M&G No. 16291.3USI1

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a ~~divisional~~continuation-in-part of U.S. ~~Patent Application No.~~patent application 12/201,595 filed on August 29, 2008, which is a division of U.S. patent application 11/209,163, filed on August 22, 2005~~, entitled "Sorbents for the Oxidation and Removal of Mercury", which claims the benefit of U.S. Provisional Application Serial No.~~ (now Patent No. 7,435,286), which claims priority from provisional application 60/605,640, filed on August 30, 2004~~, both applications~~. The disclosures of US Patent Applications 12/201,595; 11/209,163; and 60/604,640 are hereby incorporated herein by reference ~~in their entirety for all purposes.~~

~~STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT~~

~~**[0002]** 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~~to the extent appropriate.

BACKGROUND OF THE INVENTION

Technical Field of the Invention

[~~0003~~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

[~~0004~~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, ~~per~~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 ~~off gases~~offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

[~~0005~~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 ~~bag house~~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 ~~using~~ an ESP is used to collect the carbon because the contact time of the carbon with the gas is very short.

[~~0006~~0005] A major problem with existing carbon injection systems is that the sorbent is ~~initially~~relatively unreactive~~, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the~~ toward 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.

[~~0007~~0006] One solution has been to add an oxidative sorbent comprising an aluminosilicate material impregnated with a very heavy dosage of one or more oxidative metal halides plus activated carbon. For example, refer to Varma et al. (20070140940). However, the amounts of metal salts required for Hg oxidation are generally relatively large and expensive. Also, several of the salts that can be used in such a process are highly toxic. Although the metal salts are present for oxidation in this process, activated carbon is essential for getting adsorption of the Hg. As such, there is no synergistic role for the aluminosilicates as they appear to be only a support for the oxidizing salts.

[0007] Another approach has been the injection of aluminosilicate particulate such as bentonite, which contains neither oxidizing salts nor halogen complexes with a Lewis base site, and thus lacks the more powerful oxidizing capability of the said complexes as described in this application. For example, see U.S. Patent No. 7,413,719. Additionally, the injection of an aluminosilicate (kaolin or metakaolin) containing calcium hypochlorite which thermally decomposes to form halogen is also known. For example, see U.S. Patent Application No. 20030103882. Thus these and similar impregnated aluminosilicate technologies require time in flight at appropriate high temperatures to heat the impregnated salt(s) to generate an oxidation site. This clearly represents a kinetic barrier to activation in contrast to the extremely fast complexing reaction of the Lewis acid on the surface of the appropriate Lewis base sorbent described in the present patent. The kinetic barrier is only for heating up the calcium hypochlorite to decompose it to Cl atoms or molecules. Halogen (bimolecular or atomic) would complex with carbon or noncarbon at any lower temperature to form reactive oxidation sites. Also, halide would require a very high temp or strong acid to form reactive halogen or halogen complex.

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

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

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

SUMMARY

[~~0008~~0011] ~~It is thus an object~~The various embodiments of the present invention ~~to~~ overcome the various aspects of 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.

[~~0009~~0012] 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~~ any activated carbon and/or non-carbon ~~form containing a reactive~~ compound ~~produced by the reaction of bromine (or halide or other halogen) with the carbon~~, 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. ~~New methods~~Methods for in-flight preparation, introduction, and control of the ~~active~~sorbent, promoter and promoted sorbent into the mercury contaminated gas stream are described.

[~~0010~~0013] When a promoted or a non-promoted base sorbent reacts with elemental or oxidized mercury, a mercury/sorbent chemical composition is formed and, in the case of elemental mercury reacting with the promoted base sorbent, the mercury is oxidized. As discussed in further detail in other portions of the specification, the base sorbent may be either a carbon or a non-carbon material or a combination thereof. Additionally, the mercury/sorbent chemical composition may be comprised of covalent bonds, ionic bonds and/or chemical complexes between the promoted or non-promoted base sorbent and the oxidized mercury. The Lewis basic groups on the non-promoted base sorbent, or the non-promoted portions of a promoted base sorbent, are available for reaction with the Lewis acid groups of already existing oxidized mercury in the mercury containing gas. Thus, mercury may be removed from the mercury containing gas stream through the formation of multiple and various mercury/sorbent chemical compositions even within the same process. For example, multiple sites on a sorbent particulate can form multiple and various mercury/sorbent chemical compositions in the case where only a portion of the sites on the base sorbent particulate are promoted.

