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(54) **SORBENTS FOR REMOVAL OF MERCURY**

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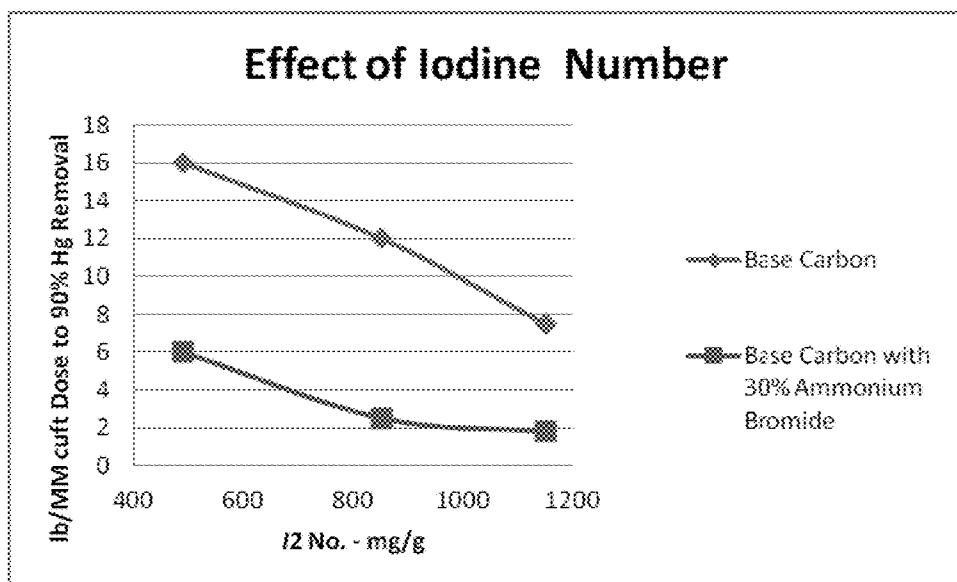
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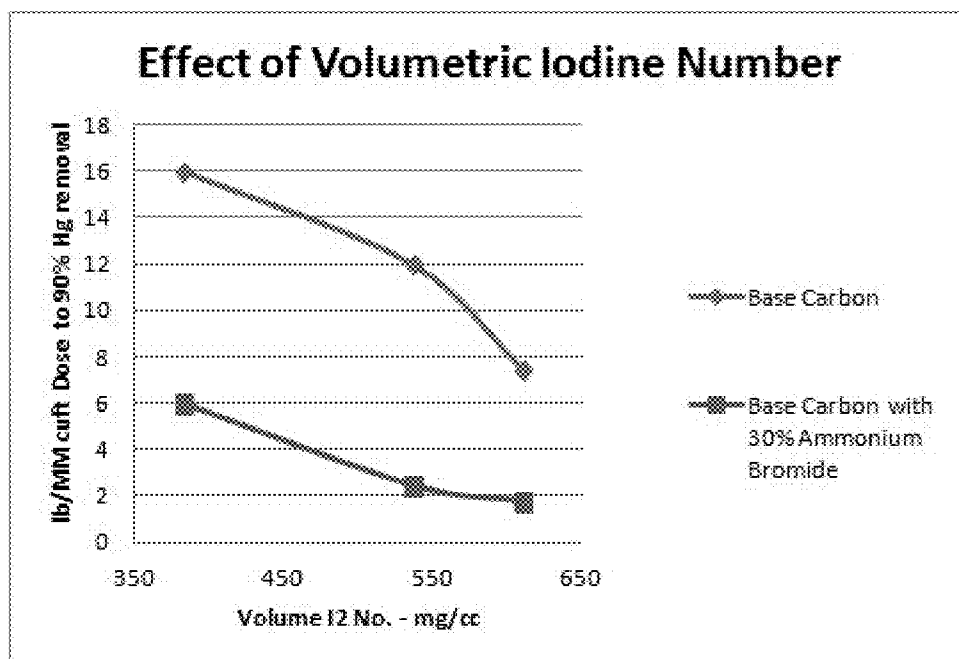
(57) **ABSTRACT**

**Related U.S. Application Data**

(60) Provisional application No. 61/658,258, filed on Jun.  
11, 2012.

Methods and systems for reducing mercury emissions from  
fluid streams are provided herein, as are adsorbent materials  
having high volumetric iodine numbers.

**FIG. 1**

**FIG. 2**

**SORBENTS FOR REMOVAL OF MERCURY****CROSS-REFERENCE TO RELATED APPLICATIONS**

**[0001]** This application claims priority to U.S. Provisional Application No. 61/658,258, entitled, "Sorbenents for Removal of Mercury," filed Jun. 11, 2012, which is incorporated herein by reference in its entirety.

**GOVERNMENT INTERESTS**

**[0002]** Not applicable

**PARTIES TO A JOINT RESEARCH AGREEMENT**

**[0003]** Not applicable

**INCORPORATION BY REFERENCE OF MATERIAL SUBMITTED ON A COMPACT DISC**

**[0004]** Not applicable

**Background**

**[0005]** Mercury is a known environmental hazard and leads to health problems for both humans and non-human animal species. Approximately 50 tons per year are released into the atmosphere in the United States, and a significant fraction of the release comes from emissions from coal burning facilities such as electric utilities. To safeguard the health of the public and to protect the environment, the utility industry is continuing to develop, test, and implement systems to reduce the level of mercury emissions from its plants. In the combustion of carbonaceous materials, it is desirable to have a process wherein mercury and other undesirable compounds are captured and retained after the combustion phase so that they are not released into the atmosphere.

