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(54) **CATALYTIC ADSORBENTS FOR MERCURY  
REMOVAL FROM FLUE GAS AND  
METHODS OF MANUFACTURE THEREFOR**

(76) Inventors: **Chien-Chung Chao**, Williamsville, NY  
(US); **Steve J. Pontonio**, Hamburg, NY  
(US)

Correspondence Address:  
**PRAXAIR, INC.**  
**LAW DEPARTMENT - M1 557**  
**39 OLD RIDGEBURY ROAD**  
**DANBURY, CT 06810-5113 (US)**

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(57) **ABSTRACT**

The present invention provides catalytic adsorbents formed from doping activated carbon with a dispersed halide salt. The catalytic adsorbents provided herein are stable and harmless at room temperature, yet allow for chemical adsorption at elevated temperatures typical of those for flue gas streams. The present invention also provides methods of manufacturing the doped activated carbon adsorbents.

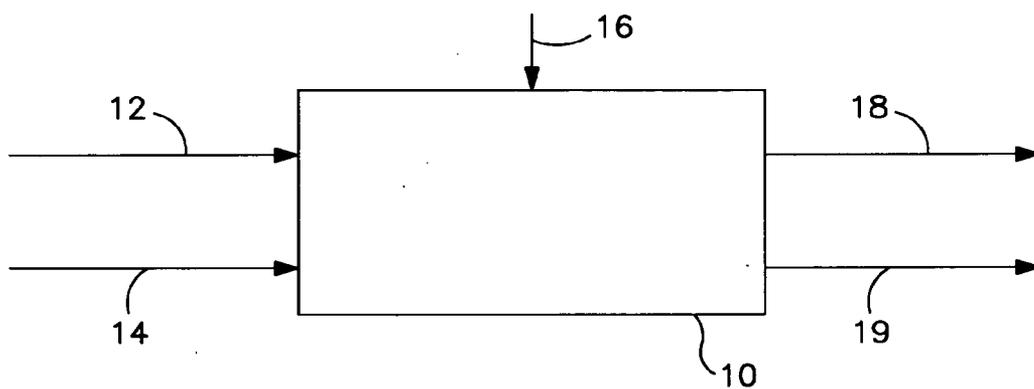


FIG. 1

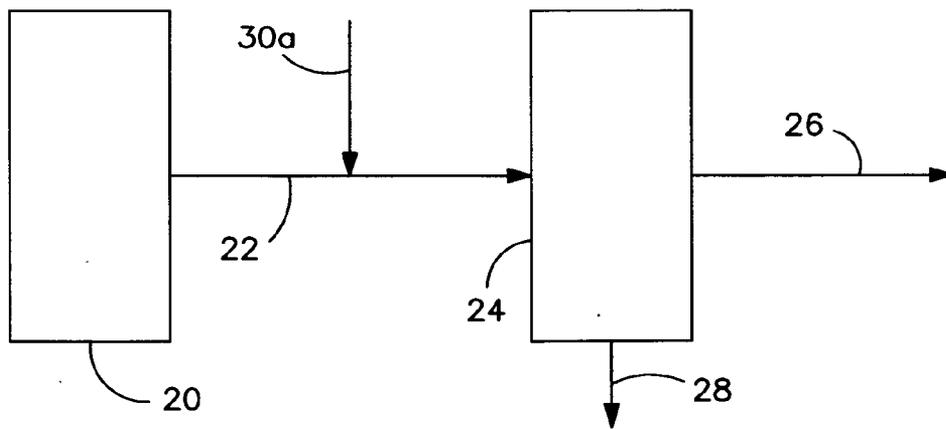
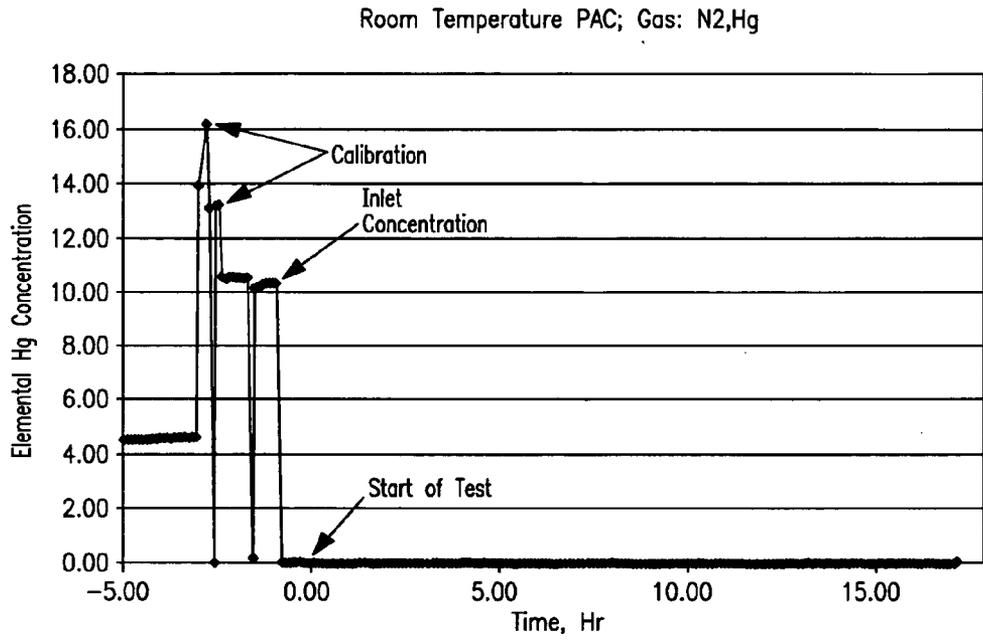
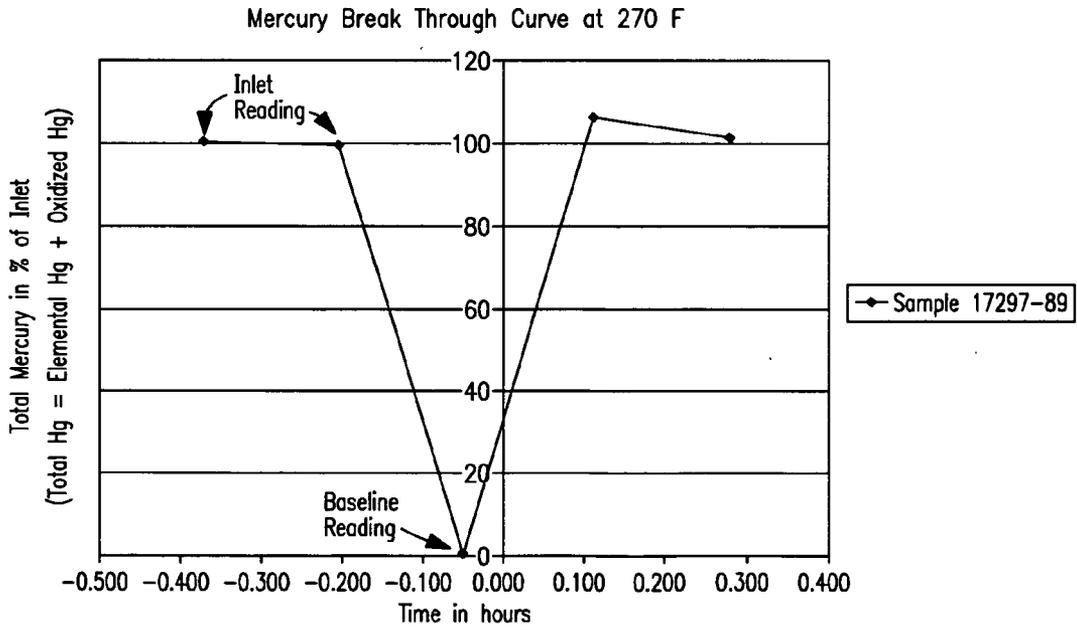