[0014] In some embodiments, a carbon and/or non-carbon promoted ~~carbon~~ sorbent and/or a combination thereof is provided comprising a ~~base activated carbon~~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.

[~~0011~~0015] In an embodiment, a promoted carbon and/or non-carbon sorbent is provided wherein the base ~~activated carbon~~sorbent is selected from the group consisting of ~~powdered~~carbon, activated carbon, ~~granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, 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 ~~flyash~~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 ~~base activated carbon~~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 ~~activated~~ sorbent (carbon, non-carbon, or their combination) may have a mass mean particle diameter greater than about 40 micrometers.

[~~0012~~0016] In another embodiment, the promoted sorbent comprises from about 1 to about 30 grams of promoter per 100 grams of base ~~activated carbon~~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.

[~~0013~~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.

[~~0014~~0018] In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the ~~primary~~base sorbent.

[~~0015~~0019] In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base ~~activated carbon~~sorbent. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base ~~activated carbon~~sorbent. In another embodiment, the promoter and optional secondary component are combined with the base ~~activated carbon substantially~~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.

[~~0016~~0020] In an embodiment, a method is provided comprising providing a granular ~~activated carbon;~~base sorbent and reacting the ~~activated carbon~~base sorbent 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 of promoter per 100 grams ~~activated carbon~~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.

[~~0017~~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 ~~activated~~ base sorbent (carbon, non-carbon, or their combination). In another embodiment, the promoter is in an organic solvent when contacting the ~~activated~~ base sorbent (carbon, non-carbon, or their combination).

[~~0018~~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.

[~~0019~~0023] In another embodiment, the method further comprises reacting the granular ~~activated~~ 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 ~~activated~~ 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, mercury removal per gram of sorbent is ~~increase~~increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

[~~0020~~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 ~~sorbent, injecting the~~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 ~~may preferably be~~is attained using less ~~than half as much carbon~~base sorbent as would be required with standard ~~(non-enhanced) carbon~~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 ~~injection of the~~base sorbent and promoter. In another embodiment the injected promoted sorbent is prepared in-flight by reacting ~~an activated~~ 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.

[~~0021~~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 ~~activated~~ the base sorbent (carbon, non-carbon, or their combination).

[~~0022~~0027] In another embodiment, the injected promoted sorbent is prepared in-flight by reacting ~~an activated~~ 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.

[~~0023~~0028] In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt~~-~~% of the promoter content. In another embodiment, the method further comprises adding to the promoted sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

[~~0024~~0029] 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 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.

[~~0025~~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 ~~injected~~promoted sorbent is prepared in-flight by reacting ~~an activated~~ a base sorbent (carbon, non-carbon, or their combination) and a promoter within the flue gas stream or in 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~~ 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.

[~~0026~~0031] In an embodiment, a method for reducing the mercury content of a mercury and ash -containing gas stream is provided wherein particulate ~~activated carbon~~carbon and/or non-carbon promoted sorbent with a mass mean size greater than 40 ~~µm is~~µmis 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 re~~-~~injected 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 co~~-~~injected 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.

[~~0027~~0032] In an embodiment, a method for reducing mercury in a mercury-containing gas to a desired level is disclosed. The method comprises reacting a carbon base sorbent with at least one promoter selected from the group consisting of molecular halogens, halides, and combinations thereof to produce a promoted carbon sorbent; allowing said promoted carbon sorbent to interact with a mercury-containing gas to capture mercury in the mercury-containing gas on the promoted sorbent to produce a cleaned gas; and monitoring the mercury content of the cleaned gas. In some embodiments, the carbon base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the carbon base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In an embodiment, the rate at which the carbon base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

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

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

[0035] In some embodiments, the base sorbent and the promoter are introduced into the mercury-containing gas at the same location or at separate locations. In some embodiments, the base sorbent or promoter or combination thereof is introduced into the mercury-containing gas at one or more locations. In some embodiments, introducing the base sorbent and the promoter comprises injecting the base sorbent and the promoter into the mercury-containing gas. In some embodiments, the promoter is introduced into the mercury-containing gas upstream of the introduction of the base sorbent. In some embodiments, the promoter is introduced upstream of a boiler or a combustion chamber. In an embodiment, the rate at which the base sorbent is introduced or the rate at which the promoter is introduced or combination thereof is adjusted according to the monitored mercury content of the cleaned gas so that the mercury content of the cleaned gas is maintained at substantially the desired level with minimal operating cost.