**[0006]** One of the most promising solutions for mercury removal from flue gas is Activated Carbon Injection (ACI). Activated carbon is a highly porous, non-toxic, readily available material that has a high affinity for mercury vapor. This technology is already established for use with municipal incinerators. Although the ACI technology is effective for mercury removal, the short contact time between the activated carbon and the flue gas stream results in an inefficient use of the full adsorption capacity of the activated carbon. Mercury is adsorbed while the carbon is conveyed in the flue gas stream along with fly ash from the boiler. The carbon and fly ash are then removed by a particulate capture device such as an Electrostatic Precipitator (ESP) or baghouse.

**SUMMARY OF THE INVENTION**

**[0007]** Various embodiments are directed to a mercury adsorptive material comprising an adsorptive material having a volumetric iodine number of greater than 450 mg/cc based on the gravimetric iodine number determined using standard test method (ASTM) D-4607 or an equivalent thereof and the apparent density determined using (ASTM) D-2854 or an equivalent thereof. In some embodiments, the volumetric iodine number is about 500 mg/cc to about 650 mg/cc. The adsorptive material can be any material known in the art including, but not limited to, activated carbon, reactivated carbon, graphite, graphene, carbon black, zeolite, silica, silica gel, clay, and combinations thereof. In some certain embodiments, the adsorptive material has a mean particle diameter (MPD) of about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ . In particular embodi-

ments, the mercury adsorptive material may include one or more oxidizing agent, such as, but not limited to, chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof, and the one or more oxidizing agent may be about 5 wt. % to about 50 wt. % of a total adsorptive material. In certain embodiments, the mercury adsorptive material may include one or more nitrogen source such as, for example, ammonium containing compounds, ammonia containing compounds, amines containing compounds, amides containing compounds, imines containing compounds, quaternary ammonium containing compounds, and combinations thereof, and the one or more nitrogen source may be about 5 wt. % to about 50 wt. % of a total adsorptive material. In some embodiments, the one or more nitrogen source may be ammonium iodide, ammonium bromide, or ammonium chloride, amine halides, a quaternary ammonium halides, organo-halides, and combinations thereof. In further embodiments, the mercury adsorptive material may include an alkaline agent such as, but not limited to, calcium carbonate, calcium oxide, calcium hydroxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium bicarbonate, trisodium hydrogencarbonate dihydrate, and combinations thereof, and the alkaline agent may be provided at a concentration of greater than or equal to about 0.15 equivalents per 100 grams of adsorptive material.

**[0008]** Other embodiments are directed to a system for removing mercury from flue gas including an adsorptive material having a volumetric iodine number of greater than 450 mg/cc based on the gravimetric iodine number determined using standard test method (ASTM) D-4607 or an equivalent thereof and the apparent density determined using (ASTM) D-2854 or an equivalent thereof. In some embodiments, the volumetric iodine number is about 500 mg/cc to about 650 mg/cc. The system can be any material known in the art including, but not limited to, activated carbon, reactivated carbon, graphite, graphene, zeolite, silica, silica gel, clay, and combinations thereof. In some certain embodiments, the adsorptive material has a mean particle diameter (MPD) of about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ . In particular embodiments, the system may include one or more oxidizing agent, such as, but not limited to, chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof, and the one or more oxidizing agent may be about 5 wt. % to about 50 wt. % of a total adsorptive material. In certain embodiments, the system may include one or more nitrogen source such as, for example, ammonium containing compounds, ammonia containing compounds, amines containing compounds, amides containing compounds, imines containing compounds, quaternary ammonium containing compounds, and combinations thereof, and the one or more nitrogen source may be about 5 wt. % to about 50 wt. % of a total adsorptive material. In some embodiments, the one or more nitrogen source may be ammonium iodide, ammonium

bromide, or ammonium chloride, amine halides, a quaternary ammonium halides, organo-halides, and combinations thereof. In further embodiments, the system may include an alkaline agent such as, but not limited to, calcium carbonate, calcium oxide, calcium hydroxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium bicarbonate, trisodium hydrogencarbonate dihydrate, and combinations thereof, and the alkaline agent may be provided at a concentration of greater than or equal to about 0.15 equivalents per 100 grams of absorptive material.

**[0009]** Further embodiments are directed to a method for mercury removal including the step of injecting an adsorptive material having a volumetric iodine number of greater than 450 mg/cc based on the gravimetric iodine number determined using standard test method (ASTM) D-4607 or an equivalent thereof and the apparent density determined using (ASTM) D-2854 or an equivalent thereof into a flue gas stream. In some embodiments, the adsorptive material may have a volumetric iodine number is about 500 mg/cc to about 650 mg/cc. The adsorptive material may be, for example, activated carbon, reactivated carbon, graphite, graphene, zeolite, silica, silica gel, clay, and combinations thereof and may have a mean particle diameter (MPD) of about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ . The adsorptive material may further include any of the additives described above.

