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

[00101] For clarity, single injection points 114, 116, and 119 are shown in FIG. 3A, although one of ordinary skill in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device(s) 204 is connected to transport line 113 or 115 (or 118, not shown) to provide signals representative of the optical density inside transport line 113, 115, or 118 as a function of time.

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

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

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

[00104] An optional continuous emission monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35 to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 207, 208, and 209 are electrically connected via optional lines 227 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and can control the preparation and injection of promoted carbon sorbent into polluted flue gas stream 15.

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

PAC ET AL. EXHIBIT 1019
Page 1580

stream 42 and/or 35 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then can adjust flow controllers 201, 202, 203, 207, 208, 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 207, 208, 209 can also be adjusted manually or by some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1582

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

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

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

[00113] In some embodiments, the secondary component(s) can include iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some embodiments, the promoted carbon sorbent can include from about 1 g to about 30 g halogen/halide per 100 g carbon nanocomposite sorbent. In some embodiments, the promoted carbon sorbent can include a secondary component in concentration of from about 1 wt% to about 15 wt% of the concentration of the halogen/halide component.

PAC ET AL. EXHIBIT 1019
Page 1583

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

Examples

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

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

Example 1.1. NanoG-CM

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

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

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

[00119] Yield of nanocomposite was 217 g.

PAC ET AL. EXHIBIT 1019
Page 1584

Example 1.2. NanoG-CB.

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

Example 1.3. Impregnation of Promotion Agent

Example 1.3.1. Ammonium bromide.

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

Example 1.3.2. Hydrogen bromide.

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

Example 1.3.3. Bromine.

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

Example 1.3.4. Sulfur.

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

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

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

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

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

Example 2.1. NanoG-ACSB.

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

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

[00129] Yield of nanocomposite was 10.2 g.

Example 2.2. NanoG-2ACSB

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

Example 2.3. NanoG-2ACSM.

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

PAC ET AL. EXHIBIT 1019
Page 1586

Example 2.4. NanoG-2ACSB-Washed.

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

Example 2.5. Impregnation of Promotion Agent.

Example 2.5.1. Ammonium bromide.

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

Example 2.5.2. Bromine.

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1587

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1588

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

Example 4. Pilot-Scale Evaluation.

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1589

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1590

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

Additional Embodiments.

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

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

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

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

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

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

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

halide promoter; promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent; contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition; and separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas.

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1592

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[00181] Embodiment 34 provides the method of any one of Embodiments 6-33, further comprising injecting the carbon nanocomposite sorbent at an injection rate and injecting separately at least one promoter at an injection rate into a gas stream whereby in-flight reaction produces the promoted sorbent, wherein the promoter is selected from the group consisting of molecular

halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per about 100 grams of carbon nanocomposite sorbent material.

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1595

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1596

CLAIMS

We claim:

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

providing or obtaining a carbon nanocomposite sorbent;

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

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

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

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

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

providing a promoter; and

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

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

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

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

providing or obtaining a carbon nanocomposite sorbent material;

providing or obtaining a halogen or halide promoter;

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

PAC ET AL. EXHIBIT 1019
Page 1597

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

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

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

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

providing or obtaining a carbon precursor;

providing or obtaining a substrate material;

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1599

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1600

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

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

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

34. The method of any one of claims 6-33, further comprising injecting the carbon nanocomposite sorbent at an injection rate and injecting separately at least one promoter at an injection rate into a gas stream whereby in-flight reaction produces the promoted sorbent, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per about 100 grams of carbon nanocomposite sorbent material.

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

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

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

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

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

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

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

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

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

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

providing or obtaining a carbon precursor;

providing or obtaining a substrate material;

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

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

providing or obtaining a halogen or halide promoter;

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

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

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

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

providing or obtaining a carbon precursor;

providing or obtaining a substrate material;

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

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

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

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

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

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

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

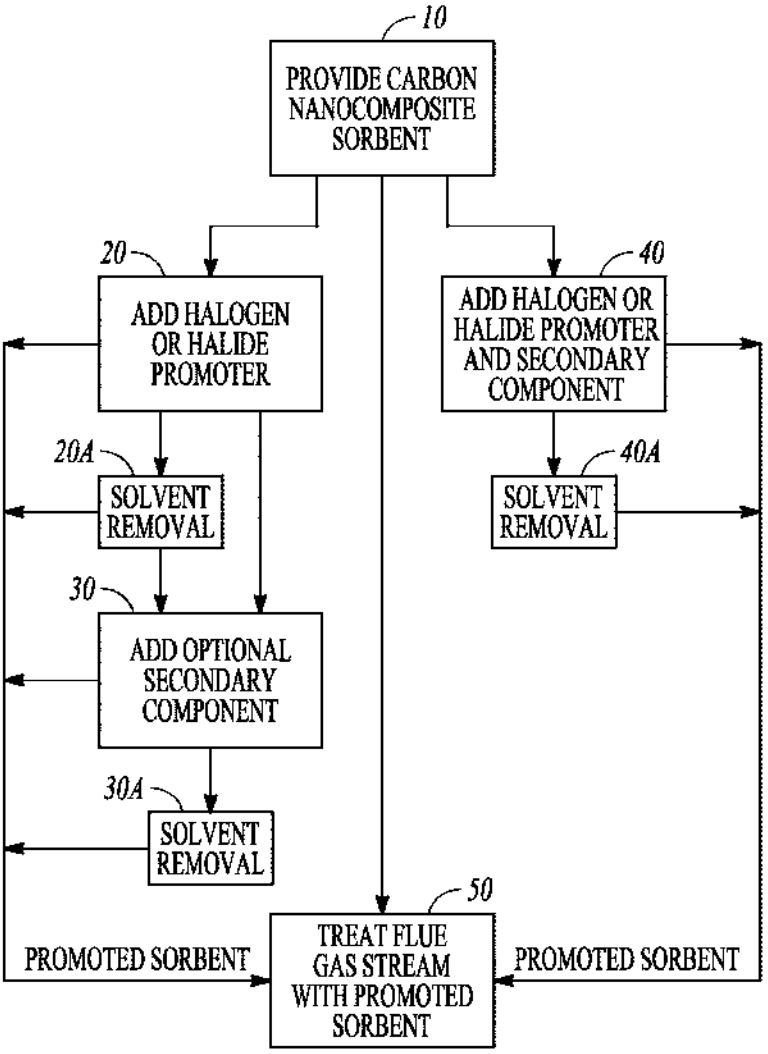

10
PROVIDE CARBON NANOCOMPOSITE SORBENT
20
ADD HALOGEN OR HALIDE PROMOTER
40
ADD HALOGEN OR HALIDE PROMOTER AND SECONDARY COMPONENT
20A
SOLVENT REMOVAL
40A
SOLVENT REMOVAL
30
ADD OPTIONAL SECONDARY COMPONENT
30A
SOLVENT REMOVAL
50
TREAT FLUE GAS STREAM WITH PROMOTED SORBENT
PROMOTED SORBENT
PROMOTED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