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

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

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

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

[~~0028~~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

[~~0029~~0041] For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

[~~0030~~0042] Figure 1 schematically illustrates methods for preparation of promoted carbon and/or non-carbon sorbents in accordance with the present invention.

[~~0031~~0043] Figure 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

[~~0032~~0044] Figure 3 schematically illustrates preparation of promoted carbon and/or non-carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system ~~m~~in accordance with the present invention, including in-flight preparation of promoted carbon and/or non-carbon sorbent.

[~~**0033]** Figure 4 is a diagram illustrating breakthrough curves for 5 wt/wt% brominated NORIT Darco FGD sorbent (37 mg+ 113 mg sand) in low-HCI (1 ppm) synthetic flue gas.~~

~~**[0034]** Figure 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg+ 113 mg sand) in low-HCI (1 ppm) synthetic flue gas.~~

~~**[0035]** Figure 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.~~

~~**[0036]** Figure 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters~~**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.

[~~0037~~0046] Figure ~~8 is a~~5A schematically illustrates an exemplary process flow diagram ~~illustrating the breakthrough curves for a brominated NORIT Darco FGD~~for in-flight preparation of a promoted carbon and/or non-carbon sorbent~~ with inert sand~~.

[~~0038]~~ ~~Figure 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.~~

~~**[0039]** Figure 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material~~**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

[~~0040~~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.

[~~0041~~0049] 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~~promoted sorbent, 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 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.

[~~0042~~0050] The treated ~~carbons~~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.

[~~0043~~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 ~~from~~in a mercury containing gas, such as a flue gas and/or product gas ~~form a~~from gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base ~~activated carbon, and~~sorbent while block 20 illustrates adding a halogen or halide promoter that reacts with the ~~carbon, illustrated at block 20,~~base sorbent 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 to produce a product-promoted sorbent suitable for injection.

[~~0044~~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 ~~activated carbon~~sorbent as shown by block 10, adding a halogen or halide promoter that reacts with the ~~carbon~~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~~ 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 to produce a product-promoted sorbent suitable for injection.

[~~0045~~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 ~~activated carbon~~sorbent as illustrated at block 10~~,~~ and adding a halogen or halide promoter and a secondary component to the ~~activated carbon~~base sorbent together, with which they react to produce a product-promoted sorbent as illustrated by block 40~~, producing a product promoted carbon sorbent~~. As above, in embodiments where vapor additions are made to the ~~activated carbon~~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.

[~~0046~~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 ~~flue~~mercury containing gas stream is treated with product -promoted carbon sorbent prepared as described above.

[~~0047~~0057] In some preferred embodiments, the ~~activated~~ carbon base sorbent provided may preferably be any of several types, as understood by those skilled in the art. For example, the ~~activated~~ 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.

[~~0048~~0058] In some preferred embodiments, the ~~activated~~ carbon base sorbent 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~~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.

[~~0049~~0059] In some preferred embodiments, the ~~activated~~ carbon base sorbent 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~~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.

[~~0050~~0060] In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the ~~base activated~~ 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).

[~~0051~~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.

[~~0052~~0062] Referring now to Figure ~~2~~4, ~~there~~a theory is illustrated~~ a theory~~ developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure ~~2~~4, ~~hydrogen bromide reacts~~a molecular bromine molecule forms a complex with the ~~unsaturated structure~~surface 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~~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 ~~bromine~~hydrogen bromide or an electrophilic or ~~a~~Lewis acid bromine compound ~~reacts~~react to form a similar structure~~, with a positive carbon that is~~. 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 ~~oxidizing the mercury with subsequent capture by the sorbent~~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.

[~~0053~~0063] ~~It~~In summary, it has now been found that the formation of the new bromide ~~compound~~complex with ~~carbon~~the metal oxide surface increases ~~their~~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 ~~carbon~~surface oxygen, 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~~appropriate metal oxide forms a similar ~~carbon~~surface bromide complex, in which the positive ~~carbon~~oxygen oxidizes the mercury with the assistance of the bromide ion.