#### DESCRIPTION OF DRAWINGS

**[0010]** In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be utilized and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

**[0011]** FIG. 1 is a graph showing the relationship between gravimetric iodine number and adsorption of mercury.

**[0012]** FIG. 2 is a graph showing the relationship between volumetric iodine number and adsorption of mercury for an adsorbent.

#### DETAILED DESCRIPTION

**[0013]** Before the present compositions and methods are described, it is to be understood that this invention is not limited to the particular processes, compositions, or methodologies described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention, which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention, the preferred methods, devices, and materials are now described. All publications mentioned herein are

incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

**[0014]** It must also be noted that as used herein and in the appended claims, the singular forms “a,” “an,” and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to “a combustion chamber” is a reference to “one or more combustion chambers” and equivalents thereof known to those skilled in the art, and so forth.

**[0015]** As used herein, the term “about” means plus or minus 10% of the numerical value of the number with which it is being used. Therefore, about 50% means in the range of 45%-55%.

**[0016]** Embodiments of the invention are directed to mercury sorbents having enhanced mercury removal capabilities in flue gas streams. Such mercury sorbents have include a mercury adsorptive material having an iodine number of greater than 300 mg/g, and in other embodiments, the mercury adsorptive material may have an iodine number from about 700 mg/g to about 1500 mg/g. In still other embodiments, these mercury sorbents may include one or more additives that may further enhance the effectiveness of the mercury adsorptive material.

**[0017]** The mercury adsorptive material of the sorbent composition of various embodiments may include any material having an affinity for mercury. For example, in some embodiments, the mercury adsorptive material may be a porous sorbent having an affinity for mercury including, but not limited to, activated carbon, reactivated carbon, graphite, graphene, zeolite, silica, silica gel, clay, and combinations thereof, and in particular embodiments, the mercury adsorptive material may be activated carbon. The mercury adsorptive material may have any mean particle diameter (MPD). For example, in some embodiments, the MPD of the mercury adsorptive material may be from about 0.1  $\mu\text{m}$  to about 100  $\mu\text{m}$ , and in other embodiments, the MPD may be about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ . In still other embodiments, the MPD of the mercury adsorptive material may be less than about 15  $\mu\text{m}$ , and in some particular embodiments, the MPD may be about 2  $\mu\text{m}$  to about 10  $\mu\text{m}$ , about 4  $\mu\text{m}$  to about 8  $\mu\text{m}$ , or about 5  $\mu\text{m}$  or about 6  $\mu\text{m}$ . In certain embodiments, the mercury adsorptive materials may have an MPD of less than about 12  $\mu\text{m}$ , or in some embodiments, less than 7  $\mu\text{m}$ , which may provide increased selectivity for mercury oxidation.

**[0018]** In certain embodiments, the mercury adsorbent may have high activity as determined by having an iodine number of greater than 300 mg/g. Iodine number is used to characterize the performance of adsorptive materials based on the adsorption of iodine from solution. This provides an indication of the pore volume of the adsorbent material. More specifically, iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration in the residual filtrate is 0.02 normal. Greater amounts of adsorbed iodine indicates that the activated carbon has a higher surface area for adsorption and a higher degree of activation activity level. Thus, a higher “iodine number” indicates higher activity. As used herein, the term “iodine number” can refer to either a gravimetric iodine number or a volumetric iodine number. Gravimetric iodine number can be determined using standard test method (ASTM) D-4607, which is hereby incorporated by reference in its entirety, or equivalent thereof. Volumetric iodine number is a

product of the gravimetric iodine number (mg of iodine adsorbed/gram of carbon) and the apparent density of the activated carbon (grams of carbon/cc of carbon), which an apparent density can be determined using ASTM D-2854, which is hereby incorporated by reference in its entirety, or an equivalent thereof. In other embodiments, granular or powdered carbon or any other form of carbon where the ASTM apparent density test cannot properly be applied, the apparent density can be determined using mercury porosimetry test ASTM 4284-12 to determine the void volume via mercury intrusion volume at 1 pound per square inch actual pressure. This intrusion volume defines the void volume of the carbon sample to allow calculation of the carbon particle density, and the apparent density is then calculated by correcting this particle density for the void fraction in a dense packed container of the carbon sample. The void fraction is 40% for a typical 3 fold range in particle size for the sample. Thus, Calculated Apparent Density (g.Carbon/cc.Carbon container)=Particle Density (g.carbon/cc.carbon particle volume)\*(100%–40% voids)/100%. The result is a volume based activity with the units of mg of iodine adsorbed per cc of carbon.

**[0019]** Adsorbent materials typically used for mercury adsorption have an iodine number, based on the gravimetric iodine number, of about 300 mg/g to about 400 mg/g, which is thought to provide equivalent performance in mercury adsorption characteristics to adsorptive materials having higher iodine numbers. Various embodiments of the invention are directed to mercury sorbents that include adsorbent materials having gravimetric iodine number for greater than 400 mg/g, greater than 500 mg/g, greater than 600 mg/g, greater than 700 mg/g, greater than 800 mg/g, greater than 900 mg/g, and so on or any gravimetric iodine number therebetween. In other embodiments, the adsorptive material may have an iodine number of from about 500 mg/g to about 1500 mg/g, about 700 mg/g to about 1200 mg/g, or about 800 mg/g to about 1100 mg/g, or any gravimetric iodine number between these exemplary ranges. In further embodiments, mercury adsorbents exhibiting an iodine number within these exemplary ranges may be an activated carbon or carbonaceous char.