FIG. 1

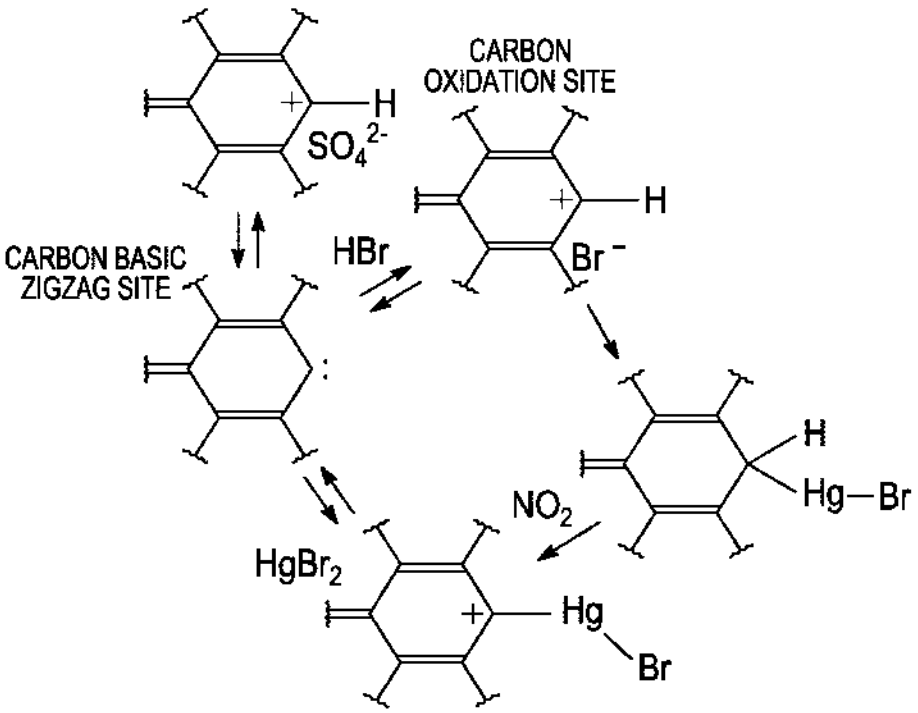

CARBON
OXIDATION SITE
H
SO_4^{2-}
H
HBr
Br^-
CARBON BASIC
ZIGZAG SITE
:
H
Hg—Br
NO_2
$HgBr_2$
Hg
Br

FIG. 2

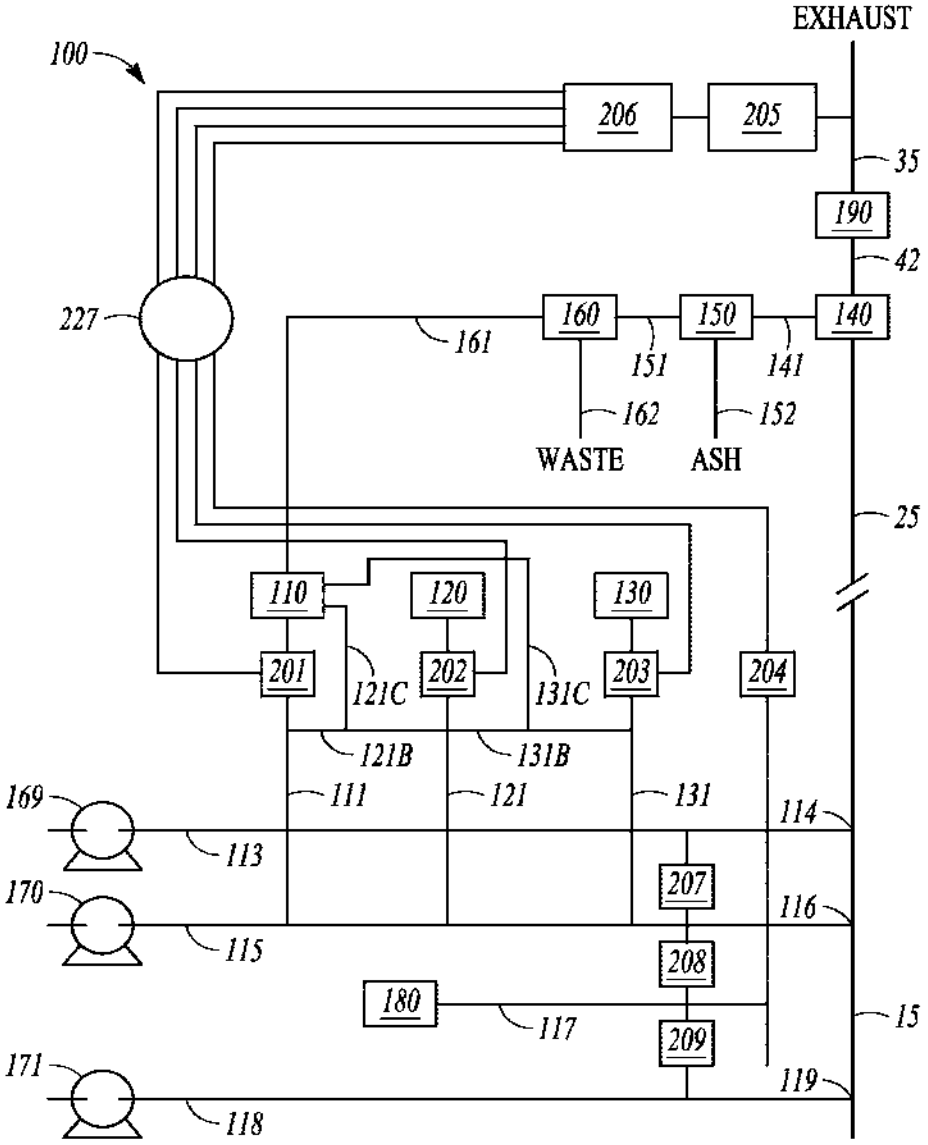

EXHAUST
100
206
205
35
190
42
227
160
150
140
161
151
141
162
152
WASTE
ASH
25
110
120
130
201
121C
202
131C
203
204
121B
131B
111
121
131
169
114
113
207
170
116
115
208
180
117
209
15
171
119
118

FIG. 3A

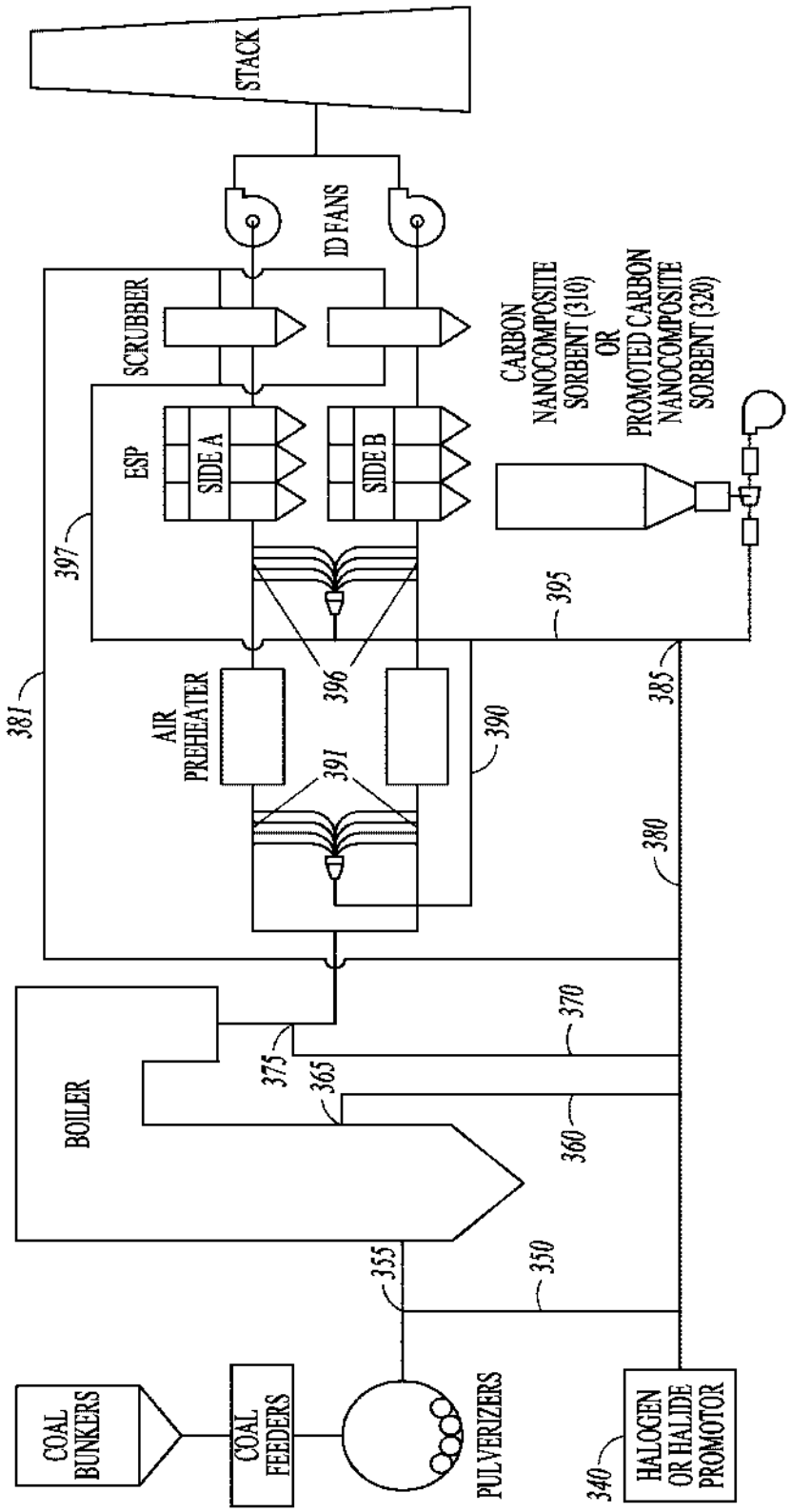

STACK
ID FANS
SCRUBBER
ESP
SIDE A
SIDE B
CARBON NANOCOMPOSITE SORBENT (310) OR PROMOTED CARBON NANOCOMPOSITE SORBENT (320)
397
395
381
396
385
AIR PREHEATER
391
390
380
370
BOILER
375
365
360
355
350
COAL BUNKERS
COAL FEEDERS
PULVERIZERS
340
HALOGEN OR HALIDE PROMOTOR