[~~0054~~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 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 ~~carbon~~base sorbents~~,~~ and flue gas mercury reduction~~,~~ in accordance with preferred embodiments of the present invention. ~~There~~In the exemplary embodiment shown, there is provided a base ~~activated carbon~~sorbent reservoir 110, ~~an optional~~a halogen/halide promoter reservoir 120, ~~an optional~~a secondary component reservoir 130, and an ~~optional akali~~alkali 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. 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 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.

[~~0055~~0070] ~~Reservoirs~~As shown, reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. ~~Optional alkali~~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.

[~~0056~~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. ~~Optical~~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.

[~~0057~~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 ~~electrostatic precipitators (hereinafter "ESP")~~ESPs, 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~~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.

[~~0058~~0074] An optional ~~Continuous Emission Monitor~~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.

[~~0059~~0075] In operation, as example, 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~~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,~~201,202,203,208, and 209 can also be adjusted manually or ~~be~~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.

[~~0060~~0076] Referring still to Figure 3, ~~there are illustrated~~ several ~~preferred~~ embodiments are illustrated 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~~sorbent from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206. The halogen/halide may be combined and react with the base

~~activated carbon~~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 ~~activated carbon~~sorbent prior to injection point 116 or downstream at point 116. This ~~option is one form of what is referred to herein as "~~results in in-flight~~"~~ preparation of a promoted~~ carbon~~ sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with the base ~~activated carbon~~sorbent prior to entering transport line 115. Still further, the halogen/halide may be contacted and react with the base ~~activated carbon~~sorbent by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebulliated or ~~fluidized~~flueidized bed of base ~~activated carbon~~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 ~~activated carbon~~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.

[~~0061~~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.

[~~0062~~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 ~~activated carbon~~sorbent, promoted ~~carbon~~sorbent, or optional secondary components. Being able to vary on-site the amount of the optional alkali component relative to base ~~activated carbon~~sorbent, promoted ~~carbon~~sorbent, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

[~~0063~~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 ~~activated carbon~~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.

[~~0064~~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 ~~fluidized~~flueidized bed of granular or fibrous ~~activated carbon~~base sorbent, with the promoted ~~carbon~~ sorbent so produced removed from the top of the bed via gas entrainment for injection.

[~~0065~~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 ~~carbon~~ sorbent may comprise from about 1 to about 30 g of halogen/halide per 100 g of base ~~activated carbon~~sorbent. In some preferred embodiments, the promoted ~~carbon~~ sorbent may comprise ~~an~~a secondary component in concentration of from about 1 to about 15 wt~~-~~% of the concentration of the halogen/halide component.

[~~0066~~0082] 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.

[~~0067~~0083] 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, H2S, SO2, H2Se, SeO2, CS2, $P2S_5$, and combinations thereof.

Halogens in Mercury Capture

[~~0068~~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 ~~a~~ hot flue gas components ~~leave~~leaves little to react with elemental mercury. The atomic elemental halogen form, which includes the ~~fluorine~~flueorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury, but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

[~~0069~~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 ~~activated carbon~~sorbent will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen -Promoted Sorbent Characteristics

[~~0070~~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 ~~carbon~~ sorbents of the present invention to successfully interact in a flue gas duct, with ~~the~~ 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 ~~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 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 ~~compound~~component formed on and/or within the ~~carbon~~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.

[~~0071~~0087] ~~It appears that the~~The inventive sorbents chemically combine ~~molecular~~ bromine~~, for example, from solution, with activated carbon (edge sites). X~~ 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 ~~activated carbon~~base sorbent 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 ~~h~~l$_2$ molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus~~,~~ an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury shown in Figure 2. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting ~~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

[~~0072~~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 ~~carbon~~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

[~~0073~~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~~NOx, 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.

[~~0074~~0090] 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,~~AC; thus more of it can be used, still resulting in overall lower costs.

~~“~~In-Flight~~”~~ Sorbent Preparation

[~~0075~~0091] ~~Furthermore, we have demonstrated that~~As stated previously, 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~~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~~ 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.

[0092] Referring to Figures SA and SB, 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 SA, 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 50l' passes through chamber 30l' 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 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

[~~0076~~0097] 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~~base sorbent injection system at the end-use site. With this technique, the halogen/halide is introduced to the ~~carbon-~~base sorbent air (or other gas, including to the flue gas or other mercury containing gas) mixture in a transport line (or ~~other~~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.
- 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 are changed or ~~reducing~~ loads are reduced, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

[~~0077~~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 ~~carbon~~ sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g., bromine) to the ~~carbon~~base sorbent structure.