**[0020]** As determined using volumetric iodine number methods, adsorbent materials for mercury adsorption may have a volumetric iodine number from about 350 mg/cc to about 800 mg/cc. In embodiments of the invention described herein, the volumetric iodine number may be greater than 400 mg/cc, greater than 500 mg/cc, greater than 600 mg/cc, greater than 700 mg/cc, and so on or any volumetric iodine number therebetween. In other embodiments, the adsorptive material may have a volumetric iodine number of from about 350 mg/cc to about 650 mg/cc, about 400 mg/cc to about 600 mg/cc, about 500 mg/cc to about 600 mg/cc, about 500 mg/cc to about 700 mg/cc, or any volumetric iodine number between these ranges. In further embodiments, mercury adsorbents exhibiting an iodine number within these exemplary ranges may be an activated carbon or carbonaceous char, and in certain embodiments, these activated carbon or carbonaceous chars exhibiting a volumetric iodine number of 400 mg/cc or greater may be combined with activated carbons and carbonaceous chars exhibiting a volumetric iodine number that is less than 400 mg/cc.

**[0021]** Without wishing to be bound by theory, adsorbent materials having an iodine number within these exemplary ranges may provide improved adsorption over adsorbent

materials having a gravimetric iodine number within the commonly used range of about 300 mg/g to about 400 mg/g. For example, in certain embodiments, about one half as much activated carbon having a gravimetric iodine number between about 700 mg/g to about 1200 mg/g or a volumetric iodine number of about 500 mg/cc to about 2200 mg/cc may be necessary to adsorb the amount of mercury adsorbed by conventional activated carbon. Thus, certain embodiments, are directed to methods in which about 5 lbs/hr to about 10 lbs/hr of activated carbon having an iodine number of from about 700 mg/g to about 1200 mg/g or a volumetric iodine number of about 500 mg/cc to about 2200 mg/cc can adsorb an equivalent amount of mercury as about 15 lbs/hr of an activated carbon having a gravimetric iodine number of about 500 mg/g (see, Example 1).

**[0022]** In still other embodiments, any of the adsorptive materials described above may be treated with one or more oxidizing agents that enhance mercury adsorption. For example, in some embodiments, the oxidizing agent may be a halogen salt including inorganic halogen salts, which for bromine may include bromides, bromates, and hypobromites, for iodine may include iodides, iodates, and hypoiodites, and for chlorine may be chlorides, chlorates, and hypochlorites. In certain embodiments, the inorganic halogen salt may be an alkali metal or an alkaline earth element containing halogen salt where the inorganic halogen salt is associated with an alkali metal such as lithium, sodium, and potassium or alkaline earth metal such as magnesium, and calcium counterion. Non-limiting examples of inorganic halogen salts including alkali metal and alkali earth metal counterions include calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and the like. The oxidizing agents may be included in the composition at any concentration, and in some embodiments, no oxidizing agent may be included in the compositions embodied by the invention. In embodiments in which oxidizing agents are included, the amount of oxidizing agent may be from about 5 wt. % or greater, about 10 wt. % or greater, about 15 wt. % or greater, about 20 wt. % or greater, about 25 wt. % or greater, about 30 wt. % or greater, about 40 wt. % or greater of the total sorbent, or about 5 wt. % to about 50 wt. %, about 10 wt. % to about 40 wt. %, about 20 wt. % to about 30 wt. %, or any amount therebetween.

**[0023]** In further embodiments, any of the adsorptive materials described above may be treated with one or more nitrogen source. The nitrogen source of such agents may be any nitrogen sources are known in the art and can include, for example, ammonium, ammonia, amines, amides, imines, quaternary ammonium, and the like. In certain embodiments, the agent may be, for example, chlorine, bromine, iodine, ammonium halide, such as, ammonium iodide, ammonium bromide, or ammonium chloride, an amine halide, a quaternary ammonium halide, or an organo-halide and combinations thereof. In some embodiments, the nitrogen containing agent may be ammonium halide, amine halide, or quaternary ammonium halide, and in certain embodiments, the agent may be an ammonium halide such as ammonium bromide. In various embodiments, the nitrogen containing agent may be provided about 5 wt. % or greater, about 10 wt. % or greater, about 15 wt. % or greater, about 20 wt. % or greater, about 25 wt. % or greater, about 30 wt. % or greater, about 40 wt. % or

greater of the total sorbent, or about 5 wt. % to about 50 wt. %, about 10 wt. % to about 40 wt. %, about 20 wt. % to about 30 wt. %, or any amount therebetween.

**[0024]** The ammonium halide, amine halide, or quaternary ammonium halide may be absent in some embodiments, in other embodiments, the ammonium halide, amine halide, or quaternary ammonium halide may be the only additive included in the sorbent composition, and in still other embodiments, the ammonium halide, amine halide, or quaternary ammonium halide may be combined with other agents such as, for example, halide salts, halide metal salts, alkaline agents, and the like to prepare a composition or sorbent encompassed by the invention. In particular embodiments, sorbent may include at least one of a halogen salt such as sodium bromide (NaBr), potassium bromide (KBr), or ammonium bromide (NH<sub>4</sub>Br).