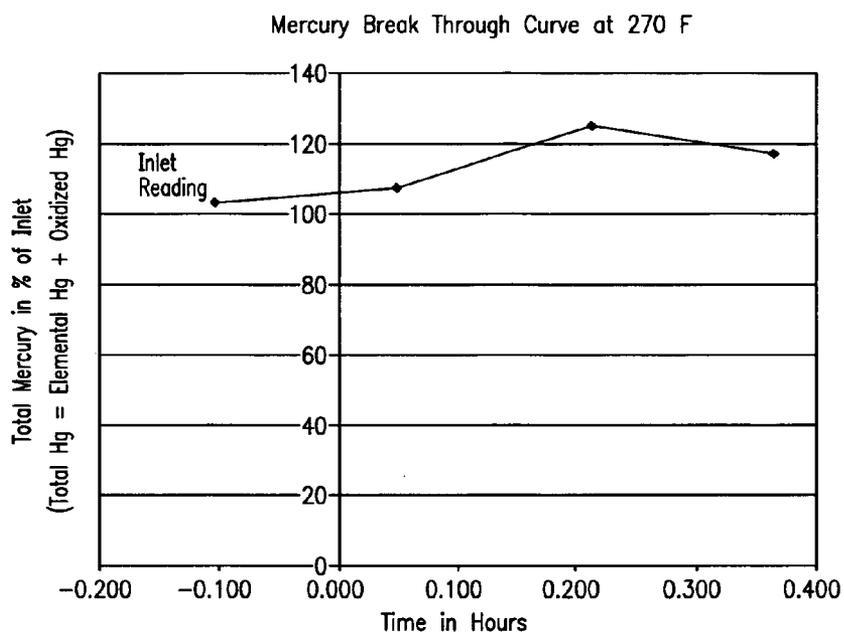
FIG. 2



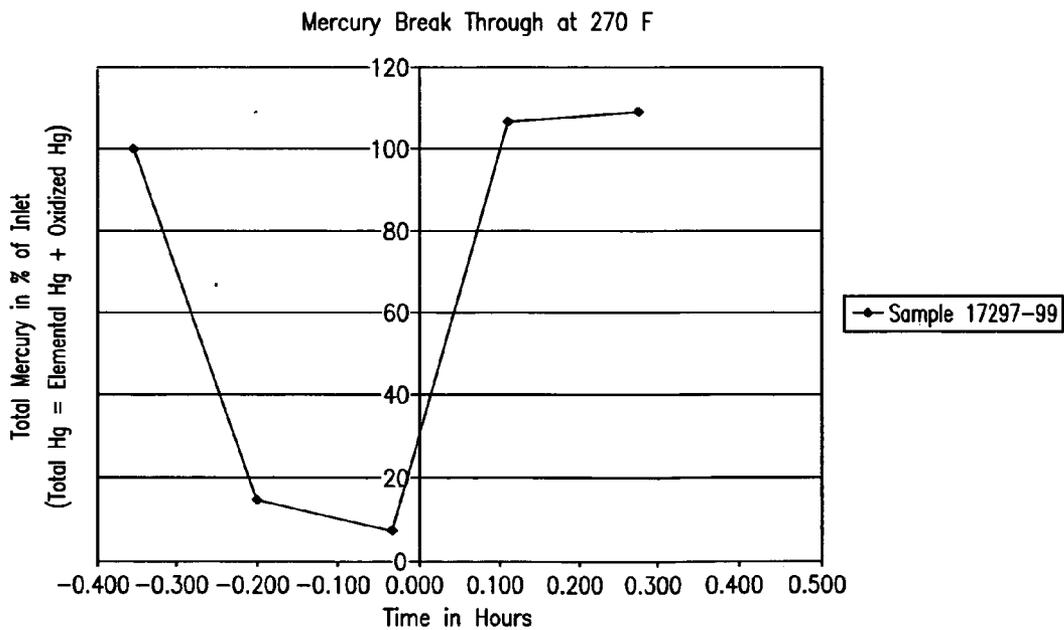
**FIG. 3**



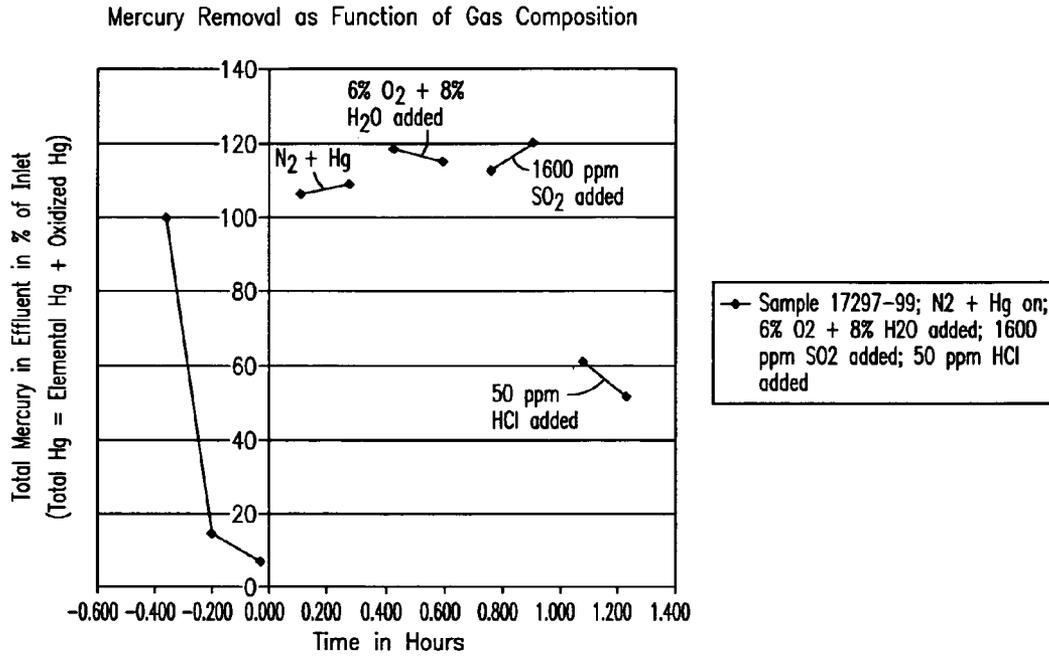
**FIG. 4**



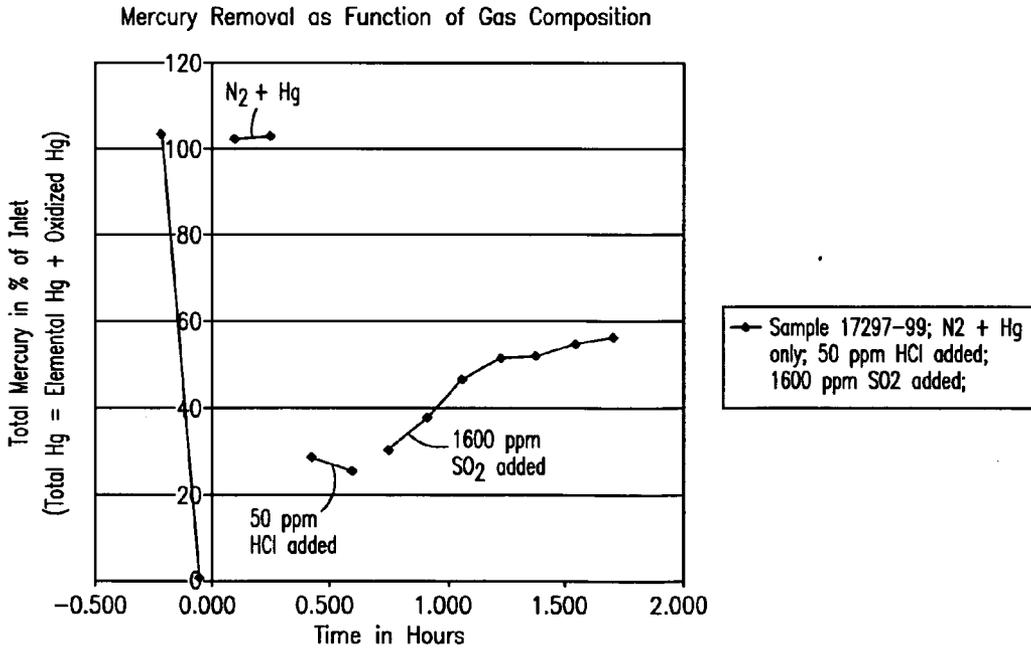
**FIG. 5**



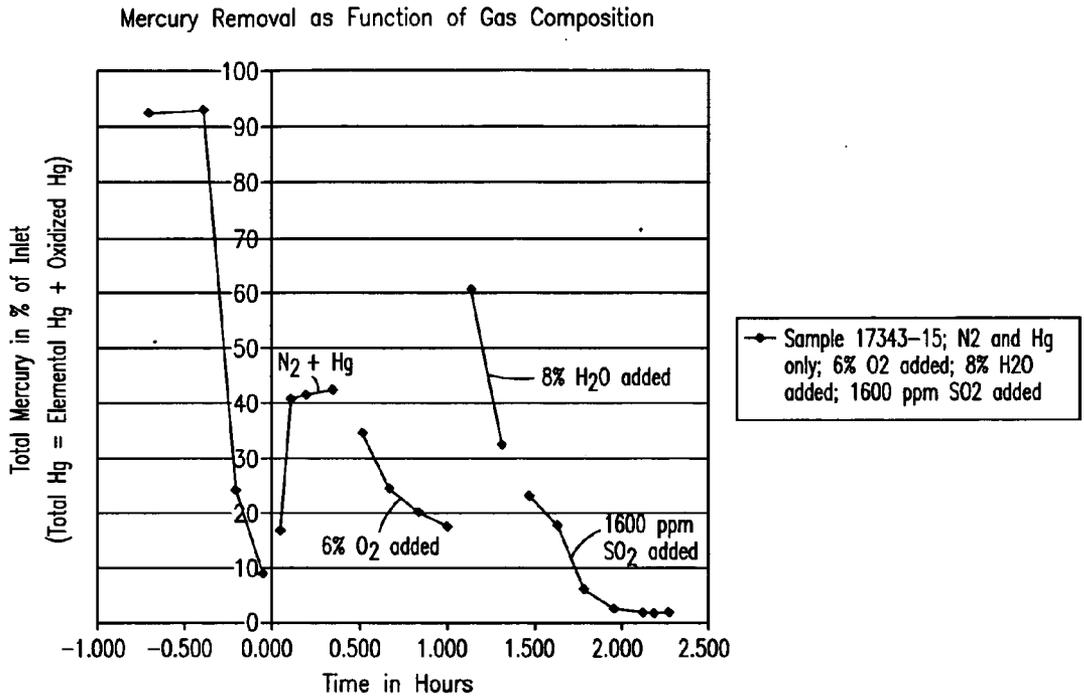