FIG. 3B

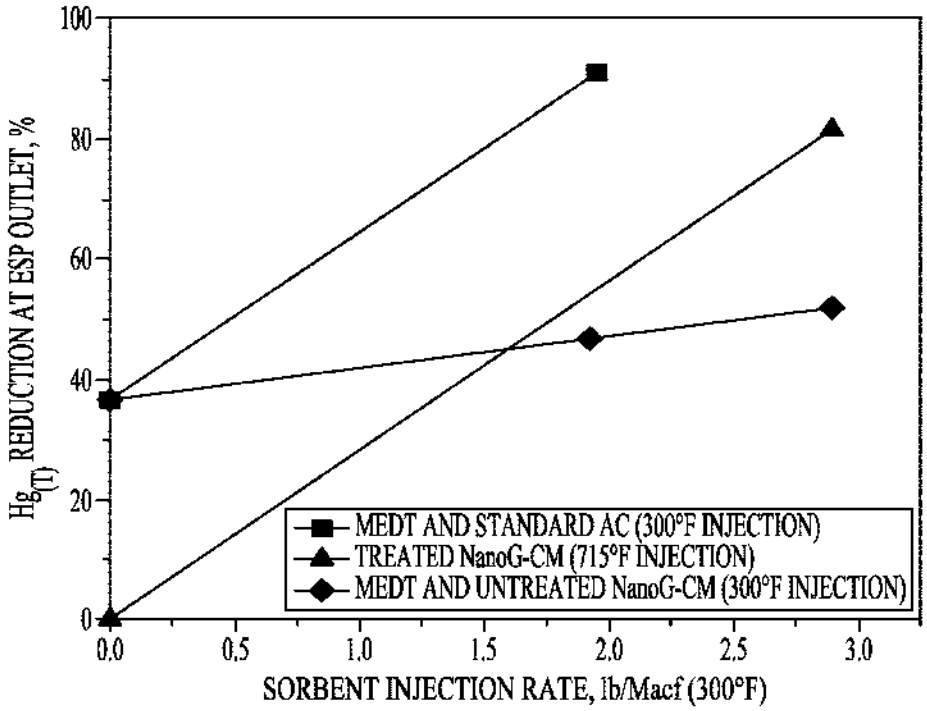

100
80
60
40
20
0
$Hg_{(T)}$ REDUCTION AT ESP OUTLET, %
0.0
0.5
1.0
1.5
2.0
2.5
3.0
SORBENT INJECTION RATE, lb/Macf (300°F)
MEDT AND STANDARD AC (300°F INJECTION)
TREATED NanoG-CM (715°F INJECTION)
MEDT AND UNTREATED NanoG-CM (300°F INJECTION)

FIG. 4

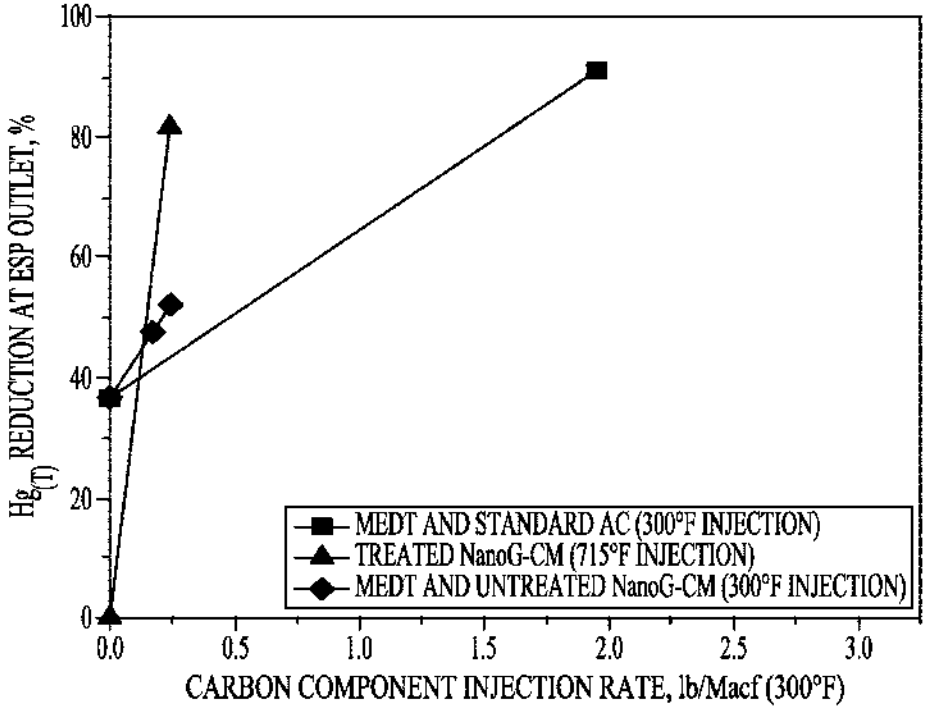

100
80
60
40
20
0
$Hg_{(T)}$ REDUCTION AT ESP OUTLET, %
0.0
0.5
1.0
1.5
2.0
2.5
3.0
CARBON COMPONENT INJECTION RATE, lb/Macf (300°F)
MEDT AND STANDARD AC (300°F INJECTION)
TREATED NanoG-CM (715°F INJECTION)
MEDT AND UNTREATED NanoG-CM (300°F INJECTION)

FIG. 5

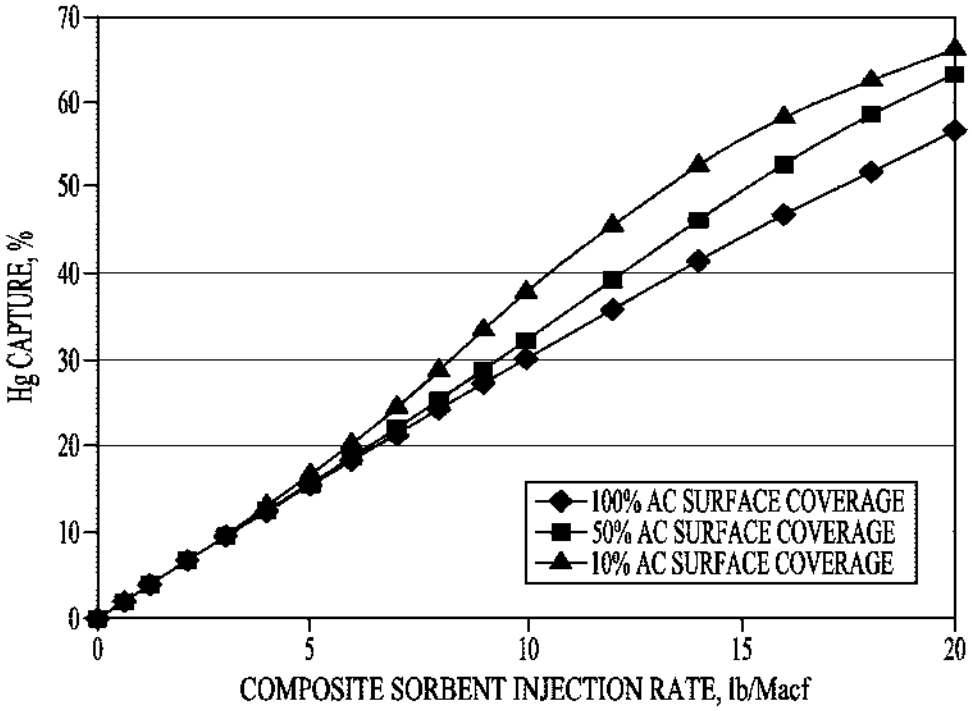

70
60
50
40
30
20
10
0
Hg CAPTURE, %
0
5
10
15
20
COMPOSITE SORBENT INJECTION RATE, lb/Macf
100% AC SURFACE COVERAGE
50% AC SURFACE COVERAGE
10% AC SURFACE COVERAGE