**[0025]** In some embodiments, the adsorbent material may be combined with an acid gas suppression agent such as, for example, alkaline agent. Numerous alkaline agents are known in the art and currently used to remove sulfur oxide species from flue gas and any such alkaline agent may be used in the invention. For example, in various embodiments, the alkaline additive may be alkali oxides, alkaline earth oxides, hydroxides, carbonates, bicarbonates, phosphates, silicates, aluminates, and combinations thereof, and in certain embodiments, the alkaline agent may be calcium carbonate (CaCO<sub>3</sub>; limestone), calcium oxide (CaO; lime), calcium hydroxide (Ca(OH)<sub>2</sub>; slaked lime), magnesium carbonate (MgCO<sub>3</sub>; dolomite), magnesium hydroxide (Mg(OH)<sub>2</sub>), magnesium oxide (MgO), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), sodium bicarbonate (NaHCO<sub>3</sub>), trisodium hydrogencarbonate dihydrate (Na<sub>3</sub>H(CO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O; trona), and combinations thereof. In various embodiments, the alkaline agent may be provided at a concentration greater than or equal to about 0.15 equivalents per 100 grams of absorptive material, wherein one equivalent of the alkaline agent is defined as the amount required to produce one mole of hydroxyl ions or to react with one mole of hydrogen ions. In particular embodiments, such alkaline agents may have a relatively high surface area such as, for example, above 100 m<sup>2</sup>/g for neat materials. High surface area materials may provide improved kinetics and capabilities for acid gas or SO<sub>x</sub> mitigation while complementing halogen compounds and other added oxidants to provide oxidation of elemental mercury. Because alkaline agents are highly polar materials that may associate and bond with water, in various embodiments, alkaline agents may be combined with the primary mercury sorbent as a physical admixture and may not generally be present on the sorbent surface or contained within the sorbent pore structure.

**[0026]** In other embodiments, the mercury adsorptive material may be treated to enhance the hydrophobicity of the adsorptive materials with, for example, one or more hydrophobicity enhancement agents that impede the adsorption and transport of water or other treatments of the sorbent that achieve similar results. Embodiments are not limited to the type of treated mercury adsorptive material or the means by which the mercury adsorptive material has been treated with a hydrophobicity enhancement agent. For example, in some embodiments, the mercury adsorptive material may be treated with an amount of one or more elemental halogen that can form a permanent bond with the surface. The elemental halogen may be any halogen such as fluorine (F), chlorine (Cl), or bromine (Br), and in certain embodiments, the elemental halogen may be fluorine (F). In other embodi-

ments, the mercury adsorptive material may be treated with a hydrophobicity enhancement agent such as a fluorine salt, organo-fluorine compound, or fluorinated polymer, such as, TEFLON®.

**[0027]** In such embodiments, treatment may be effectuated by grinding the mercury adsorptive material with the organo-fluorine compound or fluorinated polymer. In still other embodiments, carbon sorbents used as the mercury adsorptive material may be treated with mineral acids such as but not limited to, hydrochloric acid, nitric acid, boric acid, and sulfuric acid, under high temperature, e.g., greater than about 400° C. or greater than 600° C. or greater than 800° C. The concentration of the acid is not critical to such treatments and concentrations as low as 1.0 percent by weight or less may be used. Without wishing to be bound by theory, such treatment may enhance hydrophobicity and decreased activity for the catalytic oxidation of sulfur dioxide to sulfuric acid in the presence of oxygen and water. Evidence of such treatments can be found in a high contact pH and a reduced tendency for the carbon alone to decompose hydrogen peroxide when compared to the same carbon without such treatments.

**[0028]** The adsorbent material may be combined with an oxidizing agent, nitrogen containing compound, hydrophobicity agent, acid gas suppression agent, or other mercury removal agent (collectively, "additives") in any way known in the art. For example, in some embodiments, the one or more additive may be introduced onto the surface of the adsorbent material by impregnation in which the adsorbent material is immersed in a liquid mixture of additives or the liquid mixture of additives is sprayed or otherwise applied to the adsorbent material. Such impregnation processes result in an adsorbent material in which the additives are dispersed on the surface of the adsorbent material.

**[0029]** In various other embodiments, treatment of the adsorbent material may be combined with one or more additive as a dry admixture in which particles of adsorbent are separated and apart from particles of additive having substantially the same size. For example, in some embodiments, may be provided by co-milling activated carbon with one or more additive to a mean particle diameter (MPD) of less than or equal to about 12 μm, less than or equal to about 10 μm, or less than about 7 μm. Without wishing to be bound by theory, reducing the mean particle diameter of the sorbent and additives by co-milling allows for a close localization of the sorbent and the additives, but the additives are not contained within the sorbent pore structure. These dry admixtures have been found to be surprisingly effective in facilitating rapid and selective mercury adsorption. This effect has been shown particularly effective when all of components of the sorbent are combined and co-milled or otherwise sized to a mean particle diameter of less than or equal to about 12 μm. Co-milling may be carried out by any means. For example, in various embodiments, the co-milling may be carried out using bowl mills, roller mills, ball mills, jet mills or other mills or any grinding device known to those skilled in the art for reducing the particle size of dry solids.