**FIG. 6**



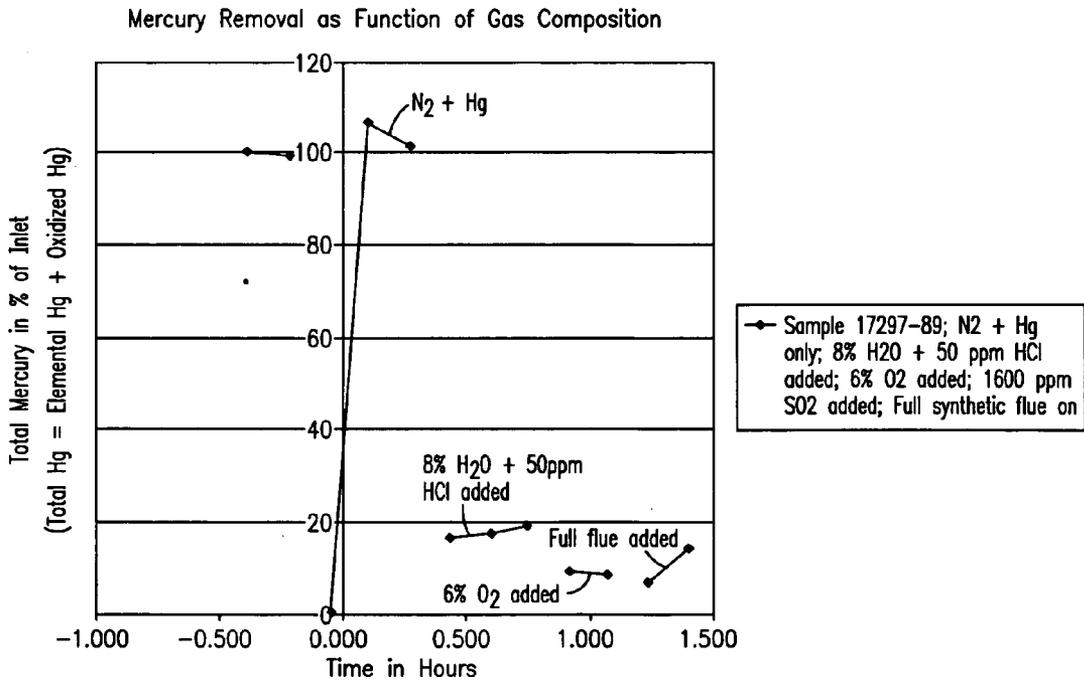
**FIG. 7**



**FIG. 8**



**FIG. 9**



**FIG. 10**

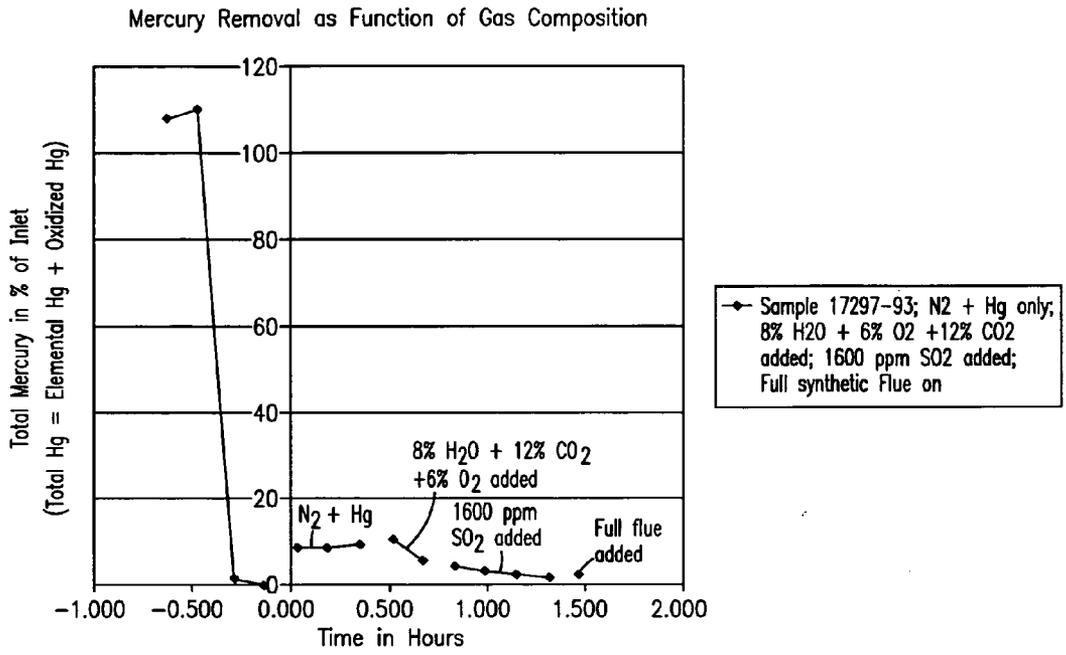


FIG. 11

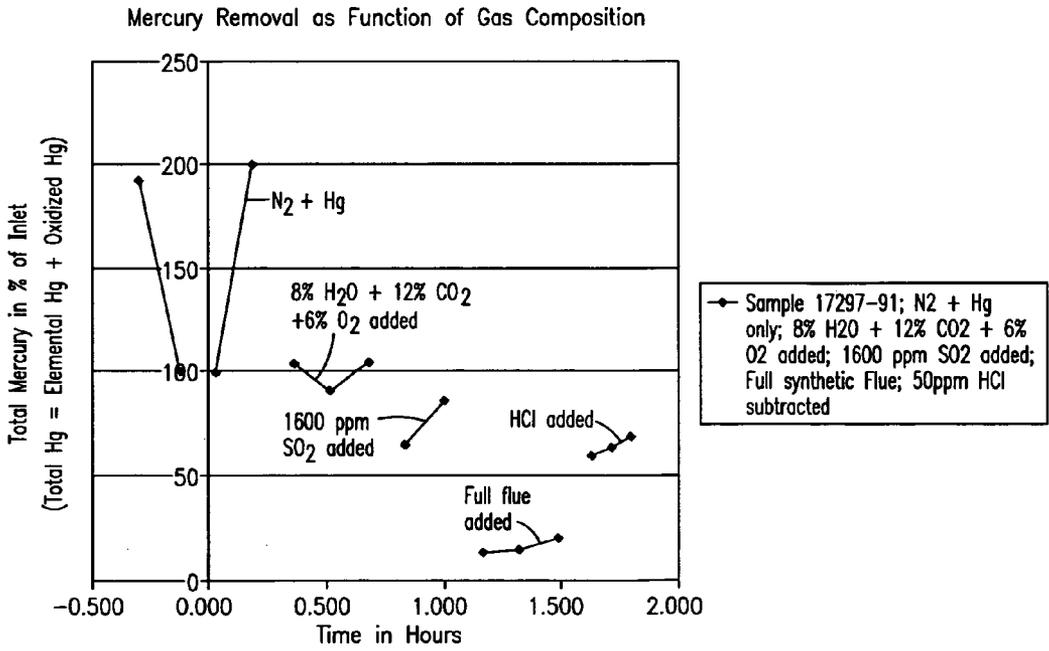
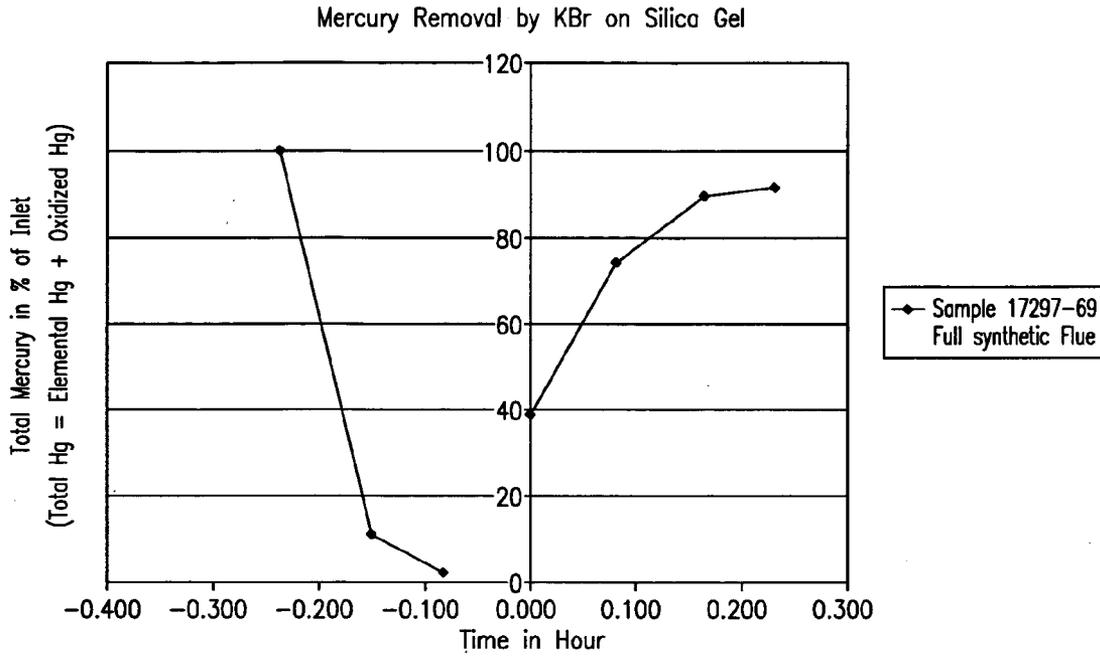
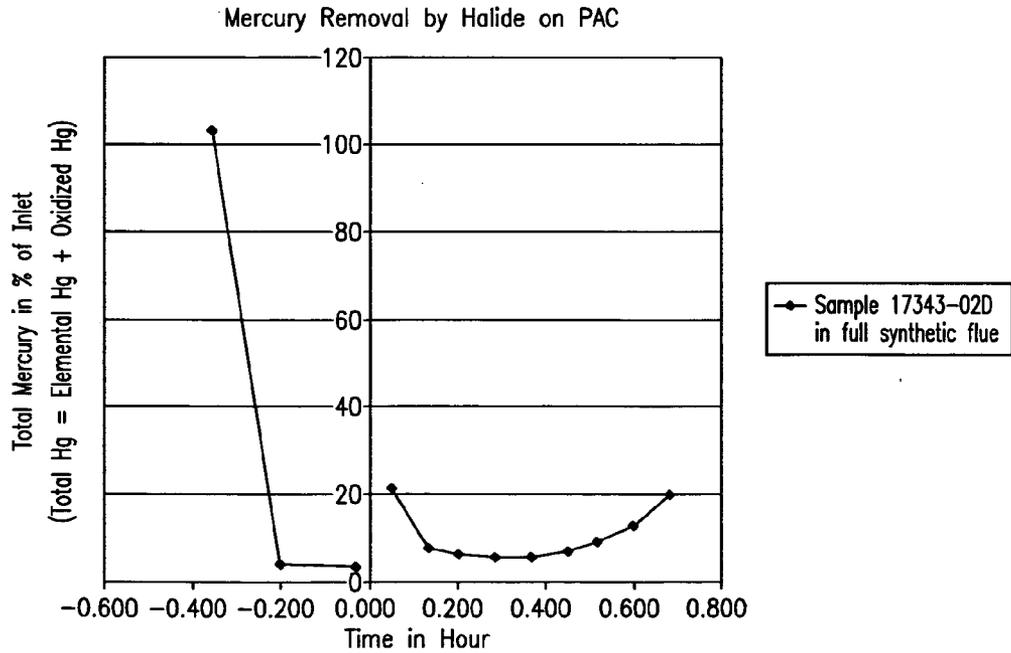