FIG. 6

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 October 2013 (31.10.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/162968 A3

(51) International Patent Classification:
B01J 20/12 (2006.01) *B01J 20/32* (2006.01)
B01D 53/02 (2006.01) *B01D 53/64* (2006.01)
B01J 20/30 (2006.01) *B01J 20/20* (2006.01)

(21) International Application Number:
PCT/US2013/036964

(22) International Filing Date:
17 April 2013 (17.04.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13/453,274 23 April 2012 (23.04.2012) US

(71) Applicant: **ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION** [US/US]; 15 North 23rd Street, Stop 9017, Grand Forks, North Dakota 58202 (US).

(72) Inventors: **OLSON, Edwin, S.**; 223 Circle Hills Drive, Grand Forks, North Dakota 58201 (US). **PAVLISH, John, Henry**; 42204 210th Street SW, East Grand Forks, Minnesota 56721 (US).

(74) Agents: **MADDEN, Robert, B.** et al.; Schwegman, Lundberg & Woessner, P.A., P.O. Box 2938, Minneapolis, Minnesota 55402 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,

[Continued on next page]

(54) Title: CARBON NANOCOMPOSITE SORBENT AND METHODS OF USING THE SAME FOR SEPARATION OF ONE OR MORE MATERIALS FROM A GAS STREAM

(57) Abstract: The present invention relates to carbon nanocomposite sorbents. The present invention provides carbon nanocomposite sorbents, methods for making the same, and methods for separation of a pollutant from a gas that includes that pollutant. Various embodiments provide a method for reducing the mercury content of a mercury-containing gas.

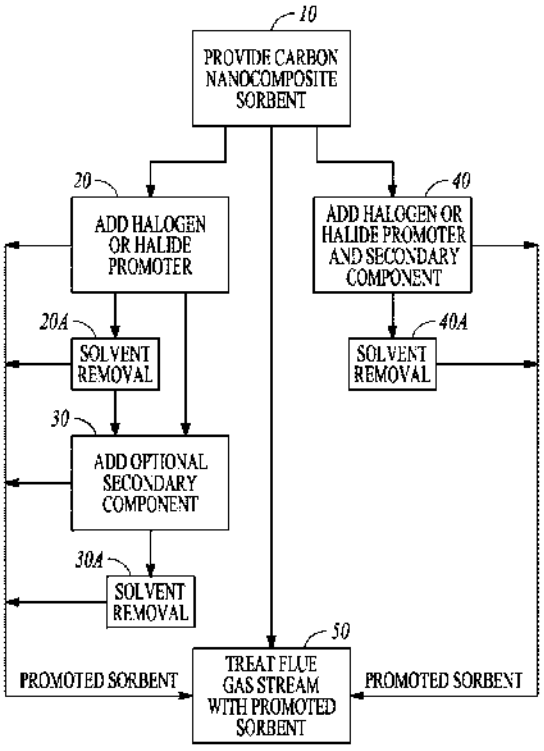


FIG. 1

WO 2013/162968 A3

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

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(88) **Date of publication of the international search report**:
27 February 2014

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/036964

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/12 B01D53/02 B01J20/30 B01J20/32 B01D53/64
B01J20/20
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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

-/--

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

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

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

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

4

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

PACETAL EXHIBIT 1019
Page 1612

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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

4

PACE PAL. EXHIBIT 1019
Page 1613

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/036964

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

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

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

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

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

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

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

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

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

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

1-5, 44, 45, 48

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

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

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

---

2. claims: 6-42, 46, 49

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

---

3. claims: 43, 47

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

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

contacting a carbon nanocomposite sorbent with a mercury-containing gas

---

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/036964

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

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 September 2014 (12.09.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/137907 A2

(51) International Patent Classification:
B01J 20/20 (2006.01)

(21) International Application Number:
PCT/US2014/019916

(22) International Filing Date:
3 March 2014 (03.03.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/773,549 6 March 2013 (06.03.2013) US

(71) Applicant: **ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION** [US/US]; 15 North 23rd Street, Stop 9017, Grand Forks, North Dakota 58202 (US).

(72) Inventors: **OLSON, Edwin S.**; 223 Circle Hills Drive, Grand Forks, North Dakota 58201 (US). **PAVLISH, John Henry**; 42204 210th Street SW, East Grand Forks, Minnesota 56721 (US).

(74) Agents: **MADDEN, Robert B.** et al.; Schwegman, Lundberg & Woessner, P.A., P.O. Box 2938, Minneapolis, Minnesota 55402 (US).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

WO 2014/137907 A2

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

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

ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

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

BACKGROUND OF THE INVENTION

[0002] Mercury (Hg) emissions have become a health and environmental concern because of their toxicity and ability to bioaccumulate. The U.S. Environmental Protection Agency (EPA) has issued regulations for the control of mercury emissions from waste-to-energy, cement production, and coal-fired power plants. Mercury in flue gas from industrial sources (e.g., power plants) can be captured by sorbents such as activated carbon, which can then be removed by particulate separation devices. The amount of standard sorbents (e.g., activated carbon) needed to serve the market is large. Standard sorbents are not always effective and become more expensive as larger amounts are used.

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

SUMMARY OF THE INVENTION

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1621

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1622

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

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

[0013] In some embodiments, counter to traditional teachings that inorganic components can hinder sorption of pollutants on activated carbon, an inorganic matrix support in the sorbent can enhance the sorption of pollutant in the activated carbon, such as on a proximate and oxidatively reactive carbon graphene layer. In various embodiments, an inorganic matrix support can stabilize the development of cationic sites on the proximate graphene carbon structures which can oxidize pollutants such as mercury. In embodiments that include an inorganic matrix-supported nanocomposite that is promoted via a hydrogen halide compound obtained from degradation or reaction of the corresponding ammonium halide, another advantageous role for the inorganic portion can be in providing a binding site for the ammonia that is released from either the decomposition or reaction of the ammonium salt. The bound ammonia can form a complex with basic character that can react with SO_2 or SO_3 in the pollutant-containing gas and can prevent their interference with the sorption of pollutants such as mercury in or near active sites on the activated carbon.

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

PAC ET AL. EXHIBIT 1019
Page 1623

DETAILED DESCRIPTION OF THE INVENTION

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

[0016] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of "about 0.1% to about 5%" or "about 0.1% to 5%" should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement "about X to Y" has the same meaning as "about X to about Y," unless indicated otherwise. Likewise, the statement "about X, Y, or about Z" has the same meaning as "about X, about Y, or about Z," unless indicated otherwise.

[0017] In this document, the terms "a," "an," or "the" are used to include one or more than one unless the context clearly dictates otherwise. The term "or" is used to refer to a nonexclusive "or" unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. Furthermore, all publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that

PAC ET AL. EXHIBIT 1019
Page 1624

of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0018] In the methods of manufacturing described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited. Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

Definitions

[0019] The term "about" as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0020] The term "substantially" as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

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

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

[0023] The term "solvent" as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Nonlimiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

[0024] The term "air" as used herein refers to a mixture of gases with a composition approximately identical to the native composition of gases taken from the atmosphere, generally at ground level. In some examples, air is taken from the ambient surroundings. Air has a composition that includes approximately 78% nitrogen, 21% oxygen, 1% argon, and 0.04% carbon dioxide, as well as small amounts of other gases.

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

[0026] As used herein, "mineral" refers to a naturally occurring solid chemical substance formed through biogeochemical processes, having, for example, characteristic chemical composition, highly ordered atomic structure, and specific physical properties.