**[0030]** Although not wishing to be bound by theory, the small MPD may improve the selectivity of mercury adsorption as the halide effectively oxidizes the mercury. As such, dry admixtures of adsorbent materials and additive may allow for a higher percentage of active halide and alkaline agents to be included in the injected sorbent. Mercury adsorbents that are impregnated with an additive by treating with an aqueous solution of the additive, for example, commercial brominated

carbon sorbents, especially those impregnated with elemental bromine, can only retain a small percentage of the additive on the surface of the adsorbent, and impregnation tends to clog the pores of porous mercury adsorbents reducing the surface area available for mercury adsorption. In contrast, the percentage of additive in a dry mixture may be greater than about 10 wt. %, greater than about 15 wt. %, greater than about 20 wt. %, or greater than about 30 wt. % and up to about 50 wt. %, up to about 60 wt. %, or up to about 70 wt. % without exhibiting a reduction in mercury adsorption efficiency.

**[0031]** While co-grinding is useful in some embodiments, adsorptive material and additives may be combined by any method. For example, in some embodiments, an adsorptive material and one or more additive may be combined by blending or mixing the materials into a single mercury sorbent that can then be injected into a flue gas stream. In other embodiments, combining may occur during use such that the adsorptive material and the one or more additive are held in different reservoirs and injected simultaneously into a flue gas stream.

**[0032]** Further embodiments are directed to methods for removing mercury from flue gas by injecting a mercury adsorbent including a mercury sorbent described above including an adsorbent material and one or more oxidizing agent, nitrogen containing compound, hydrophobicity agent, acid gas suppression agent, or other mercury removal agent into a flue gas stream. The sorbents described herein may be used to adsorb mercury in any flue gas stream. For example, the sorbents of various embodiments may be used in flue gas streams having no or extremely low  $\text{SO}_3$  content or flue gas streams containing high concentrations of other acid gases such as  $\text{HCl}$ ,  $\text{HF}$ , or  $\text{NO}_x$  species.

**[0033]** In some embodiments, the mercury adsorptive material and one or more additive may be combined prior to injection into the flue gas stream by, for example, mixing or blending, the mercury adsorptive material with the one or more additives. In other embodiments, the mercury adsorptive material and one or more additives may be injected separately into the flue gas stream and combined in the flue gas stream itself. In still other embodiments, the mercury adsorbent material and the one or more additives may be introduced into a flue gas stream in different portions of the flue gas stream. For example, in some embodiments, all adsorbent materials and additives may be introduced into the flue gas stream simultaneously and at the same portion of the flue gas stream. In other embodiments, an additive such as, for example, a halide salt may be introduced into a boiler or a upstream portion of the flue gas stream and the adsorbent and one or more additional additives may be introduced into the flue gas stream either simultaneously or separately in one or more downstream portions of the flue gas stream.

### EXAMPLES

**[0034]** Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contained within this specification. Various aspects of the present invention will be illustrated with reference to the following non-limiting examples.

#### Example 1

**[0035]** Activated carbons of various activity levels were investigated for their ability to remove mercury from flue gas.

Activity was based on the gravimetric iodine number (ASTM D-4607) and volumetric iodine number which the gravimetric iodine number converted to a volumetric basis using the density of the granular material (ASTM D2854). Carbons were all approximately 7  $\mu\text{m}$  in size and were injected into test flue gas upstream of the electrostatic precipitator (ESP) either alone or in a dry admixture with 30% w/w ammonium bromide. Results are reported based on lbs/hr required to remove 90% of the mercury in the flue gas stream.

**[0036]** FIGS. 1 and 2 shows performance curves for base carbons (no additive) and the base carbon in a dry admixture of 30% w/w ammonium bromide. FIG. 1 shows the relationship of gravimetric iodine number (mg/g) to the amount of adsorbent required to reach 90% mercury removal, and FIG. 2 shows the relationship between volumetric iodine number (mg/cc) and the amount of adsorbent required to 90% mercury removal. Table 1 shows the apparent density and gravimetric iodine number used to calculate the volumetric iodine number.

TABLE 1

| Apparent Density (g/cc) | Gravimetric Iodine Number (mg/g) | Volumetric Iodine Number (mg/cc) |
|-------------------------|----------------------------------|----------------------------------|
| 0.78                    | 490                              | 382                              |
| 0.63                    | 850                              | 536                              |
| 0.53                    | 1150                             | 610                              |

**[0037]** As illustrated in FIGS. 1 and 2, 15.4 lbs/hr of carbon having an gravimetric iodine number of 462 mg/g and a volumetric iodine number of about 382 mg/cc is required to remove 90% of the mercury from the flue gas stream. In contrast, about 8.3 lbs/hr is required to remove 90% of the mercury from the flue gas stream with activated carbon having a gravimetric iodine number of 1150 mg/g and a volumetric iodine number of about 610 mg/cc. This provides an about 45% reduction in the amount of activated carbon required to remove 90% of the mercury from a flue gas stream when the activity as determined by iodine number is increased by 40%.