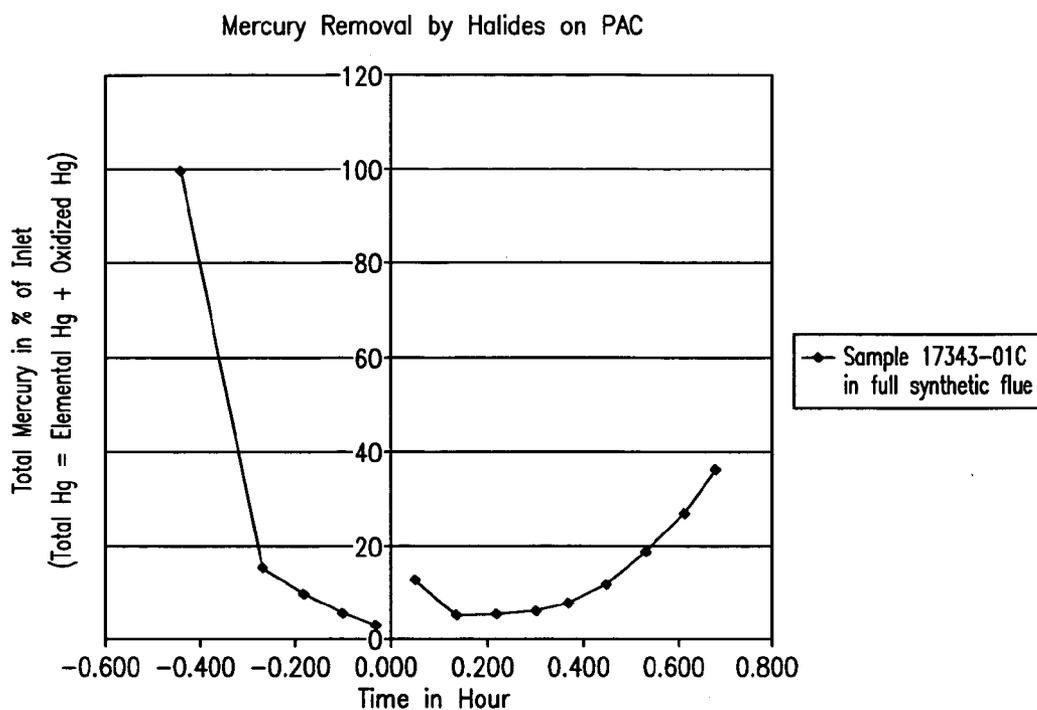
FIG. 12



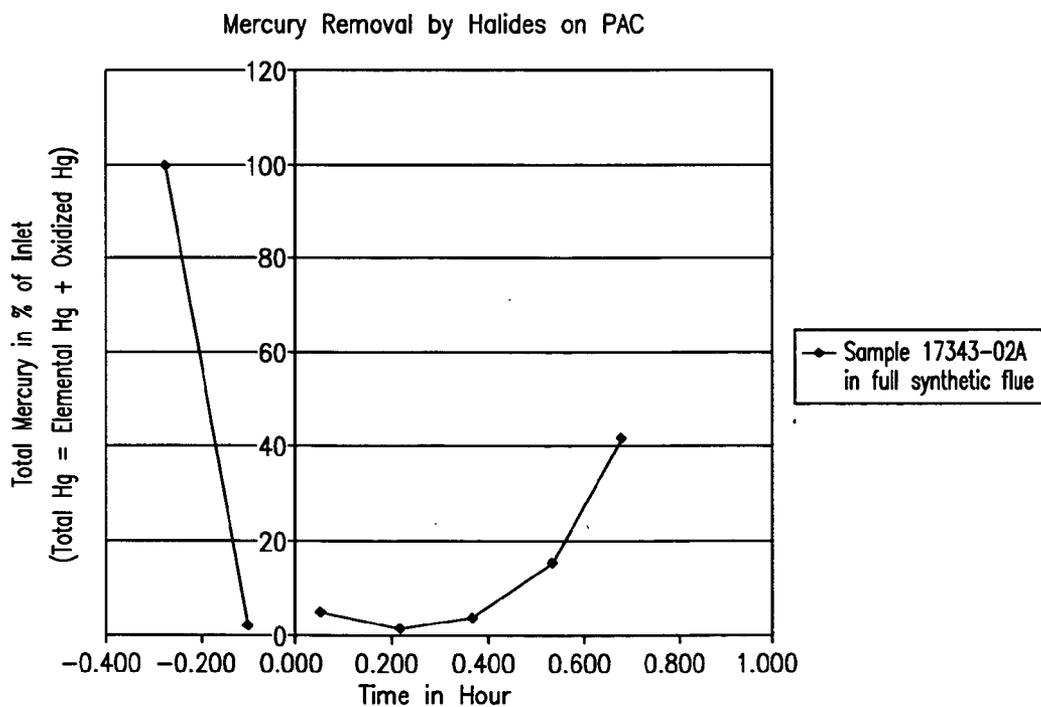
**FIG. 13**



**FIG. 14**



**FIG. 15**



**FIG. 16**

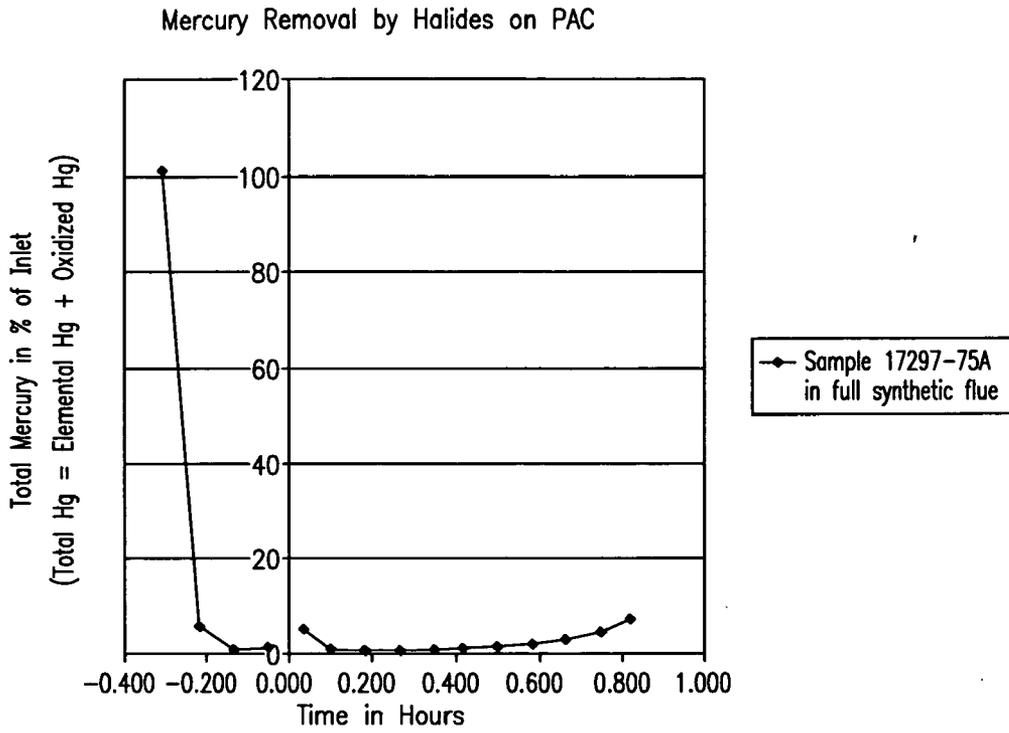


FIG. 17

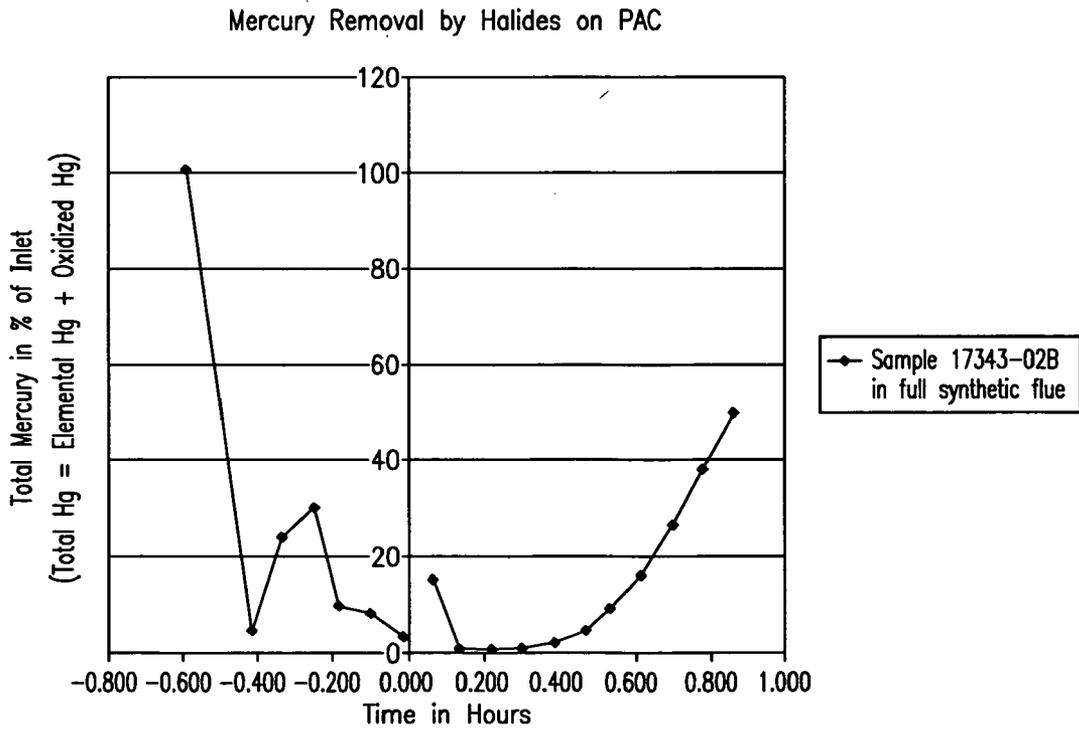
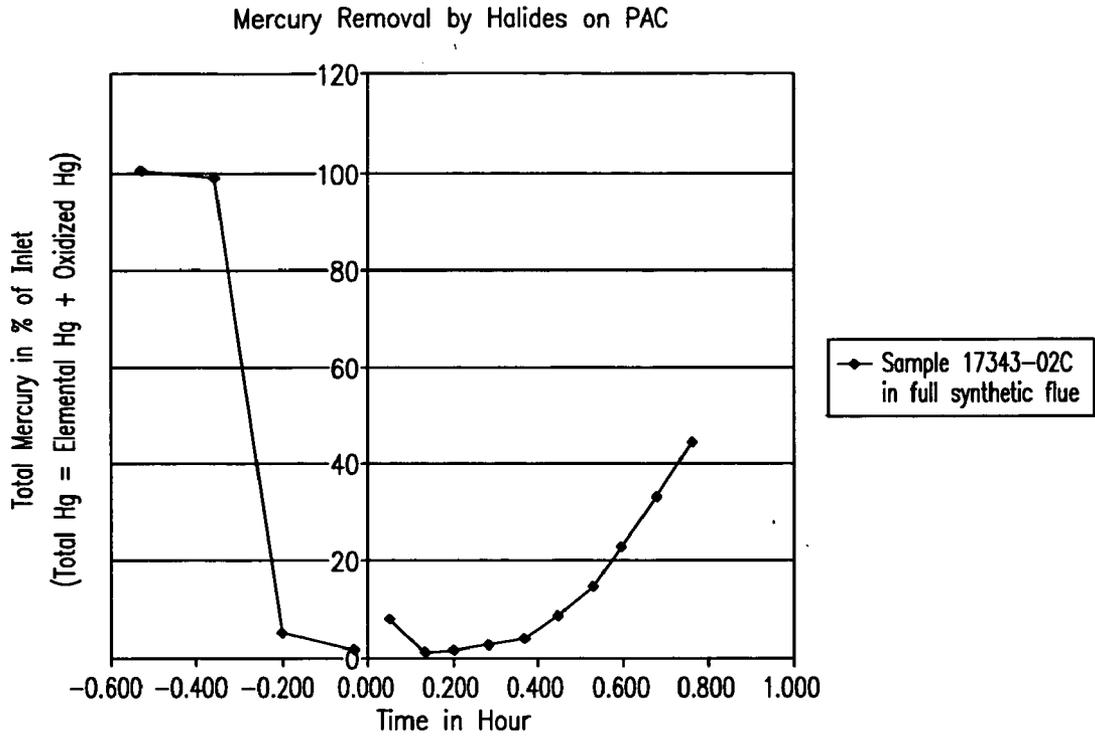
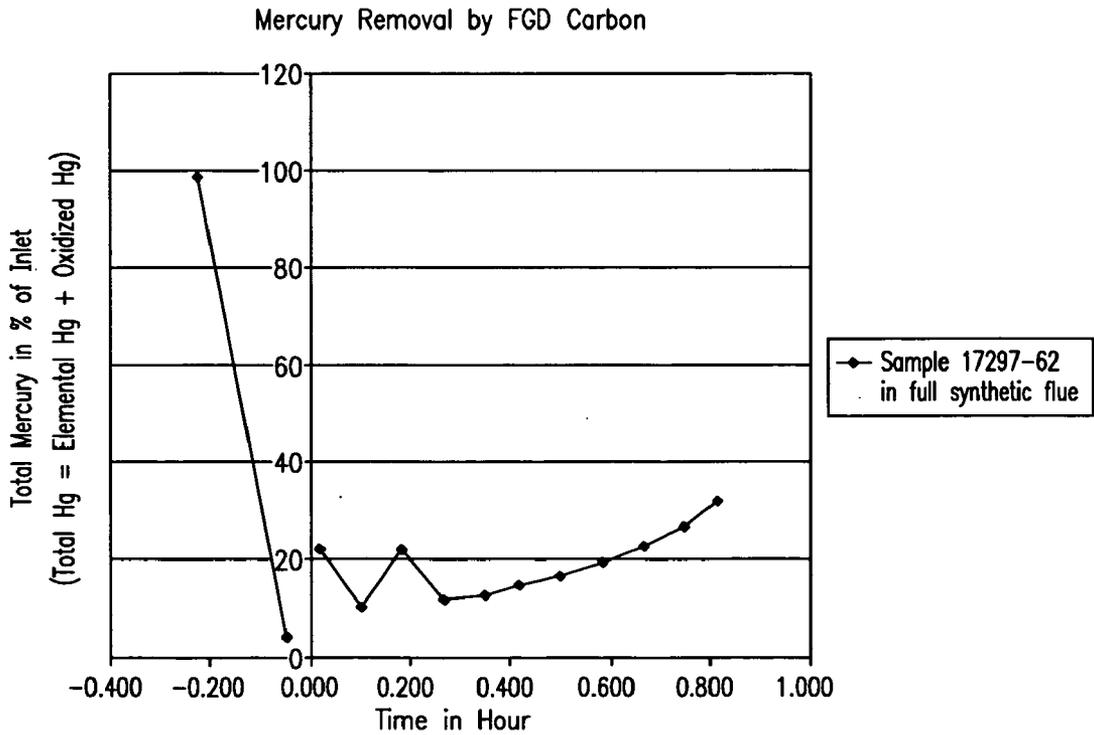


FIG. 18



**FIG. 19**



**FIG. 20**

## CATALYTIC ADSORBENTS FOR MERCURY REMOVAL FROM FLUE GAS AND METHODS OF MANUFACTURE THEREFOR

### TECHNICAL FIELD

[0001] The present invention relates generally to catalytic adsorbents for use in the removal of mercury from flue gas streams and methods of manufacturing such catalytic adsorbents.

