscopy, it has been determined that bromine or HBr added to carbon black forms chemical compounds within a carbon structure.

A body of theory has been developed from scientific evidence to explain the nature of the promotion effect of the bromine compounds. This principle is illustrated in FIG. 2, which in step 1 shows the reaction of the hydrogen bromide with the unsaturated structure of the activated carbon. This may be a carbene species on the edge of the graphene sheets 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.

We now teach that the formation of the new bromide compound with carbon increases the reactivity of the carbon forms toward mercury and other pollutants. The resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation results from the promotion effect of the halide exerted on the developing positive charge on the mercury during the

BHE et al. EXHIBIT 1023
Page 451

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, which stabilizes the positive charge developing on the mercury and lowers 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 forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Prior Art Publications

The earliest patents that relate to mercury capture on a sorbent are actually not for flue gas mercury control but for capture of mercury from air or other gas mixtures on a carbon or other sorbent. These patents were based on a model that recognized the affinity of halogens for mercury, rather than the formation of a reactive carbon. These patents are discussed below according to the type of halogen used for impregnation.

One patent that teaches a halogen impregnation (Stock, U.S. Patent 1,984,164, issued in 1934) describes the use of activated carbon or other solid impregnated with a halogen for removing Hg from air. The impregnation method is not specified. This seems to be the most general claim with respect to halogen impregnation. All the statements and claims appear to refer to halogen or iodine, but the patent does not appear to address bromides or other halides or bromide compounds or even specifically iodide or an iodine compound. The only example in the description is iodine impregnation. The patent also is restricted to air systems and did not pertain to flue gas systems with reactive acid gases. The description did not assume that the iodine formed a reactive carbon species.

Japanese Patent JP 49-43197 describes the treatment of Hg-contaminated electrolysis cell gas using a metal iodide salt on a support. A similar treatment using a resin impregnated with a metal iodide is described in JP 50-6438. These patents do not appear to represent a carbon bromide compound as specified in this patent application.

BHE et al. EXHIBIT 1023
Page 452

Another early patent (Hilgen, U.S. Patent 3,849,267, issued in 1974) describes a method for Hg removal from a gas which claims mixing molecular chlorine (Cl_2) with the gas to be cleaned and passing it through a nonporous sorbent such as glass wool and NaCl (not carbon). This was evidently not an obvious extension of the Stock patent, since a halogen was introduced as part of the gas phase being cleaned.

A later patent (deJong, et al., U.S. Patent 4,196,173, issued in 1980) describes a method for Hg removal in air which claims using a bed of activated carbon impregnated with halogen-only Cl_2 is specified in the other claims and examples, and it is prepared by flowing the Cl_2 stream through a carbon bed.

An improved sorbent for mercury in air was patented by Revoir and Jones (U.S. Patent 3662523, issued in 1972), in which ICl and ICl_3 vapors were impregnated into the activated carbon. No explanation of the increased activity was provided. Since these compounds are interhalogen compounds, the patent did not infringe Stock.

U.S. Patent 5,891,324 describes an activated carbon containing an acid (HCl, H_2SO_4, or H_3PO_4) for the removal of mercury contained in a liquid phase, such as would occur in a process steam in the oil industry. In this case, the model presented was that mercury is adsorbed from the liquid into the solid carbon phase at relatively low temperatures.

In U.S. Patent Application 2004/0003716, a method is described for removing mercury from a combustion gas. This method employs an exposure of a finely powdered activated carbon to a molecular bromine gas at an elevated temperature or to HBr to produce a sorbent with good mercury removal ability when injected into the flue gas duct. The model for the efficacy of the Nelson sorbent is not clearly stated, so it can be presumed that the reasoning for using bromine is the simple premise that some bromine form will help capture the mercury, as does iodine and chlorine. The methods for incorporation of the bromine in the Nelson application are not the same as with the present invention, and the Nelson method will not produce the identical carbon bromide species that are obtained in the art described in this application. The Nelson method lacks many of the features

BHE et al. EXHIBIT 1023
Page 453

described in this application that impart exceptional activity to the sorbent in a convenient way, for example, the addition of smaller amount of a second more powerful promoting agent, the use of facile solvent systems, including aqueous bromine, and the use of in-flight bromine treatment. Additionally, the patent application does not mention regeneration, recycling, or reuse, or the use of moving contactors or larger particle size to facilitate sorbent-ash separation.

Embodiments of the Invention.

A sorbent that is initially very reactive in oxidizing mercury can be used in very small amounts to achieve high capture efficiencies, thus lowering operation costs and lessening the disposal problem. In addition, further disposal reduction is made possible by recycling and reusing the sorbent that is produced using this technology. The time interval for the mercury and sorbent to interact in a flue gas duct and the subsequent collection of the mercury on the sorbent and ash may be very short- only seconds. This requires the sorbent to have high capacity and be very reactive toward mercury. A sorbent can be utilized in a very finely powdered form (e.g., 1-10 μm) to minimize mass transfer limitations. But, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. One feature of this invention is the process to prepare a sorbent containing a bromide 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 effective capture of the mercury.

One possible way to do this is to chemically combine molecular bromine from solution with activated carbon (edge sites). X-ray photoelectron spectroscopy established that the addition of bromine formed a chemical compound in the carbon structure. Thus, the sorbent does not represent a molecular bromine halogen form but a new chemically modified carbon structure. This may not occur with the less reactive iodine, where an I_2- molecular complex can exist on the carbon basal plane. In the bromine case, it is actually the carbon that oxidizes the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can be generated by the addition of bromine,

BHE et al. EXHIBIT 1023
Page 454

hydrogen bromide, or combinations of bromine and other elements as described herein. Chlorine treatment resulted in lower-activity carbons because the chloride anion was less 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.