**[0038]** FIGS. 1 and 2 also show performance curves for carbons including 30% w/w additive (ammonium bromide) is combined with the activated carbon in a dry admixture before being injected into the flue gas upstream of the ESP. Initially, a 40% reduction in the amount of activated carbon (from 15.4 lbs/hr to 6.2 lbs/hr) necessary to remove 90% of the mercury from the flue gas stream was observed by the addition of ammonium bromide to the activated carbon having an gravimetric iodine number of 462 mg/g. The adsorption of mercury is further enhanced by the introduction of adsorbent having higher activity based on iodine number. Specifically, 1.8 lbs/hr of activated carbon is necessary to remove 90% of the mercury from the flue gas when activated carbon having a gravimetric iodine number of 1150 mg/g and a volumetric iodine number of about 610 mg/cc. This represents a 60% reduction in the amount of activated carbon necessary to reduce the amount of mercury in a full gas stream by 90%. Additionally, the performance curves resulting from activated carbon ammonium bromide mixtures exhibit a non-linear relationship which could be indicative of a synergistic interaction between ammonium bromide addition and both volumetric and gravimetric iodine activity.

**[0039]** FIG. 2 also shows a non-linear decrease in the amount of carbon required when the volumetric iodine number is above about 500 mg/cc when ammonium bromide is



present as an admix. Additionally in FIG. 2, increasing the volume iodine value of the base carbon does not have a large effect on the performance of this material.

What is claimed is:

1. A mercury adsorptive material comprising an adsorptive material having a volumetric iodine number of greater than about 450 mg/cc.

2. The mercury adsorptive material of claim 1, wherein the volumetric iodine number is about 500 mg/cc to about 650 mg/cc.

3. The mercury adsorptive material of claim 1, wherein the volumetric iodine number is about 500 mg/cc to about 700 mg/cc.

4. The mercury adsorptive material of claim 1, wherein the adsorptive material is selected from the group consisting of activated carbon, reactivated carbon, graphite, graphene carbon black, zeolite, silica, silica gel, clay, and combinations thereof.

5. The mercury adsorptive material of claim 1, wherein the adsorptive material is an activated carbon derived from coal.

6. The mercury adsorptive material of claim 1, wherein the adsorptive material has a mean particle diameter (MPD) of about 1  $\mu$ m to about 30 min.

7. The mercury adsorptive material of claim 1, further comprising one or more oxidizing agent.

8. The mercury adsorptive material of claim 7, wherein the one or more oxidizing agent is selected from the group consisting of chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

9. The mercury adsorptive material of claim 7, wherein the one or more oxidizing agent comprises about 5 wt. % to about 50 wt. % of a total adsorptive material.

10. The mercury adsorptive material of claim 1, further comprising one or more nitrogen source.

11. The mercury adsorptive material of claim 10, wherein the one or more nitrogen source is selected from the group consisting of ammonium containing compounds, ammonia containing compounds, amines containing compounds, amides containing compounds, imines containing compounds, quaternary ammonium containing compounds, and combinations thereof.

12. The mercury adsorptive material of claim 10, wherein the one or more nitrogen source is selected from the group consisting of ammonium iodide, ammonium bromide, or ammonium chloride, amine halides, a quaternary ammonium halides, and combinations thereof.

13. The mercury adsorptive material of claim 10, wherein the one or more nitrogen source comprises about 5 wt. % to about 50 wt. % of a total adsorptive material.

14. The mercury adsorptive material of claim 1, further comprising an alkaline agent.

15. The mercury adsorptive material of claim 14, wherein the alkaline agent is selected from the group consisting of alkaline agent may be calcium carbonate, calcium oxide, calcium hydroxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium bicarbonate, trisodium hydrogendicarbonate dihydrate, and combinations thereof.

16. The mercury adsorptive material of claim 14, wherein the alkaline agent is provided at a concentration of greater than or equal to about 0.15 equivalents per 100 grams of absorptive material.

17. A mercury adsorptive material comprising:

an adsorptive material having a volumetric iodine number of greater than about 450 mg/cc;

one or more oxidizing agent; and

one or more nitrogen source.

18. The mercury adsorptive material of claim 17, wherein the volumetric iodine number is about 500 mg/cc to about 650 mg/cc.

19. The mercury adsorptive material of claim 17, wherein the volumetric iodine number is about 500 mg/cc to about 700 mg/cc.

20. The mercury adsorptive material of claim 17, wherein the adsorptive material is selected from the group consisting of activated carbon, reactivated carbon, graphite, graphene carbon black, zeolite, silica, silica gel, clay, and combinations thereof.

21. The mercury adsorptive material of claim 17, wherein the one or more oxidizing agent is selected from the group consisting of chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

22. The mercury adsorptive material of claim 17, wherein the one or more nitrogen source is selected from the group consisting of ammonium iodide, ammonium bromide, or ammonium chloride, amine halides, a quaternary ammonium halides, and combinations thereof.

23. A mercury adsorptive material comprising:

an adsorptive material having a volumetric iodine number of greater than about 450 mg/cc;

one or more oxidizing agent; and

one or more alkaline agent.

24. The mercury adsorptive material of claim 23, wherein the volumetric iodine number is about 500 mg/cc to about 650 mg/cc.

25. The mercury adsorptive material of claim 23, wherein the volumetric iodine number is about 500 mg/cc to about 700 mg/cc.