### BACKGROUND OF THE INVENTION

[0002] The toxicity of mercury to humans and the environment has long been known. It is known for example that mercury exposure can cause neurological damage in humans. A particularly devastating example of the harmful effects of mercury occurred in Minamata, Japan in the 1950's where organic mercury byproducts of acetaldehyde production were discharged into the local bay. The byproducts were consumed and metabolized by fish. By consuming fish in the bay, wide spread neurological damage and birth defects among the local population were reported.

[0003] Coals used for generating electric power often contain about 0.1 ppm mercury. In the United States alone, about 50 tons of mercury are discharged as vapor in stack gas every year. Through chemical and biological processes, this mercury can become concentrated in fish by many thousand fold, thereby entering human food supplies at harmful levels.

[0004] The effort to remove trace mercury from air, water, natural gas, and other industrial streams has a long history, however; removing mercury from coal burning flue gas streams is a very different problem.

[0005] Prior art techniques for removing mercury from air or hydrocarbons at room temperature generally have limited relevance to removing mercury from flue gas streams. Mercury has a high atomic weight and adsorption temperature is a significant issue. At room temperature, the dispersion interaction with carbon is sufficient to immobilize mercury atoms. At about 300° F. (the temperature of many flue gas streams), however, physical adsorption is no longer able to hold down the volatile elemental mercury.

[0006] In addition, sufficient contact time with rapidly moving flue gas streams is another issue for mercury removal. The total time for flue gas, from generation by combustion to exit through the stack, is often less than 10 seconds. Either as injected powder, where adsorbent fly amid flue gas is for about 2 seconds, or as filter cake on bags in a bag house, the contact time between flue gas and activated carbon captured by the filter is less than one second.

[0007] The demand on reactivity and reaction kinetics by flue gas cleaning can not be properly tested by conventional packed beds. Conventional packed beds are insufficient for flue gas cleaning because the volume of flue gas is so large, the cost for compressing it to push it through a packed bed is prohibitive.

[0008] Further issues relating to the removal of mercury from flue gas include the small, yet potentially toxic, concentration levels of mercury in the flue gas streams. The concentration of mercury in flue gas streams is in  $\mu\text{g}/\text{m}^3$

whereas the concentration of mercury in many other industrial processes is on the order of  $\text{mg}/\text{m}^3$ . Much early work considered effluents containing mercury in the  $5 \mu\text{g}/\text{m}^3$  range (that is not much lower than the initial concentration of mercury in the flue gas) as fully purified.

[0009] Above all, prior art techniques consider the adsorption of mercury as an event between the adsorbent and the mercury. While this is true in air or hydrocarbon streams at room temperature, flue gas contains highly polar and reactive components that can play both an interfering and enabling role for mercury removal. One model composition used for flue gas contains about: 6%  $\text{O}_2$ , 12%  $\text{CO}_2$ , 8%  $\text{H}_2\text{O}$ , 1600 ppm  $\text{SO}_2$ , 400 ppm  $\text{NO}$ , 50 ppm  $\text{HCl}$ , 20 ppm  $\text{NO}_2$ , and  $12 \mu\text{g}/\text{m}^3$  elemental Hg.

[0010] Prior art attempts to remove mercury from flue gas have included various techniques. One approach has focused on adding halogen salts into coal prior to combustion such that the combustion process generates hydrogen halide gases and then injecting powder carbon downstream into the flue gas at a lower temperature. Some mercury is captured by interaction between the hydrogen halide gases, activated carbon and mercury. Another approach has been to add hydrogen halides or elemental halogen together with activated carbon to a lower temperature flue gas.

[0011] U.S. Pat. No. 1,984,164 to Karlsruhe proposes carbon or silica gel or other adsorbents impregnated with elementary halogen for removal of mercury from room air. Other prior art attempts have included adding halide salts to coal before combustion since these salts are known to be very stable. The combustion process oxidizes halides to halogen and further reacts with hydrogen to yield hydrogen halides. For example, U.S. Pat. No. 5,435,980 to Felsing et al. suggest adding chloride or a chlorine containing material into the coal before or during combustion or adding  $\text{HCl}$  into flue gas upstream of or in the drying-absorption zone.

[0012] U.S. Patent Application No. 2004/0003716 A1 to Nelson, Jr. discloses a method for removing mercury and mercury containing compounds from combustion gas by injecting an adsorbent into the flue stream. The sorbent is prepared by treating a carbonaceous substrate with a bromine containing gas. Bromine gas is known to be highly toxic by inhalation, ingestion or skin contact.  $\text{HBr}$  is also known to be corrosive. In addition, bromine and  $\text{HBr}$  compounds are reactive and can easily be added onto alkenes. Further, bromine is reactive with aromatics.

[0013] U.S. Pat. No. 6,533,842 B1 to Maes et al. disclose powder adsorbents which contain about 40% carbon, 40% calcium hydroxide, 10% cupric chloride and 10%  $\text{KI}_3$  impregnated carbon to remove mercury from a high temperature, high moisture gas stream.

[0014] In December 2000, the United States Environmental Protection Agency (EPA) made its regulatory decision that mercury emissions from coal-fired electric generating plants need to be controlled.

[0015] In the field of the mercury removal from flue gas streams, it would therefore be desirable to provide adsorbents having improved adsorbent characteristics in the flue gas temperature range and that can be economically and efficiently manufactured.

### BRIEF SUMMARY OF THE INVENTION

[0016] The present invention provides catalytic adsorbents in which a halide salt is dispersed on activated carbon and

the oxidation catalytic activity of the activated carbon promotes the formation of mercury halide. At the same time, the adsorbent qualities of activated carbon retain the mercury halides thus formed. The present invention recognizes that while the halide salts are stable and harmless at room temperature, these doped activated carbon compounds form mercury halogen compounds at elevated temperatures typical of those found in flue gas streams, and in the presence of reactive components typical of flue gas. These mercury halogen compounds are retained on the surface of the activated carbon. Moreover, the increased adsorbent capacity and faster rate of adsorption result in a need for smaller quantities of adsorbent relative to an undoped activated carbon formed from the same starting material.

[0017] A catalytic adsorbent composition for removal of mercury from a flue gas stream thus includes an activated carbon having a dopant (i.e., a halide salt) dispersed thereon. The cation of the dopant used for the halide salt in accordance with the present invention can be an alkaline, alkaline earth, or transition metal (e.g., Na, Ca, Mg, Cu and K). The anion involved can be bromide or chloride. Particularly preferred dopants include, but are not limited to, NaCl, CaCl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, NaBr, KBr, CaBr<sub>2</sub> and MgBr<sub>2</sub>.

[0018] The halide salt is inert with respect to mercury and the activated carbon at room temperature. At elevated temperatures (e.g., 200-570° F.) and in the presence of typical flue gas compositions, mercury halogen compounds are formed and retained on the activated carbon. While not intending to be bound by any theory, it is believed that any or all of the following or a combination of the following may occur. An oxidant (for example, oxygen from the flue gas or oxidant on the activated carbon) oxidizes the mercury and the anion of the dopant provides a counter ion for the mercury ion as oxidized by the oxidant. Alternatively, the oxidant oxidizes the anion in the salt and the oxidized anion in turn oxidizes the mercury to form a mercury halogen compound on the activated carbon. In addition or in the alternative, acidic gases present in the flue gas react with the dopant salt to yield a hydrogen halide. The hydrogen halide is then oxidized by an oxidant and yields a halogen compound. The halogen compound then reacts with the mercury to form a mercury halogen compound that are then adsorbed by the activated carbon.

[0019] The present invention also provides methods of manufacturing such doped activated carbon adsorbents that are both economical and safe. The catalytic adsorbents of the present invention can be made from a variety of methods. In one embodiment, the catalytic adsorbents can be formed by placing an activated carbon in an aqueous solution containing a halide salt to form a mixture, stirring the mixture until a homogeneous slurry is formed and drying the activated carbon such that water from the aqueous solution evaporates and the halide salt is dispersed on the surface of the activated carbon.

[0020] In another exemplary method of manufacture, the catalytic adsorbents can be made by injecting a presoaked carbonaceous feedstock into a reaction chamber together with oxidizing gases such as air and/or steam. The carbonaceous feedstock and the oxidizing gases are injected into the reaction chamber under conditions and for a residence time sufficient to form a powder activated carbon having a dopant dispersed on the surface of the powder activated

carbon. In this method, the reaction chamber can be a batch type reactor such as a tube furnace or a reactor designed for continuous mode operation (e.g., a fluidized bed reactor). The dopant is formed of a cation selected from the group including an alkaline metal, an alkaline earth metal, and a transition metal (e.g., Na, K, Mg, Ca and Cu) while the anion is selected from bromide and chloride. In some embodiments, the dopant may be selected from the group including: NaCl, KCl, CaCl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, NaBr, KBr, CaBr<sub>2</sub> and MgBr<sub>2</sub>.

[0021] The catalytic adsorbents of the present invention are suitable for use in the removal of mercury from a gas stream containing an oxidant and/or acidic gases at an elevated temperature such as a flue gas stream exiting a boiler or combustion process. In this process, the catalytic adsorbents of the present invention are injected into the flue gas stream for an in-flight mode of mercury capture. As discussed above, the dopant is inert with respect to the mercury at room temperature. At flue gas temperatures and in the presence of the activated carbon, oxidant and/or acidic gases, however, the dopant effectively removes mercury from the flue gas stream. The mercury is retained on the activated carbon in the form of mercury halogen compounds and can be separated from the flue gas stream together with the flyash.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0022] For a more complete understanding of the present invention and the advantages thereof, reference should be made to the following Detailed Description taken in conjunction with the accompanying drawings in which:

[0023] FIG. 1 illustrates one embodiment for manufacturing catalytic adsorbents in accordance with the present invention;

[0024] FIG. 2 illustrates a method of using the catalytic adsorbents in accordance with the present invention;

[0025] FIGS. 3-6 illustrate graphs relating to Example 1;

[0026] FIGS. 7-12 illustrate graphs relating to Example 2;

[0027] FIG. 13 illustrates a graph relating to Example 3; and

[0028] FIGS. 14-20 illustrate graphs relating to Example 4.