Description

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

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

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

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

Activated carbon sorbent including nitrogen.

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1628

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

[0034] In some embodiments, at least some of the carbon in the activated carbon is in the graphene form of carbon. The graphene form of carbon can, in some embodiments, include higher concentrations of locations suitable as active sites. In some examples, certain parts of graphene carbon can have the highest concentrations of locations suitable as active sites: in some examples at the edges, in some examples in non-edge locations. Such locations suitable as active sites may be activated via treatment with halide or halogen, as described herein. In various embodiments, the carbon in the activated carbon sorbent can be at least about 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%, 99.9 wt%, 99.99 wt%, or more than about 99.999 wt% graphene form of carbon.

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1630

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

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

PAC ET AL. EXHIBIT 1019
Page 1631

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1632

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

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

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

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

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

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

[0047] The method of reducing the pollutant content in a pollutant-containing gas can include contacting a pollutant-containing gas with the activated carbon sorbent. The contacting forms a pollutant-sorbent composition. The contacting can be any suitable contacting. In some embodiments, contacting the pollutant-containing gas with the activated carbon sorbent can include adding or injecting the activated carbon sorbent into the pollutant containing gas. For example, the contacting can occur in the gas. In another embodiment, the contacting can occur in an aqueous liquid. In another example, the contacting can occur in the gas, and subsequently contacting can also occur in an aqueous phase such as a scrubber.

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

[0049] The pollutant-sorbent composition can be any suitable composition including the pollutant or an oxidized or otherwise chemically transformed form of the pollutant and the activated carbon sorbent. In some embodiments, mercury is absorbed in its elemental form by the sorbent; the mercury-sorbent composition can include the sorbent and the elemental form of mercury. In some embodiments, the mercury is converted by the sorbent via a chemical reaction, such as oxidation, such that the mercury from the gas is transformed into an organomercury compound including the carbon framework

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

[0050] In some examples, elemental mercury or transformed mercury can remain absorbed to the sorbent until the mercury-sorbent composition has been removed in a later separation step. For example, elemental mercury or transformed mercury can be absorbed, or reacted and absorbed, into or onto the sorbent composition, such that after separating the pollutant-sorbent composition from the pollutant-containing gas, the separated gas has about 1% or less, 3%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.9%, 99.99%, or about 99.999% or more of the mercury that was originally present in the pollutant-containing gas. In some embodiments, elemental mercury or transformed mercury can be released from the mercury-sorbent composition; for example, less than about 1 wt%, 3 wt%, 5 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, or less than about 99 wt% of the mercury can be released from the mercury-sorbent composition prior to separation of the mercury-sorbent composition from the gas. In some examples, the majority of absorbed elemental or transformed mercury can remain part of the mercury-sorbent composition until the mercury-sorbent composition is removed in a later separation step. In some examples, transformed mercury that is released from the mercury-sorbent composition can be later removed from the gas via the separation step or another step. In some examples, elemental or transformed mercury that has been released from the mercury-sorbent composition can contact activated carbon sorbent to form a mercury-sorbent composition, to be removed later via the separation step.

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

electrostatic precipitator (ESP), a baghouse, a wet scrubber, a filter, cyclone, fabric separator, or any combination thereof. In some embodiments, an electrostatic precipitator can be used, followed by a scrubber. In other embodiments, an electrostatic precipitator can be used without a scrubber, or another particulate separator can be used. Some devices that can function as particulate separators can also have other functions, for example a scrubber can also remove SO_2 or SO_3. In embodiments that include contacting of the mercury with a sorbent in an aqueous phase, e.g. in a scrubber, the removal of mercury from the gas that occurs within the aqueous phase by reaction or interaction of the mercury with the sorbent in the aqueous phase can be considered separation of the mercury-sorbent composition from the gas.

[0052] In some examples, by separating the particulates from the mercury-containing gas, at least about 20 wt%, 30 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, 96 wt%, 97 wt%, 98 wt%, 99 wt%, 99.9 wt%, 99.99 wt%, or about 99.999 wt% or more mercury can be removed from the mercury-containing gas stream. As discussed herein, the mercury can be removed in the form of elemental mercury, or in the form of a transformed mercury, such as an organomercury compound including the mercury bound to the carbon framework of the activated carbon or as Hg(II) complexed with a suitable counterion.

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

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

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

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

alkali or alkaline-earth element, and a compound or material including the same. In various examples, the addition of an alkaline component separately or with the carbon sorbent can result in improved mercury capture. Various factors can impact the effectiveness of the alkaline addition, such as, for example, flue gas pollutants, flue gas constituents (e.g., SO_2, NO_x, Se, HCl, and the like), operating temperature, mercury form, and mercury concentration. In some examples, the alkaline-to-activated-carbon ratio can be adjusted to optimize for a given set of site conditions.

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

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

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

Method of making activated carbon including nitrogen.

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

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

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

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

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

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

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

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

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

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

Promoted activated carbon sorbent including nitrogen.

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

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

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

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

[0070] The promoting of the sorbent material can occur before addition or injection into a gas stream, during addition or injection into a gas stream, after addition or injection into a gas stream, or a combination thereof, wherein the gas stream can be a mercury-containing gas stream, a transport stream, or a combination thereof. In some examples, the promoter can be added to the sorbent before the promoter and the sorbent react, such that the heat of the gas stream into which the promoter is added causes the promoting of the sorbent. For example, the promoter can be added as a gas, as a gas dissolved in a liquid, or as a solid such as a salt, or other substance (e.g., acid) dissolved in liquid (e.g., water), for example, hydrobromic acid. In examples wherein the promoter is added in a liquid such as water, the water can be allowed to dry, which can allow the promoter to adhere to, impregnate, or react with the activated carbon sorbent, or a combination thereof. In some examples, a pre-added promoter can be an ammonium salt, such as an ammonium chloride, an ammonium bromide, or an ammonium iodide, including, for example, mono-, di-, tri-, or tetraalkyl ammonium halides, or NH_4^+ halide salts. In some examples, the promoter can be added to the sorbent near to or at the time of promoting; for example, the promoter can be added to a gas stream with the sorbent or such that it contacts the sorbent within a heated gas stream, such as a mercury-containing gas stream or a feed gas stream. In some examples, the promoter can be NH_4Br.

[0071] In some embodiments, a promoter precursor transforms into the halogen or halide promoter that reacts with the activated carbon sorbent to give the activated carbon material. The promoter precursor can be any suitable precursor that can transform into the halogen or halide promoter. In some embodiments, the promoter precursor can be at least one of on the unpromoted sorbent and added or injected with the unpromoted sorbent. In some embodiments, the promoter can be HBr, and in some examples, the HBr can be provided via degradation or reaction of a promoter precursor such as ammonium bromide, sodium bromide, or calcium bromide. The promoter can be HCl, and in some examples, the HCl can be provided via degradation or reaction of a promoter precursor such as ammonium chloride, sodium chloride, or calcium chloride. The promoter can be HF, and in some examples, the HF can be provided via degradation or reaction of a promoter precursor such as ammonium fluoride, sodium fluoride, or calcium fluoride. In some examples, the promoter (e.g., HBr or HCl) or promoter precursor (e.g., NH_4Br, NaBr, $CaBr_2$, NH_4Cl, NaCl, $CaCl_2$) can be added or injected in the flue gas separately from the activated carbon sorbent or with the activated carbon sorbent (e.g., can be applied to the sorbent pre-injection, added or injected simultaneously at the same location, or added or injected simultaneously at different locations). In some examples, NaCl, $CaCl_2$, NaBr, or $CaBr_2$ can be added with uncombusted material such as uncombusted coal.

Inorganic matrix-support or nanocomposites.