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, exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound from a second halogen, such as HBr. 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).

Furthermore, we demonstrated that the sorbent can be readily treated with any combination of bromine and the second component in-flight using vapors of these components contacting the very fine carbon particles dispersed in air or other gas stream that conveys the particles to the flue gas duct. There is no particular temperature requirement for this contact. This technology is very simple to implement, so it will result in a great cost savings to the utility using this technology for mercury capture.

A unique, nonobvious technique for preparation of the treated carbon is through combining the treatment system with the carbon injection system at the end-use site. With this technique, the halogen is introduced to the carbon-air mixture in the transport line (or other part of the sorbent storage and injection system). Benefits over current concepts to treat sorbents off-site include the following:

- 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.
- This process uses existing hardware and operation procedures.

BHE et al. EXHIBIT 1023
Page 455

- This 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.
- This process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as needed when changing fuels or reducing loads, thus further optimizing the economics.
- This 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 invention, a process for preparing and regenerating carbon sorbents whose activity for mercury capture is promoted by the addition of bromine to the carbon structure.

The invention applies to use of a sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Examples of the composition of the sorbent are a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Alternatively, the sorbent is on a moving contactor consisting of particles or fibers containing the compositions listed in the previous sentence. Either type can be regenerated; the poisoning contaminants from the flue gas are 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 art of adding a reagent (such as peroxide, gold, triiodide, etc.) to the sorbent. The activated carbon sorbent treated with bromine and/or the other 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 incorporated by reference herein.

Although the invention is described herein as a sorbent material, 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

BHE et al. EXHIBIT 1023
Page 456

the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific exemplary embodiments.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility. Of course, the invention can also be used in any other desired type of facility. FIG. 11 shows a boiler for burning pulverized coal. The facility utilizes various devices to clean the exhaust of the boiler. In this example, a baghouse or ESP is used to collect particulates in the exhaust. A scrubber and sorbent bed are also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In the example shown, the sorbent is injected into the flue gas after the boiler. The additive can be injected where desired (e.g., before, after, or within the boiler).

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize the invention. Where possible, the mercury control technology of the present invention will utilize measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent levels in this way will ensure mercury removal requirements are met with the minimal sorbent requirements and therefore the associated costs will be minimized. In one example, the emissions are measured at the stack.

Carbon Sorbent

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, galium, 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 accept electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The

BHE et al. EXHIBIT 1023
Page 457

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.

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several powdered carbon sorbents, 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. Adding a second component to the solution was demonstrated to improve 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. 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 has been treated with 0.1 N HBr, collecting the powder by centrifugation and drying, revealed that the mercury capture activity is 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 indicates that it not only captures mercury at the same level as before (100% capture) but is enhanced such that its capacity is prolonged by several minutes.

BHE et al. EXHIBIT 1023
Page 458

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.

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 of 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.

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 carbons were collected in the baghouse at 350E to 375EF. Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/Macf resulted in mercury effluent concentrations of 3.8-4.2 $\mu g/m^3$ (representing 62%-58% removal of the mercury from the gas), and at 2.0 lb/Macf, 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-treated carbon.

Addendum: Other References to Hg Sorption

Sorbent Beds with Particulate Removal

Carbon beds have also been utilized for mercury capture in flue gas. The German Patent 34 26 059 describes the use of a very thick carbon bed for treatment of flue gases containing polyhalogenated compounds. Although the system employed at Dusseldorf would also have the potential for Hg removal (for example, see the Streng reference), it is not very practical to use such a thick bed. Spent sorbent is burned and not regenerated. The carbons are not pretreated.

The GE-Mitsui-BF system (Tsuji, K.; Shiraishi, I.; Dague, R.F. Proceedings, Sixth International Symposium, Air & Water Management Assoc., New Orleans, LA, March 10-12, I993) employs 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

BHE et al. EXHIBIT 1023
Page 459

mercury is converted to the elemental form, which desorbs from the sorbent. Attrition of the sorbent results in a significant sorbent cost. The carbons are not pretreated.

Sorbent Injection After Particulate Removal

A process of injecting manganese oxide sorbent particles is described in U.S. Patent Application 2002/0150516. Regeneration is claimed by removal of spent oxide particles from the reaction zone and rinsing with dilute aqueous acid.

Sorbent Beds After Particulate Removal

Of particular 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 teaches several examples of this type of configuration and sorbent processing.

U.S. Patent 5,607,496 teaches the oxidation of mercury on a metal oxide sorbent bed and subsequent absorption to 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 the metal sulfates, which poison the bed. High temperatures are proposed to regenerate the bed. However, Hg is only partially removed from the sorbent at temperatures up to 500°C. The sorbents do not work effectively after regeneration using this technique; the problem may be that manganese sulfate formed during the sorption cycle does not completely decompose back to an active manganese oxide form.

U.S. Patent 6,383,981 describes a fixed MnO_2 or Fe_2O_3 bed for removal of Hg from a hydrocarbon stream. No regeneration method appears to be included.

A recent U.S. Patent application (2001/0003116) 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 polyfunctional complex-forming reagent containing the catalyst active component

BHE et al. EXHIBIT 1023
Page 460