[0029] Similar reference characters refer to similar parts throughout the several views of the drawings.

#### DETAILED DESCRIPTION

[0030] The present invention provides catalytic adsorbents suitable for use in the removal of mercury from flue gas streams at elevated temperatures. The catalytic adsorbents of the present invention include compositions having an activated carbon with a dopant dispersed on the activated carbon. The dopant is a halide salt. The cation of the dopant can be an alkaline, alkaline earth, or transition metal while the anion of the dopant can be bromide or chloride. The catalytic adsorbents of the present invention can be formed from a variety of methods.

[0031] The present invention also provides methods of using these compositions for mercury capture at elevated

temperature in the presence of acidic gases and/or oxidative gases that are commonly found in flue gas streams generated by coal burning.

[0032] The mercury capture action is a synergistic combination of components in the adsorbent compositions, the flue gas stream as well as the flue gas stream temperature. Activated carbon doped with bromide salts may be particularly preferred adsorbents as the bromide salts appear to require less assistance from acidic and/or oxidative gases in the flue gas stream and appear to be particularly effective at removing mercury from the flue gas stream.

[0033] As discussed hereinabove, alkaline, alkaline earth and transition metal halides are harmless salts and inert to mercury and activated carbon at room temperature. At about 200°-570° F. (e.g., 270° F.), however, and in the presence of acidic gases and/or oxidative gases of flue gas, these doped activated carbon compositions are capable of capturing mercury with high efficiency. Unused halide salts remain in their salt form.

[0034] The catalytic adsorbents of the present invention also perform well in flue gas streams generated by burning low chloride coal (e.g., Powder River Basin (PRB) coal from Wyoming) where current adsorbents such as FGD carbon do not function efficiently.

[0035] The present invention thus provides for halide salts to be dispersed on activated carbon such that the salts retain their chemical inertness at room temperature, but react with mercury in hot flue gas to yield non volatile mercury halide. More particularly, at temperatures in the range of about 200-570° F., and in the presence of acidic and/or oxidative gas from the flue gas, halide salts react with mercury and assist the activated carbon to capture the mercury, which is present in very low concentrations in flue gas streams. The catalytic adsorbents of the present invention utilize the very fast kinetics at elevated temperatures to optimize both physical adsorption as well as chemical adsorption. The reactivity of the halide salts as used herein is thus a cooperative phenomenon.

[0036] As discussed hereinbelow, the catalytic adsorbents of the present invention can be made from a variety of methods. The adsorbents can be made from commercially available powdered activated carbon (PAC) or from raw carbonaceous material. Exemplary PACs suitable for use in the invention include, but are not limited to, FGD (available from Norit America, Inc.), ashless activated carbon powder made from purified petroleum coke and carbon fiber powder made by carbonization of rayon fiber. It will be appreciated that other activated carbons can also be used in the present invention.

[0037] The catalytic adsorbents of the present invention can be made from various techniques. In one embodiment of the invention, the adsorbents can be manufactured by soaking activated carbon in an aqueous solution of halide salts. This approach is an economical and safe process relative to treating activated carbon with hydrogen halides or halogen gases.

[0038] In this embodiment, the minimum amount of water necessary to make a solution of the salt is utilized. The cation of the dopant can be an alkaline, alkaline earth, or transition metal. The anion involved can be bromide or chloride. Suitable salts for use in the invention therefore

include, but are not limited to, NaCl, CaCl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, NaBr, KBr, CaBr<sub>2</sub> and MgBr<sub>2</sub>. In some embodiments, KBr, NaBr or CaBr<sub>2</sub> may be preferred and in some embodiments, NaBr or KBr may be the most preferred salt.

[0039] The PAC, preferably in powder form, is placed in the aqueous solution and the mixture is stirred until it becomes a homogeneous slurry and such that there is sufficient contact time between the salt solution and PAC that the salt solution becomes dispersed on the PAC. It will be appreciated by those skilled in the art that the PAC has porosity such that the solution and hence the halide salt will disperse into the PAC.

[0040] In this approach, the amount of salt necessary for the aqueous solution is determined based on the amount of PAC and the ratio of the salt to PAC that is desired for a particular adsorbent (i.e., the dopant level in the desired PAC determines the concentration of the salt solution). In some embodiments, the ratio of the dopant level to that of the PAC is 1:10,000 to 30:100. In more preferred embodiments, the ratio of dopant to PAC is 1:1000 to 10:100 and in other embodiments, the ratio of dopant to PAC is 0.5:100 to 7:100.

[0041] The salt solution containing the PAC is allowed to soak and then allowed to sufficiently dry such that the PAC is free flowing. During this time, the water evaporates and the salt enters the pore volume of the PAC and becomes dispersed on the surface of the PAC. After the PAC is dried, it is in powder form. It may be ground and passed through an appropriate size desired mesh. While not to be construed as limiting, the PAC may be passed through a 200 mesh. In this manner, the PAC can be used for mercury removal at less than or equal to a 200 mesh material. It will be appreciated by those skilled in the art that the adsorbent can be treated for appropriate size depending on the intended use of the adsorbent. For example, smaller mesh (e.g., 400 mesh) may be desirable in some applications.

[0042] It is believed that the catalytic adsorbents of the present invention will perform well for mercury removal from flue gas streams at elevated temperatures given the dispersed salts on the surface of the PAC. While not intending to be bound by any theory, it is believed that the salt is inert with respect to elemental mercury at room and high (i.e. in the range of combustion zone) temperatures. At elevated temperatures of about 200-570 F (for example, at about 270-300 F), however, and in the presence of oxidative and/or acidic gases in the flue gas, and the doped activated carbon, mercury in the flue gas stream can be oxidized and effectively removed therefrom.

[0043] An alternative method to soaking a PAC in an aqueous solution as described above is to spray water droplets containing the desired halide salt on the PAC in a manner such that the halide salts become dispersed as discussed above. Such an approach can be used in connection with the activated char produced in commonly owned U.S. patent application Ser. No. \_\_\_\_\_ entitled "Production of Activated Char Using Hot Gas" to Bool et al., filed on even date herewith. The entire contents of U.S. patent application Ser. No. \_\_\_\_\_ are incorporated herein by reference.

[0044] An alternative method for manufacturing catalytic adsorbents suitable for use in the present invention is shown in **FIG. 1**. In this embodiment, the catalytic adsorbents can

be manufactured by presoaking a prepulverized carbonaceous feedstock in an aqueous solution of an alkaline, alkaline earth or transition halide salt. Alternatively, the prepulverized carbonaceous feedstock may be soaked in an alcohol (e.g., ethanol) solution containing the alkaline, alkaline earth or transition halide salt. The presoaked feedstock is then exposed to an oxidizing gas mixture such as air and steam at an elevated temperature in a reaction chamber to produce catalytic adsorbents and an exhaust gas.

[0045] The final concentration of the catalytic adsorbent is determined as in the prior embodiment (i.e. the ratio of the dopant to activated carbon is predetermined in order to determine the concentration of the salt solution), except that in this embodiment, the loss of carbon due to combustion in the reaction chamber must be taken into account. One can therefore determine the concentration based on the yield of the final product to account for the loss of carbon due to combustion.

[0046] As illustrated in **FIG. 1**, carbonaceous feedstock **16** is injected into reaction chamber **10**. In some embodiments, carbonaceous feedstock **16** is not yet activated and can be selected from various types of feedstock such as coal or biomass materials. The feedstock can be prepulverized to an appropriate size, for example from about 5-200 microns.

[0047] The carbonaceous feedstock **16** is also presoaked as discussed above prior to injection into reaction chamber **10** with a solution containing the desired halide salt. In this embodiment, the solution can be formed from water or ethanol, although water may be preferred.

[0048] Oxidizing gases **12** and **14** (e.g., air **12** and steam **14**) are injected into reaction chamber **10** simultaneous with or nearly simultaneous with carbonaceous feedstock **16**. Preferably, the steam is preheated and is injected at a temperature of about 1800 F.

[0049] Reaction chamber **10** may be selected from a variety of reactors such as single batch reactors where the feedstock is suspended on a filter media and reactant gases pass through the feedstock (e.g., a tube furnace) or continuous reactors whereupon the gas temperature, composition and feedstock residence time can be controlled for optimal conditions (e.g., a fluidized bed reactor). One type of a continuous process reactor may be a Plow Mixer, available from Scott Equipment Company.

[0050] Heat for reaction chamber **10** can be provided by from various sources, for example, the reaction chamber can be electrically heated or heated by a flame. Alternatively or in addition to such heat, reaction chamber **10** may be heated from the temperature of the feedstock and/or steam. It will be appreciated by those skilled in the art that the desired temperature within the reaction chamber depends on several factors, including temperature of the air and/or oxidizing gases, amount of oxygen, stoichiometric ratio of oxygen to feedstock and/or temperature of the feedstock. The heat may be provided from any source so long as it is sufficient to generate flue gas **18** and adsorbent **19**. Typically, the temperature within the furnace will be between about 1450-2700° F., and more preferably between about 1650-2200° F. When the stoichiometric ratio of oxygen to feedstock is greater than one, the contact time between the oxidizing gas and the feedstock becomes more significant because more of the feedstock will be consumed and therefore impact prod-

uct yield. When the stoichiometric ratio is less than one, the contact time will be less critical.

[0051] The residence time of the carbonaceous feedstock **16**, reactive oxidizing gases (such as air **12** and steam **14**) within reaction chamber **10** is long enough such that flue gas **18** and adsorbent **19** are generated within chamber **10**. The residence time of the carbon is independent of the gas and can be independently controlled. This can be significant because sufficient time is necessary to devolatilize and partially oxidize the feedstock. While the residence time is short, it is important that it be long enough to adequately activate the carbon. In some embodiments, the residence time may be on the order of minutes. It will be appreciated that if the residence time is too long or there is too much oxygen or steam, adsorbent yield will be negatively impacted.

[0052] Adsorbent **19** is removed from reaction chamber **10** and is ready for use as a mercury removal adsorbent from flue gas streams at elevated temperatures. Flue gas **18** typically includes combustion gases such as CO<sub>2</sub>, CO, N<sub>2</sub> and H<sub>2</sub>O. Any unreacted, partially combusted (e.g., CO) or volatile gases in gas stream **18** can be further combusted.

[0053] Yet another alternative embodiment for manufacturing catalytic adsorbents for use in accordance with the present invention can be found in commonly owned U.S. patent application Ser. No. \_\_\_\_\_, entitled "Production of Activated Char Using Hot Gas" to Bool et al., filed on even date herewith. The entire contents of U.S. patent application Ser. No. \_\_\_\_\_ are incorporated herein by reference.