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

PAC ET AL. EXHIBIT 1019
Page 1643

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

[0073] For example, the method of reducing the pollutant content in a pollutant-containing gas can include obtaining or providing a substrate material. The substrate material can be any suitable substrate. For example, the substrate can be at least one of diatomaceous earth, a clay, a zeolite, or a mineral. The method can include contacting the carbon precursor and the substrate material, to provide a sorbent starting material. The contacting can take place in any suitable fashion. The contacting mixes the carbon precursor and the substrate material, such that when the conglomeration is heated (or subjected to any other suitable source of energy), the carbon nanocomposite or supported sorbent is formed. The contacting can be performed such that the carbon precursor is approximately evenly distributed on the substrate. In some examples, water or another solvent can be added to help distribute the carbon precursor on the substrate. In examples where water is included in the mixture of the carbon precursor and the substrate, the conglomeration can be dried prior to the heating. The drying can occur in any conventional manner (e.g., convective, conductive, microwave, and the like), including by heating near or above the boiling point of the solvent, in the case of water (e.g., 50°C-120°C or higher), at atmospheric pressure, under pressure, or under a vacuum.

[0074] The substrate can include any suitable porous material. For example, the substrate material can be diatomaceous earth, zeolites, porous minerals (e.g., clays) including, for example, smectites (e.g., montmorillonite, bentonite, nontronite, saponite), kaolins, illites, chlorites, sepiolite, or attapulgites. In some examples, the substrate can include polymers, non-metals, metals, metalloids, ceramics or mixtures, and blends, as well as composites and alloys thereof. The materials can be synthetic or naturally occurring or naturally derived materials. Examples of synthetic polymers include any common thermoplastics and thermosetting materials. Examples of metals include aluminum, titanium, copper, steel, and stainless steel. Examples of ceramics include any form of alumina, zirconia, titania, and silica. Examples of naturally occurring or naturally derived materials include wood, wood composites, paper, cellulose acetate, and geologic formations such as granite or limestone.

PAC ET AL. EXHIBIT 1019
Page 1644

Examples of non-metals include various forms of carbon such as graphite or carbon. Examples of metalloids include silicon or germanium. The porous material can be a construction material such as concrete or asphalt.

[0075] In some examples, the substrate material can be present in from about 1 wt% to about 99 wt%, about 20 wt% to about 80 wt%, or about 40 wt% to about 60 wt% of the starting material for the carbon nanocomposite sorbent. Wt% in this paragraph refers to the percentage by weight based on the total weight of the carbon precursor and the substrate material.

[0076] The method can include processing (e.g., heating, vibrating, sonicating, microwaving, or otherwise adding energy to) the sorbent starting material, to provide the activated carbon sorbent. The contacted composition of the carbon precursor and the substrate can then be processed (e.g., heated, vibrated, sonicated, microwaved, or other suitable addition of energy) to form the carbon nanocomposite or inorganic matrix-supported sorbent. The processing can take place at any suitable temperature, such that the sorbent is sufficiently formed, for example heating to about 50°C, 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C, 1000°C, 1100°C, or about 1200°C or higher. The processing can take place for any suitable time, such that the carbon nanocomposite is sufficiently formed, for example, greater than about 1 min, 2 min, 5 min, 10 min, 30 min, 1 h, 1.5 h, 2 h, 3 h, 4 h, 5 h, 10 h, or greater than about 24 h. The heating can take place in any suitable apparatus, for example, a unit that substantially excludes oxygen, e.g., that allows heated inert gas air to flow around the mixture being heated. In one example, the heating occurs in a furnace having an inert gas environment therein. The processing can be accelerated, or lengthened, depending on the apparatus and the nanocomposite or supported material.

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

PAC ET AL. EXHIBIT 1019
Page 1645

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

Method of making an active carbon sorbent including nitrogen.

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

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

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

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

Examples

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

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

Example 1a. Carbon precursor.

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

Example 1b. Char precursor.

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

Example 1c. Wood charcoal precursor.

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

PAC ET AL. EXHIBIT 1019
Page 1647

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

Example 1d. Wood charcoal – alanine.

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

Example 2. Tube reactor testing.

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

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

PAC ET AL. EXHIBIT 1019
Page 1648

Example 3. Filter bed testing.

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

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

Example 4a. Vinylpyrrolidone-acrylic acid copolymer.

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

Example 4b. Vinylpyrrolidone-vinyl acetate copolymer.

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

Example 4c. Poly(vinylpyrrolidone).

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

PAC ET AL. EXHIBIT 1019
Page 1649

Example 4d. Poly(vinylpyrrolidone).

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

Example 4c. Wood-derived charcoal.

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

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

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

Example 4g. Steam activation.

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1650

Example 5b. Sulfamic acid.

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

Example 5c. Carbonized lignite.

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

Example 5d. Steam activation.

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

Example 6. Preparation of Nitrogen-Containing Pitches.

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1651

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1652

Example 7. Preparation of Nitrogen-Impregnated Carbon.

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

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

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

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

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

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

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

Example 9a. Simulation of the Sulfuric Acid Accumulation.

PAC ET AL. EXHIBIT 1019
Page 1653

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

Example 9b. Packed-Bed Tests.

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

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

PAC ET AL. EXHIBIT 1019
Page 1654

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

PAC ET AL. EXHIBIT 1019
Page 1655

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

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

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

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

Example 9c. Test Results.

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

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

PAC ET AL. EXHIBIT 1019
Page 1657

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1658

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

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

Additional Embodiments.

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

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1660

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1661

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1662

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1664

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1667

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1668

CLAIMS

What is claimed is:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1670

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1671

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

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

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

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

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

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

obtaining or providing a carbon precursor comprising nitrogen; and

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1672

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

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

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

obtaining or providing a substrate material;

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1673

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1674

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

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

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

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

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

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

obtaining or providing a carbon precursor comprising nitrogen;

obtaining or providing a substrate material;

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

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

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

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

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

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

obtaining or providing an unpromoted carbon sorbent comprising nitrogen;

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

52. The method of claim 51, further comprising:

obtaining or providing a carbon precursor comprising nitrogen;

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

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

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

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1677

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1678

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

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

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

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

Electronic Acknowledgement Receipt

EFS ID:	32666047
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
Filer Authorized By:	Jordan Rivard Golomb
Attorney Docket Number:	4820.001US9
Receipt Date:	18-MAY-2018
Filing Date:	
Time Stamp:	15:43:16
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		15974343_IDS_5-18-2018.pdf	575228 931f0cb8b82162217aff9955d8f68887b130ebff	yes	24

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Miscellaneous Incoming Letter	1	1
	Miscellaneous Incoming Letter	2	3
	Transmittal Letter	4	5
	Information Disclosure Statement (IDS) Form (SB08)	6	24

Warnings:					
Information:					
2	Foreign Reference	0001_ca1099490a.pdf	405337 99a899b3d0dcecf2f3ebc4284c17d7fa871771e4	no	11
Warnings:					
Information:					
3	Foreign Reference	0002_ca2150529a1.pdf	818730 2cb79324896ad7f99cfc66f7e422c5485a34fcdc	no	25
Warnings:					
Information:					
4	Foreign Reference	0003_ca2327602a1.pdf	763633 35387d39264bef6f21fe538e10be8d03e9faddf6	no	23
Warnings:					
Information:					
5	Foreign Reference	0004_ca2400898a1.pdf	543617 9ed04ec3926a57f2d7ddedff2d643078374 6b805	no	14
Warnings:					
Information:					
6	Foreign Reference	0006_ca2757309a1.pdf	2176673 75a8fc2d98460187fb2d93754aa7f36a4a679189	no	40
Warnings:					
Information:					

7	Foreign Reference	0007_ca2757309c.pdf	2285367 1da7414f16f7b9fdc8e8ce879649a87b9289d1bf	no	46
Warnings:					
Information:					
8	Foreign Reference	0008_cn101048218a.pdf	2290088 899b8353333ad2d664a0f24add9afc03606866dd	no	48
Warnings:					
Information:					
9	Foreign Reference	0009_cn101053820a.pdf	876976 b4fdabc4e42a6e94df37213f4be168cbbb111f75	no	13
Warnings:					
Information:					
10	Foreign Reference	0010_cn101293196a.pdf	805367 d768bdc9e3330a196aa15c8581dd8fbffc91e479	no	10
Warnings:					
Information:					
11	Foreign Reference	0011_cn_101816922a.pdf	933126 0c04a771d5e95994a2fec33ee2367c9b78da9fd7	no	7
Warnings:					
Information:					
12	Foreign Reference	0012_cn102413899a.pdf	2165232 a717567ef8813c2d6465a24073294954a444842d	no	28
Warnings:					
Information:					
13	Foreign Reference	0013_cn104519410a.pdf	2684441 32fafac762fae05afa6afb57b353afcbe95613a7	no	36
Warnings:					
Information:					