Sorbent Injection Location

[~~0078~~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~~ carbon~~ sorbent comprise a powdered modified ~~activated carbon~~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 ~~activated carbon~~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

[~~0079~~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 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 co~~-~~pending, commonly owned PCT ~~patent application~~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

[~~0080~~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.

~~*Promoted Carbon Sorbents*~~

~~[0081] 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.~~

~~[0082] 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

[~~0083~~00102] To more clearly illustrate the present invention, ~~several examples are~~an example is presented below. ~~These examples are~~This example is intended to be illustrative, and no limitations to the present invention should be drawn or inferred from the ~~examples~~example presented herein.

Example 1 -~~Preparation and Testing of Halogenated Carbon (& Comparative Example)~~Non-carbon-Promoted Sorbent Tests at Full-Scale Plants

~~*Gas Phase Halogenation*~~

~~[0084] 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 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 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 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 the bromine has completely reacted with the carbon to produce the brominated carbon.~~

~~**[0085]** 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***~~

~~**[0086]** 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.~~

~~**[0087]** 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: 02 (6%), CO_2 (12%), SO_2 (600 ppm), NO (120 ppm) NO_2 (6 ppm), HCl (1 ppm), Hg^o (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 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.~~

~~**[0088]** 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).~~

~~**[0089]** 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***~~

~~**[0090]** 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***~~

~~**[0091]** 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.***~~

~~**[0092]** 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***~~

~~**[0093]** 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***~~

~~**[0094]** 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***~~

~~**[0095]** 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 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***~~

~~**[0096]** 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.~~

~~**[0097]** 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***~~

~~**[0098]** 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 0_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 NOx 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.~~

~~**[0099]** 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 m3/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.~~

~~**[00100]** 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 m3/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***~~

~~**[00101]** 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").~~

~~**[00102]** 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 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*~~

~~**[00103]** 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*~~

~~**[00104]** 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.~~

~~**[00105]** The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 µg/m3) 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 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/Ebulliated Bed Preparation*~~

~~**[00106]** 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 ebulliated 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*~~

~~**[00107]** 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).~~

~~**[00108]** In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 μg/m3. 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 μg/m3 (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*~~

~~**[00109]** 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.~~

~~**[00110]** 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 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 IIB - Addition of Optional Alkaline Component - Pilot-Scale*~~

~~**[00111]** 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.~~

~~**[00112]** 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*~~

~~**[00113]** 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*~~

~~**[00114]** 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*~~

~~**[00115]** A phosphohalogenated sorbent was prepared from PBr_3 using the method described m Example 5, except granular Calgon F400 was used.~~

~~*Testing in Hydrogen Atmosphere - Procedure*~~

~~**[00116]** 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.~~

~~**[00117]** 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***~~

~~**[00118]** 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.~~

~~**[00119]** 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~~

[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 interstitial spaces. Each base sorbent was injected upstream from the ESP.

[00104] The flue gas flow rate for the test was approximately 23 million dsft^3/hr with a corresponding mercury flow rate of 0.0097 lbs Hg/hr. Initial mercury concentration in the flue gas prior to the introduction of the base sorbent or promoted sorbent was approximately 0.000417 lbs Hg/million dsft^3.

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

Table 1

~~Times for 50% Breakthrough~~

~~Maximum Observed Hg Concentrations for~~**. Test Data for Non Carbon-Promoted Sorbents**

~~(10% Hydrogen Streams)~~

~~**Sorbent**~~	~~**Temp (ºC)**~~	~~**50% breakthrough (min)**~~	~~**Maximum [Hg] (µg/m3)**~~	~~**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~~

~~**[00120]**~~

Base Sorbent Material	**Base Sorbent Injection Rate (lb/hr)**			**Promoter Injection Rate (lb/hr)**			**Percent Removal of Mercury (%)**		
	Low	Ave.	High	Low	Ave.	High	Low	Ave.	High
Perlite	100	150	200	0	0	0	37	40	43
	100	150	200	20	25	35	55	72	74
Pumacite	100	150	200	0	0	0	25	25	25

	100	150	200	20	25	50	52	60	65
Clay-Based Mix of Silica and Alumina	100	150	200	0	0	0	50	52	54
	100	150	200	20	25	30	58	65	74

[00106] While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only~~,~~ and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

[~~00121~~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.

[~~00122~~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.

[~~00123~~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.