[0054] In this embodiment, the feedstock is presoaked with an aqueous or ethanol solution as discussed above. The presoaked feedstock is then treated to produce activated char as discussed in commonly owned U.S. patent application Ser. No. \_\_\_\_\_, entitled "Production of Activated Char Using Hot Gas".

[0055] Catalytic adsorbents of the present invention can also be formed by dry mixing a prepulverized raw carbonaceous material with a halide salt powder. In this embodiment, the raw carbonaceous material and halide salt powder are mixed together in dry form. The mixture can then be injected and processed as discussed hereinabove with regard to **FIG. 1** or as shown in commonly owned U.S. patent application Ser. No. \_\_\_\_\_, entitled "Production of Activated Char Using Hot Gas". The temperature within the reaction zone will be at or above the melting point of the halide salt such that the halide salt melts and wets the surface of the carbonaceous material. Consequently, the salt can be dispersed in the carbonaceous material.

[0056] Referring now to **FIG. 2**, an exemplary system for using the catalytic adsorbents of the present invention is shown. Flue gas **22** is formed as a result of combustion in a furnace or boiler **20**. While flue gas **22** can vary in composition and temperature, a typical composition can include: 6% O<sub>2</sub>, 12% CO<sub>2</sub>, 8% H<sub>2</sub>O, 1600 ppm SO<sub>2</sub>, 400 ppm NO, 50 ppm HCl, 20 ppm NO<sub>2</sub>, and 12 µg/m<sup>3</sup> elemental Hg and can be in the temperature range of about 200-570 F. Catalytic adsorbent **30a**, which can be formed from any of the methods described hereinabove, can be injected upstream of particulate collection device (PCD) **24**. Particulate collection device **24** is typically a baghouse or electrostatic precipitators (ESPs). Adsorbent **30a** is injected into flue gas

stream **22** upstream of PCD **24** such that there is sufficient residence time for the catalytic adsorbent to capture and remove mercury from flue gas **22**.

[0057] Particulates and adsorbent containing mercury are removed from PCD **24** by stream **28**. Flue gas **26** thus contains less mercury than flue gas **22** and may be sent to the stack.

[0058] In some embodiments, it may be desirable to inject the catalytic adsorbent into the flue gas downstream of the PCD. Such processes are currently being investigated by others.

[0059] As discussed above, it is believed that the catalytic adsorbents of the present invention will perform well for mercury removal from flue gas streams at elevated temperatures given the dispersed salts on the surface of the PAC.

#### EXAMPLES

[0060] As will be seen hereinbelow, physical adsorption of PAC at about 270° F. is not sufficient to retain elementary mercury without HCl as a promoter. In contrast, doped PAC function well without HCl; however, the presence of HCl, O<sub>2</sub> and/or SO<sub>2</sub> function as promoters for a doped PAC.

[0061] In some examples, doped PAC were prepared by treating three types of commercially available PAC. In other examples, doped PAC was prepared by activation of halide salt treated coal.

[0062] The first commercial PAC used is FGD carbon, available from Norit America, Inc. It is made from lignite coal and contains about 30 weight percent ashes. In powder form, it is widely tested and accepted as a bench mark for activated carbon for mercury removal from flue gas. The second PAC was ashless activated carbon available from Carbon Resource, Inc. It is typically made from purified petroleum pitch and contains a trace amount of ash. It is generally sold in bead form. For mercury removal in the following examples, it was ground, sieved and the -400 mesh portion was used. The third PAC that was used was activated carbon fiber ACF-1300/200, also available from Carbon Resources, Inc. It is made from rayon and typically received in cloth form. This material was ground and screened through 400 mesh sieve before use.

[0063] To prepare halide salt doped PAC from coal, coal was soaked in an aqueous or ethanol halide salt solution. The doped coals were activated in a stream of oxygen, nitrogen and steam in temperature range of about 1800° F.

[0064] Two tests were used to evaluate the adsorbents: a fixed bed test and a residence chamber test. In the fixed bed test, the fixed bed consisted of 150 mg adsorbent supported on a quartz filter of about 63.5 mm in diameter. The details of the test setup are described in papers published by EERC, as published for example at the Mercury Control Technology R&D Program Review Meeting on Aug. 12-13, 2003 at Pittsburgh, Pa. Gas streams containing mercury as well as components of flue gas were passed through the thin bed. The break through of mercury was monitored and spent adsorption beds were collected and analyzed.

[0065] In the residence time chamber test, a slip stream from a power plant at Pleasant Prairie, Wis. was made to pass through chambers of different length. Adsorbent was injected at one end of the chamber to flight with the flue gas stream. At the other end of the chamber, the adsorbent was separated from the flue gas stream and the cleaned flue gas was analyzed for Hg content to determine the efficiency of the adsorbent. The chamber length was used to determine the contact time between the flue gas and the adsorbent. Details of the residence time chamber apparatus (designed by the Electric Power Research Institute (EPRI)) can be found in published papers (see e.g., "Assessment of Low Cost Novel Sorbents for Coal Fired Power Plant Mercury Control", Combined Power Plant Air Pollutant Control Mega Symposium (Washington, D.C., Aug. 30-Sep. 2, 2004).

#### Example 1

[0066] This example demonstrates that at room temperature, undoped PAC is a good adsorbent for elemental mercury and a promoter would appear to provide no additional benefit. At 270° F., however, physical adsorption is overwhelmed by kinetic energy and adsorption by undoped PAC and without a promoter was inadequate.

[0067] Fixed bed tests were conducted on four samples in a stream which contained nitrogen and about 13 µg/m<sup>3</sup> of elemental mercury. The tests conditions and results are summarized in Table 1 and FIGS. 3-6. The undoped FGD carbon sample was tested at room temperature and achieved 100% mercury removal for more than 15 hours with no sign of mercury breakthrough. For samples tested at 270° F., all three types of activated carbon reached almost 100% breakthrough immediately (0% removal).

TABLE 1

Sample #	Sample Name	Sample treatment	Test Temp	Test gases composition and sequence	Comments on Test Results
	FGD carbon	As received	72 F.	N <sub>2</sub> + Hg	100% Hg removal for 15 hrs; no any sign of breakthrough
17297-89	FGD carbon	Vacuum activated at 1100 F.	270 F.	N <sub>2</sub> + Hg	Breakthrough occurred immediately
17343-13	Carbon fiber	6 N HCl extraction and heating at 1800 F. in N <sub>2</sub>	270 F.	N <sub>2</sub> + Hg	Breakthrough occurred immediately.

TABLE 1-continued

Sample #	Sample Name	Sample treatment	Test Temp	Test gases composition and sequence	Comments on Test Results
17297-99	Ashless carbon	6 N HCl extraction and heating at 1800 F. in N <sub>2</sub>	270 F.	N <sub>2</sub> + Hg	Breakthrough occurred immediately

[0068] 6 N HCl extraction was used in Sample Numbers 17343-13 and 17297-99 to remove any trace ashes. Heating in N<sub>2</sub> at 1800° F. is intended to remove oxidizing species on the commercially obtained PAC. Neither treatment changed the adsorption behavior of the PAC.

#### Example 2

[0069] This example demonstrates how halide salts as a dopant alter the flue gas, mercury and carbon interaction so as to promote mercury adsorption from the flue gas stream. In this Example, thin fixed beds of PAC samples were exposed to different gas mixtures in sequence. All experi-

ments started with nitrogen and mercury (about 13μ gm/cubic meter). Other components of the flue were added into the stream sequentially or in sequential combination toward a composition of synthetic flue gas, which is typified as: 6% O<sub>2</sub>, 12% CO<sub>2</sub>, 8% H<sub>2</sub>O, 1600 ppm SO<sub>2</sub>, 400 ppm NO, 20 ppm NO<sub>2</sub>, 50 ppm HCl, 12-14 μg/m<sup>3</sup> Hg, with the balance being N<sub>2</sub>.

[0070] Two type of PAC (ashless and FGD) and three dopants (KBr, NaBr, and NaCl) were used in the experiments. Detail of the experiments are summarized in Table 2. The breakthrough curves are given in FIGS. 7-12.

TABLE 2

Sample #	Sample Name	Sample Description	Test gases composition and sequence	Comments on Test Results
17297-99	Ashless carbon	6 N HCl extraction and heating at 1800 F in N <sub>2</sub>	1. N <sub>2</sub> + Hg; 2. 6% O <sub>2</sub> + 8% H <sub>2</sub> O added; 3. 1600 ppm SO <sub>2</sub> added; 4. 50 ppm HCl added	Removed Hg only after HCl was added to the test gas
17297-99	Ashless carbon	6 N HCl extraction and heating at 1800 F in N <sub>2</sub>	1. N <sub>2</sub> +; Hg; 2. 50 ppm HCl added; 3. 1600 ppm SO <sub>2</sub> added	HCl promoted Hg adsorption, SO <sub>2</sub> caused decline of Hg removal
17343-15	KBr doped Ashless carbon	15:100 ratio of KBr:Carbon	1. N <sub>2</sub> + Hg; 2. 6% O <sub>2</sub> added; 3. 8% H <sub>2</sub> O added; 4. 1600 ppm SO <sub>2</sub> added	Adsorbed Hg in N <sub>2</sub> stream. Both O <sub>2</sub> and SO <sub>2</sub> promoted Hg removal
17297-89	FGD carbon	Vacuum activated at 1100° F.	1. N <sub>2</sub> + Hg; 2. 8% H <sub>2</sub> O + 50 ppm HCl added; 3. 6% O <sub>2</sub> added; 4. Full Flue added	Removed Hg only after HCl was added to the test gas
17297-93	NaBr doped FGD	15:100 ratio of NaBr:Carbon	1. N <sub>2</sub> + Hg; 2. 8% H <sub>2</sub> O + 12% CO <sub>2</sub> + 6% O <sub>2</sub> added; 3. 1600 ppm SO <sub>2</sub> added; 4. Full Flue added	Adsorbed Hg in N <sub>2</sub> stream. Both O <sub>2</sub> and SO <sub>2</sub> promoted Hg removal
17297-91	NaCl doped FGD	15:100 ratio of NaCl:Carbon	1. N <sub>2</sub> + Hg; 2. +8% H <sub>2</sub> O + 12% CO <sub>2</sub> + 6% O <sub>2</sub> added; 3. 1600 ppm SO <sub>2</sub> added; 4. Full Flue added; 5. —HCl added	CO <sub>2</sub> and SO <sub>2</sub> were weak promoters. The presence of HCl was important for Hg removal

Example 3

[0071] This example demonstrates that a physical adsorbent such as silica gel, doped with KBr, did not remove mercury from the flue gas.

[0072] The same thin fixed bed method as in Examples 1 and 2 was used in this Example. The details of sample preparation, test conditions and results are given in Table 3 and FIG. 13.

TABLE 3

Sample #	Sample Name	Sample Description	Test gases composition and sequence	Comments on Test Results
17297-69	KBr doped silica gel	The weight ratio of KBr:Silica = 15:100	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 micro gram +	The concentration of Hg reduction was less than 10%.