14	Foreign Reference	0015_cn1048173a.pdf	421978 de0ead7795b037f704de7ee61bf790e37a19b86e	no	8
Warnings:					
Information:					
15	Foreign Reference	0018_de_10233173a1.pdf	4086015 8b8a964d7caf137656186a1964129b7d05396dc8	no	22
Warnings:					
Information:					
16	Foreign Reference	0022_ep0208490a1.pdf	403919 de9e231ae9fb42faf38c8851471570bbd152317f	no	14
Warnings:					
Information:					
17	Foreign Reference	0025_ep_1570894a1.pdf	2556949 74dbd4247b95cda68483b96a40554c4cadcbf14c	no	14
Warnings:					
Information:					
18	Foreign Reference	0026_fr_2529802a1.pdf	2589381 9c84d5f36c9c6144d3f55393c18d8e868201dabf	no	21
Warnings:					
Information:					
19	Foreign Reference	0027_gb2122916a.pdf	950227 c1e188a1709693fc5877c0ed1365312caf8a4654	no	20
Warnings:					
Information:					
20	Foreign Reference	0028_jph09256812a.pdf	258113 b3a255862a2fa059050f44ad12112260961 35f23	no	7
Warnings:					
Information:					

21	Foreign Reference	0029_jp4943197.pdf	167397 3e974cc391e4dd4180613de8ec8e6d036f6b0885	no	4
Warnings:					
Information:					
22	Foreign Reference	0030_jp_49_053590a.pdf	747232 c83b55e3a583e513403751fa0b9a5dc9455065bb	no	7
Warnings:					
Information:					
23	Foreign Reference	0031_jp_49_066592a.pdf	594755 c55fb23565e1813eb429a3b7688b3781e23dbdb4	no	5
Warnings:					
Information:					
24	Foreign Reference	0033_jp506438.pdf	185329 76546bda5f2132ecba7a74f648b3413 1e55e4581	no	4
Warnings:					
Information:					
25	Foreign Reference	0034_jp_51_003386a.pdf	778988 63bf0c9c74dc737babda177daaec33f6c3201e35	no	8
Warnings:					
Information:					
26	Foreign Reference	0035_jps544868a.pdf	408454 dd05f5dd124377ecb1639c2f81255ec3329325d4	no	6
Warnings:					
Information:					
27	Foreign Reference	0037_su_1163892a.pdf	536907 260272adf2ba6f2d577605f95c2d6ce3c2569b72	no	5
Warnings:					
Information:					

28	Foreign Reference	0039_wo2001062368a1.pdf	389681 d3e80b7764340442f9dfbfbe1982e54628b52377	no	14
Warnings:					
Information:					
29	Foreign Reference	0040_wo2002028513a2.pdf	2519010 c95a3e1fdd84e9657e1b4e8da1a43019a4a85ef8	no	88
Warnings:					
Information:					
30	Foreign Reference	0041_wo2003072241a1.pdf	1646314 89232d768701243697efbd65d4ff5dfd8fbcaa5f	no	59
Warnings:					
Information:					
31	Foreign Reference	0042_wo_2004_089501a2.pdf	3583158 11bf7151f49f8a2b3b72d66e34339f683639f3ff	no	28
Warnings:					
Information:					
32	Foreign Reference	0043_wo2004094024a2.pdf	546734 56ca8b8297d11cd63f6b018084ba326aaa9396bc	no	26
Warnings:					
Information:					
33	Foreign Reference	0044_wo2006039007a2.pdf	1252233 a8d92b906e06e265b48388f210e3aaf9633e40e8	no	41
Warnings:					
Information:					
34	Foreign Reference	0046_wo2006099611a1.pdf	1780317 faa15ff4d51d0a1a0934d1d13035b0892d2905b3	no	64
Warnings:					
Information:					

35	Foreign Reference	0047_wo2009018539a3.pdf	72047 910cdaf1e5cc0e85700bb9fc4513a9e61084aca2	no	3
Warnings:					
Information:					
36	Foreign Reference	0048_wo2010123609a1.pdf	734312 2848d99b2ba578f647bb020f80ba203259ad4a89	no	41
Warnings:					
Information:					
37	Foreign Reference	0049_wo2013162968a2.pdf	2778381 3cc1f3941f59f3f4c6e4fb161cc1532761579cb0	no	64
Warnings:					
Information:					
38	Foreign Reference	0050_wo2013162968a3.pdf	55214 9f6c24f6e46a833cb19036ce02b2fa5c3de198d3	no	8
Warnings:					
Information:					
39	Foreign Reference	0051_wo2014137907a2.pdf	433227 84bb0ae526885106e8f4192088a71536e8e77e38	no	62
Warnings:					
Information:					
40	Foreign Reference	0052_3338013us1_aarn_110110.pdf	569783 15d4650c2b35a299aac0aeca2b1912eebbc0222f	no	17
Warnings:					
Information:					
41	Non Patent Literature	0053_3338013us1_foar_042710.pdf	226806 54e2e4584745c25e8b00d34558fe3598fa81f0fe	no	8
Warnings:					
Information:					

42	Non Patent Literature	0054_3338013us1_oarn_100609.pdf	236242 005b7fc6e5678e963f96245dcce6e936fd0c7374	no	8
Warnings:					
Information:					
43	Non Patent Literature	0055_10554018_noar_011912.pdf	386736 95e15b1deb28503566d358c83368e44261eae54f	no	7
Warnings:					
Information:					
44	Non Patent Literature	0056_3338013us1_aarn_020810.pdf	274003 470134d14c05fbf74d02682ace8ea1062ebf2a6a	no	9
Warnings:					
Information:					
45	Non Patent Literature	0057_3338013us1_rerr_r_081009.pdf	30401 df00c89c533b62f984a731108ae67585d1b2af4a	no	1
Warnings:					
Information:					
46	Non Patent Literature	0058_3338013us1_rerr_060909.pdf	160351 3c176eeee0bef35e7c7d2313c2d99ce3a0cff245	no	5
Warnings:					
Information:					
47	Non Patent Literature	0059_advisory_action_04_21_08.pdf	494017 84d44f202dfb53cdce534143d0fd9832c435ce9f	no	3
Warnings:					
Information:					
48	Non Patent Literature	0060_final_oa_01_23_2008.pdf	3300353 0cbc72ed6725fbeb6bb332f6d7d24006ebf955f4	no	20
Warnings:					
Information:					

49	Non Patent Literature	0061_non_final_oa_08_13_07.pdf	2460713 620767db73fbcba3fdd9bee433cbaeeca9e913c0	no	14
Warnings:					
Information:					
50	Non Patent Literature	0062_3338005us1_noar_101408.pdf	324774 3e15c9b9f15a9cc8e25e740d8e5cf1f7c8745c48	no	7
Warnings:					
Information:					
51	Non Patent Literature	0063_prel_azmend_02_27_07.pdf	1892558 be4fa4848c53c06b878178c5f588cc4bfce6fd76	no	9
Warnings:					
Information:					
52	Non Patent Literature	0064_response_03_24_08.pdf	5212373 db73bf45f8cbf52c9e83eece465d4b6e5a54fb45	no	29
Warnings:					
Information:					
53	Non Patent Literature	0065_3338005us1_rrr_070907.pdf	47669 b1613c811d9810abc7f75edabf4bb99c686e69e2	no	2
Warnings:					
Information:					
54	Non Patent Literature	0066_3338005us1_aarn_111307.pdf	932282 72bd33ac10a9b4b33cc60a353a66f83b3ecd9b3a	no	19
Warnings:					
Information:					
55	Non Patent Literature	0067_3338005us1_rerr_060707.pdf	210625 2f95c7dff73172e628c1474133138527ba4382515	no	6
Warnings:					
Information:					

56	Non Patent Literature	0068_3338002us1exir4511.pdf	166822 47042bd4d180b41ec9f5074c4c9a8e544d2b32d1	no	3
Warnings:					
Information:					
57	Non Patent Literature	0069_3338002us1_foar_051111.pdf	709112 304c546f052994db285a97824e62058e44a59bcd	no	15
Warnings:					
Information:					
		Total Files Size (in bytes):	65435707		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s): Edwin S. Olson et al.
Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

Docket No.:	4820.001US9	Serial No.:	15/974,343
Filed:	May 8, 2018	Due Date:	N/A
Examiner:	Unknown	Group Art Unit:	Unknown
Customer No.:	21186	Confirmation No.:	1072

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

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

X Communication Concerning Prior and Copending Applications (2 pgs.)
X Information Disclosure Statement (2 pgs.), Form 1449 (19 pgs.) Copies of Cited References (325).