26. The mercury adsorptive material of claim 23, wherein the adsorptive material is selected from the group consisting of activated carbon, reactivated carbon, graphite, graphene carbon black, zeolite, silica, silica gel, clay, and combinations thereof.

27. The mercury adsorptive material of claim 23, wherein the one or more oxidizing agent is selected from the group consisting of chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypoiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

28. The mercury adsorptive material of claim 23, wherein the alkaline agent is selected from the group consisting of alkaline agent may be calcium carbonate, calcium oxide, calcium hydroxide, magnesium carbonate, magnesium

hydroxide, magnesium oxide, sodium carbonate, sodium bicarbonate, trisodium hydrogendicarbonate dihydrate, and combinations thereof.

29. A system for removing mercury from flue gas, the system comprising an adsorptive material having a volumetric iodine number of greater than 450 mg/cc.

30. The system of claim 29, wherein the volumetric iodine number is about 500 mg/cc to about 650 mg/cc.

31. The system of claim 29, wherein the volumetric iodine number is about 500 mg/cc to about 700 mg/cc.

32. The system of claim 29, wherein the adsorptive material is selected from the group consisting of activated carbon, reactivated carbon, graphite, graphene carbon black, zeolite, silica, silica gel, clay, and combinations thereof.

33. The system of claim 29, wherein the adsorptive material is an activated carbon derived from coal.

34. The system of claim 29, wherein the adsorptive material has a mean particle diameter (MPD) of about 1  $\mu\text{m}$  to about 30 min.

35. The system of claim 29, further comprising one or more oxidizing agent.

36. The system of claim 35, wherein the one or more oxidizing agent is selected from the group consisting of chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

37. The system of claim 35, wherein the one or more oxidizing agent comprises about 5 wt.

38. The system of claim 29, further comprising one or more nitrogen source.

39. The system of claim 38, wherein the one or more nitrogen source is selected from the group consisting of ammonium containing compounds, ammonia containing compounds, amines containing compounds, amides containing compounds, imines containing compounds, quaternary ammonium containing compounds, and combinations thereof.

40. The system of claim 38, wherein the one or more nitrogen source is selected from the group consisting of ammonium iodide, ammonium bromide, or ammonium chloride, amine halides, a quaternary ammonium halides, and combinations thereof.

41. The system of claim 38, wherein the one or more nitrogen source comprises about 5 wt.

42. The system of claim 29, further comprising an alkaline agent.

43. The system of claim 42, wherein the alkaline agent is selected from the group consisting of alkaline agent may be calcium carbonate, calcium oxide, calcium hydroxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium bicarbonate, trisodium hydrogendicarbonate dihydrate, and combinations thereof.

44. The system of claim 42, wherein the alkaline agent is provided at a concentration of greater than or equal to about 0.15 equivalents per 100 grams of absorptive material.

45. A method for mercury removal comprising:

injecting an adsorptive material having a volumetric iodine number of greater than 450 mg/cc.

46. The method of claim 45, wherein the volumetric iodine number is about 500 mg/cc to about 650 mg/cc.

47. The method of claim 45, wherein the volumetric iodine number is about 500 mg/cc to about 700 mg/cc.

48. The method of claim 45, wherein the adsorptive material is selected from the group consisting of activated carbon, reactivated carbon, graphite, graphene carbon black, zeolite, silica, silica gel, clay, and combinations thereof.

49. The method of claim 45, wherein the adsorptive material is an activated carbon derived from coal.

50. The method of claim 45, wherein the adsorptive material has a mean particle diameter (MPD) of about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ .

51. The method of claim 45, further comprising one or more oxidizing agent.

52. The method of claim 51, wherein the one or more oxidizing agent is selected from the group consisting of chlorine, bromine, iodine, ammonium bromide, ammonium chloride, calcium hypochlorite, calcium hypobromite, calcium hypiodite, calcium chloride, calcium bromide, calcium iodide, magnesium chloride, magnesium bromide, magnesium iodide, sodium chloride, sodium bromide, sodium iodide, potassium tri-chloride, potassium tri-bromide, potassium tri-iodide, and combinations thereof.

53. The method of claim 51, wherein the one or more oxidizing agent comprises about 5 wt.

54. The method of claim 45, further comprising one or more nitrogen source.

55. The method of claim 54, wherein the one or more nitrogen source is selected from the group consisting of ammonium containing compounds, ammonia containing compounds, amines containing compounds, amides containing compounds, imines containing compounds, quaternary ammonium containing compounds, and combinations thereof.

56. The method of claim 54, wherein the one or more nitrogen source is selected from the group consisting of ammonium iodide, ammonium bromide, or ammonium chloride, amine halides, a quaternary ammonium halides, and combinations thereof.

57. The method of claim 54, wherein the one or more nitrogen source comprises about 5 wt.

58. The method of claim 45, further comprising an alkaline agent.

59. The method of claim 58, wherein the alkaline agent is selected from the group consisting of alkaline agent may be calcium carbonate, calcium oxide, calcium hydroxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium bicarbonate, trisodium hydrogendicarbonate dihydrate, and combinations thereof.

60. The method of claim 58, wherein the alkaline agent is provided at a concentration of greater than or equal to about 0.15 equivalents per 100 grams of absorptive material.

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