TABLE 3-continued

Sample #	Sample Name	Sample Description	Test gases composition and sequence	Comments on Test Results
			N <sub>2</sub> (full synthetic flue)	

Example 4

[0073] This example analyzed the effectiveness of various halide salts as dopants. Doped ashless carbons were tested by thin fixed bed methods as in Examples 1-3 in synthetic flue. The results are compared with undoped FGD.

[0074] The thin fixed bed test is to simulate the function of a bag house in a power plant. The efficiency of adsorbent is analyzed by the percent of mercury removal from the flue gas. All doped samples reached higher mercury removal than undoped FGD carbon. The results are given below in Table 4 below. The breakthrough curves are shown in FIGS. 14-20.

TABLE 4

Sample #	Sample Name	Sample Description	Test gases composition and sequence	Comments on Test Results
17343-02D	KCl doped ashless carbon	15:100 ratio of KCl:Carbon	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue)	Best removal at about 95% level
17343-01C	NaCl doped ashless carbon	15:100 ratio of NaCl:Carbon	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue)	Best removal at about 93% level
17343-02A	NaBr doped ashless carbon	15:100 ratio of NaBr:Carbon	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue)	Best removal at about 98% level
17297-75A	KBr:Carbon = 15:100	15:100 ratio of KBr:Carbon	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue)	Best removal at about 100% level
17343-02B	CaBr <sub>2</sub> doped ashless carbon	15:100 ratio of CaBr <sub>2</sub> :Carbon	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue)	Best removal at about 100% level
17343-02C	MgBr <sub>2</sub> doped ashless carbon	15:100 ratio of MgBr <sub>2</sub> :Carbon	1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO	Best removal at about 95% level

TABLE 4-continued

Sample #	Sample Name	Sample Description	Test gases composition and sequence	Comments on Test Results
17297-62	FGD carbon	From Norit Amercia, a reference	400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue) 1. O <sub>2</sub> 6% + CO <sub>2</sub> 12% + H <sub>2</sub> O 8% + SO <sub>2</sub> 1600 ppm + NO 400 ppm + HCl 50 ppm + NO <sub>2</sub> 20 ppm + Hg 14 µg/m <sup>3</sup> + N <sub>2</sub> (full flue)	Best removal at about 90% level

## Example 5

[0075] This example used a residence time chamber test to demonstrate the effectiveness of bromide salt doped PAC in an “in flight adsorption” and the quality of PAC made by direct activation of bromide salt doped coal.

[0076] Residence time chamber test. The residence time chamber used in this Example was an EPRI 8-inch diameter tube setup as discussed above. A slip stream of 30 acfm flue was taken out from a coal burning boiler duct for flow through this tube. Adsorbent is injected at one end of the tube. At each of the middle section and exit end of this tube, there are one outlet sampling tubes to allow measurement at two different residence times. The mercury concentrations were measured at the inlet as well as the sampling outlets to determine the mercury removal efficiency of the adsorbents.

[0077] The residence time chamber simulates the situation of a plant which has only an electrostatic precipitator (ESP), therefore mercury removal depends on inflight adsorption. Typical inflight time is about 2 seconds. In the example, the

sampling outlets allow about 2 and 4 seconds of residence time. Three groups of adsorbents were tested. The first group of samples were prepared by doping FGD PAC with an aqueous bromide salt solution. The second group of samples were prepared by activation of halide salt doped coal in a tube furnace at 1650° F. to 2000° F. in a stream containing, oxygen, nitrogen and water. The third group of samples were prepared by activation of halide salt doped coal by a burner as in commonly owned U.S. patent application Ser. No. \_\_\_\_\_, entitled “Production of Activated Char Using Hot Gas” to Bool et al., filed on even date herewith, with or without further steam activation at 1800° F.

[0078] Undoped FGD carbon samples were also tested to serve as a reference. The test results are given in Table 5. The percentage of Hg removal is calculated by dividing outlet mercury concentration with the inlet mercury concentration. Since there is no way to determine how much mercury is removed by the cylinder wall, the reported number is the sum of inflight removal plus removal by wall effect.

TABLE 5

Sample #	Sample Name	Sample Description	Injection rate lb/mmacf	Temp (° F.)	Inlet Hg µg/Nm <sup>3</sup>	Outlet Hg ¼ sec	% Hg Removal (2 sec)	% Hg Removal (4 sec)
17297-22	FGD/KBr	FGD carbon doped with 7:100 ratio of KBr:FGD	5.8	300	9	1.75/0.9	81	90
17297-23	FGD/KBr/CuBr <sub>2</sub>	FGD carbon with 6:1:100 ratio of KBr:CuBr <sub>2</sub> :FGD	5.7	300	8.7	1.3/0.7	85	92
	FGD	No doping	6	300	6.4	3.3/2.8	48	56
17343-76	Activated PRB coal predoped with CaBr <sub>2</sub>	7:100 ratio of CaBr <sub>2</sub> :Coal. Activated in tube furnace	6	300	10.3	3.0/2.0	71	80
17343-77	Activated PRB coal predoped	7:100 ratio of NaBr:coal.	6	300	9.5	2.1/1.5	78	84

TABLE 5-continued

Sample #	Sample Name	Sample Description	Injection rate lb/mm <sup>2</sup> ac <sup>2</sup>	Temp (° F.)	Inlet Hg µg/Nm <sup>3</sup>	Outlet Hg ¾ sec	% Hg Removal (2 sec)	% Hg Removal (4 sec)
17343-83B	with NaBr Activated PRB coal predoped with CaBr <sub>2</sub>	Activated in tube furnace 5:100 ratio of (CaBr <sub>2</sub> :½H <sub>2</sub> O):coal. Activated In tube furnace	6	300	9.9	2.8/1.8	72	82
78B	Activated PRB coal predoped with KBr	7:100 ratio of KBr:coal. Activated in burner	6	300	9.8	3.5/2.2	64	78
42A-15-1000	Activated PRB coal predoped with KBr	7:100 ratio of KBr:coal. Activated in burner, then steamed at 1800 F. (15 min)	6	300	9	1.7/1.2	81	87

## Example 6

[0079] The chemical form of dopant in PAC. Activation of bromide salt doped coal is at a temperature close to 1800° F. This raises the question whether the bromide salt retains its ionic form. Chemical analyses of bromide salt doped coal

before and after activation are shown in Table 6. Bromide salt maintains its inert ionic form. This may be particularly advantageous because bromination of carbon can create unknown and undesirable organic bromide compounds. It is therefore desirable to avoid the formation of such compounds.

TABLE 6

Sample #	Sample Name	Sample Description	Ionic bromine mmol/gm	Total bromine mmol/gm	Na mmol/gm
17343-85A	NaBr doped PRB coal	NaBr:PRB coal = 5:100 Before activation	0.43	0.48	0.17
17343-85B	17343-85A after activation	tube furnace at 1800 F, purged with 10% O <sub>2</sub> , 90% N <sub>2</sub> saturated with water vapor at 194 F.	0.65	0.70	0.26
17343-88A	NaBr doped PRB coal	NaBr:PRB coal = 1:100 before activation	0.09	0.08	0.03
17343-88B	17343-88A after activation	tube furnace at 1800 F, purged with 10% O <sub>2</sub> , 90% N <sub>2</sub> saturated with water vapor at 194 F.	0.11	0.12	0.05

[0080] It should be appreciated by those skilled in the art that the specific embodiments disclosed above 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.

What is claimed is:

1. A catalytic adsorbent composition for removing mercury from a flue gas stream at elevated temperatures, comprising:

an activated carbon having a halide salt dispersed thereon, the halide salt having a cation and an anion.

2. The composition of claim 1, wherein the cation is selected from the group comprising: an alkaline metal, an alkaline earth metal, and a transition metal.

3. The composition of claim 2, wherein the cation is selected from the group consisting of: Na, Mg, Ca, Cu and K.

4. The composition of claim 1, wherein the anion is selected from the group comprising: bromide and chloride.

5. The composition of claim 1, wherein the halide salt is selected from the group consisting of: NaCl, KCl, CaCl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, NaBr, KBr, CaBr<sub>2</sub>, MgBr<sub>2</sub> and mixtures thereof.

6. The composition of claim 5, wherein the halide salt is NaBr, KBr or mixtures thereof.

7. A method of making a catalytic adsorbent for use in the adsorption of mercury from flue gas streams at elevated temperatures, comprising:

placing a powder activated carbon in an aqueous solution containing a halide salt having a cation and an anion to form a mixture;

stirring the mixture until a homogeneous slurry is formed;

drying the powder activated carbon such that water from the aqueous solution evaporates and the halide salt is dispersed on the surface of the powder activated carbon.

8. The method of claim 7, wherein the cation is selected from the group comprising: an alkaline metal, an alkaline earth metal, and a transition metal.

9. The method of claim 8, wherein the cation is selected from the group consisting of: Na, Mg, Ca, Cu and K.

10. The method of claim 7, wherein the anion is selected from the group comprising: bromide and chloride.

11. The method of claim 7, wherein the halide salt is selected from the group consisting of: NaCl, CaCl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, NaBr, KBr, CaBr<sub>2</sub>, MgBr<sub>2</sub> and mixtures thereof.

12. The method of claim 11, wherein the halide salt is NaBr, KBr or mixtures thereof.

13. A method of making catalytic adsorbent for use in the adsorption of mercury from flue gas streams at elevated temperatures, comprising:

injecting a presoaked carbonaceous feedstock into a reaction chamber; and

injecting at least one oxidizing gas into the reaction chamber;

injecting steam into the reaction chamber,

wherein the carbonaceous feedstock, the air and the steam are injected into the reaction chamber under conditions and for a residence time sufficient to form an activated carbon having a halide salt having a cation and an anion dispersed on the surface of the activated carbon.

14. The method of claim 13, wherein the oxidizing gas comprises: air, oxygen, steam, nitrogen or combinations thereof.

15. The method of claim 13, wherein the reaction chamber is a tube furnace.

16. The method of claim 13, wherein the reaction chamber is a fluidized bed reactor.

17. The method of claim 13, wherein the cation is selected from the group comprising: an alkaline metal, an alkaline earth metal, and a transition metal.

18. The method of claim 17, wherein the cation is selected from the group consisting of: Na, Ca, Cu and K.

19. The method of claim 13, wherein the anion is selected from the group comprising: bromide and chloride.

20. The method of claim 13, wherein the halide salt is selected from the group consisting of: NaCl, KCl, CaCl<sub>2</sub>, CuCl<sub>2</sub>, CuBr<sub>2</sub>, NaBr, KBr, CaBr<sub>2</sub>, MgBr<sub>2</sub> or mixtures thereof.

21. The method of claim 19, wherein the halide salt is NaBr, KBr or mixtures thereof.

22. A method for removing mercury from a gas stream at an elevated temperature, the method comprising:

injecting a catalytic adsorbent containing an activated carbon and a dopant, the dopant having a cation and an anion into the gas stream;

adsorbing mercury onto the catalytic adsorbent; and

removing the mercury containing catalytic adsorbent from the gas stream.

23. The method of claim 22, wherein the gas stream contains oxidative gas, acidic gas or a combination thereof.

24. The method of claim 22, wherein the gas stream contains an inert gas.

25. The method of claim 24, wherein the inert gas comprises nitrogen.

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