If not provided for in a separate paper filed herewith, please consider this a PETITION FOR EXTENSION OF TIME for sufficient number of months to enter these papers and please charge any additional fees or credit overpayment to Deposit Account No. 19-0743. If applicable, any papers or fees supplied herewith are considered to be timely filed pursuant to 37 C.F.R. § 1.7(a), the response period falling on a Federal Holiday, Saturday or Sunday being extended to the next succeeding business day.

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
Customer No.: 21186

By: /Nicholas P. Lanzatella/
Nicholas P. Lanzatella
Reg. No. 63,803

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s):	Edwin S. Olson et al.	Examiner:	Unknown
Serial No.:	15/974,343	Group Art Unit:	Unknown
Filed:	May 8, 2018	Docket:	4820.001US9
Customer No.:	21186	Confirmation No.:	1072
Title:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY		

COMMUNICATION CONCERNING PRIOR OR COPENDING APPLICATION(S)

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

Pursuant to the guidance of MPEP §§ 2001.06(b) and 2004(9), Applicant would like to bring the following additional application(s) to the Examiner's attention. The identification of these applications is not intended to suggest that the subject matter claimed in any listed application is, or has been, substantially similar to any claim or claims in the present application.

Serial No./ Patent No.	Filing Date	Attorney Docket	Title
11/209,163 7,435,286	August 22, 2005	4820.001US1	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
12/201,595	August 29, 2008	4820.001US2	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
12/419,219 8,168,147	April 6, 2009	4820.001US3	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
13/427,665 8,512,655	March 22, 2012	4820.001US4	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
13/966,768 8,821,819	August 14, 2013	4820.001US5	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
14/318,270 9,757,689	June 27, 2014	4820.001US6	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
14/712,558	May 14, 2015	4820.001US7	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
15/951,970	April 12, 2018	4820.001US8	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

15/589,359	May 8, 2017	4820.003US2	ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME
14/195,360 9,669,355	March 3, 2014	4820.003US1	ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME
15/382,114	December 16, 2016	4820.004US1	PROMOTED AMMONIUM SALT-PROTECTED ACTIVATED CARBON SORBENT PARTICLES FOR REMOVAL OF MERCURY FROM GAS STREAMS
15/449,112	March 3, 2017	4820.005US1	SORBENT COMPRISING CARBON AND NITROGEN AND METHODS OF USING THE SAME
12/429,058 8,652,235	April 23, 2009	4820.007US1	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
14/102,896 9,468,886	December 11, 2013	4820.007US2	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
15/295,594	October 17, 2016	4820.007US3	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
15/978,760	May 14, 2018	4820.007US4	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
15/853,029	December 22, 2017	4820.018US1	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

Respectfully submitted,

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
P.O. Box 2938
Minneapolis, MN 55402
(651) 305-2704

Date 5-18-2018 By /Nicholas P. Lanzatella/

Nicholas P. Lanzatella
Reg. No. 63,803

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s):	Edwin S. Olson et al.	Examiner:	Unknown
Serial No.:	15/974,343	Group Art Unit:	Unknown
Filed:	May 8, 2018	Docket:	4820.001US9
Customer No.:	21186	Confirmation No.:	1072
Title:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY		

INFORMATION DISCLOSURE STATEMENT

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

In compliance with the duty imposed by 37 C.F.R. § 1.56, and in accordance with 37 C.F.R. §§ 1.97 *et. seq.*, the enclosed materials are brought to the attention of the Examiner for consideration in connection with the above-identified patent application. Applicant respectfully requests that this Information Disclosure Statement be entered and the documents listed on the attached PTO 1449 Form be considered by the Examiner and made of record. Pursuant to the provisions of MPEP 609, Applicant requests that a copy of the PTO 1449 Form, initialed as being considered by the Examiner, be returned to the Applicant with the next official communication.

Pursuant to 37 C.F.R. § 1.97(b), it is believed that no fee or statement is required with the Information Disclosure Statement. However, if an Office Action on the merits has been mailed after filing of the application or after the filing of the most recent RCE, the Commissioner is hereby authorized to charge the required fees to Deposit Account No. 19-0743 in order to have this Information Disclosure Statement considered.

Pursuant to 37 C.F.R. § 1.98(a)(2), copies of cited U.S. Patents and Published Applications, and Non-Published Applications identifiable by USPTO Serial Number, are no longer required to be provided to the Office. Applicant acknowledges the requirement to submit copies of foreign patent documents and non-patent literature in accordance with 37 C.F.R § 1.98(a)(2).

The Examiner is invited to contact the undersigned at the telephone number indicated if there are any questions regarding this communication.

Respectfully submitted,

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
P.O. Box 2938
Minneapolis, MN 55402
(651) 305-2704

Date 5-18-2018 By /Nicholas P. Lanzatella/
Nicholas P. Lanzatella
Reg. No. 63,803

RJC:jj

Electronic Acknowledgement Receipt

EFS ID:	32666239
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
Filer Authorized By:	Jordan Rivard Golomb
Attorney Docket Number:	4820.001US9
Receipt Date:	18-MAY-2018
Filing Date:	
Time Stamp:	15:51:26
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Non Patent Literature	0070_3338002us1_oarn_011911.pdf	593730 7f8aa0c06fe0fed9013dd5e7dbef31d19d160773	no	14

Warnings:

Information:					
2	Non Patent Literature	0071_3338002us1_aarn_040711.pdf	236498 7c9e24377a6c16e185a8ad74a30836ad211cbab9	no	12
Warnings:					
Information:					
3	Non Patent Literature	0072_3338002us1_aarf_070811.pdf	64625 9ac7538078d5b6be00ecc6b93b155e1535da3177	no	11
Warnings:					
Information:					
4	Non Patent Literature	0073_final_oa_03_10_10.pdf	2110264 f70df96789e1399043a65ffb672e75105aefce5a	no	13
Warnings:					
Information:					
5	Non Patent Literature	0074_nonfinal_oa_04_16_2009.pdf	3456715 7c6715ac00c178a4fbfa2ab16d79b4e5f46ed8d3	no	21
Warnings:					
Information:					
6	Non Patent Literature	0075_3338005us2_aarn_101609.pdf	941267 f0930a6985c30c175659cd4e028a054b1066c932	no	18
Warnings:					
Information:					
7	Non Patent Literature	0076_final_oa_10_14_10.pdf	2948656 8055c6d962e9b46e218e8d7346fc8da95c5ea1eb	no	17
Warnings:					
Information:					
8	Non Patent Literature	0077_non_final_oa_1_15_10.pdf	2215453 5c08704d4d1f12ccc2862fa926143809726de9471	no	13
Warnings:					
Information:					

9	Non Patent Literature	0078_non_final_oa_2_23_11.pdf	2855787 f1908dfd01ea961b55bcb3bbdfa381a28f0ed846	no	17
Warnings:					
Information:					
10	Non Patent Literature	0079_non_final_oa_8_4_11.pdf	2735467 10b167a90bc02271551210f56c671d6ed77d6874	no	16
Warnings:					
Information:					
11	Non Patent Literature	0080_12419219__noar_011012.pdf	394260 b06b4a44a6f35a5b09056baedcedae5867364b91	no	7
Warnings:					
Information:					
12	Non Patent Literature	0081_3338005us3_pamd_040609.pdf	195365 d8ab462775e75df0ec1f1b712ebeb3938eb980ff	no	7
Warnings:					
Information:					
13	Non Patent Literature	0082_response_02_14_11.pdf	3136755 21824c5e4c71de110f91d29608632fda104dc64a	no	19
Warnings:					
Information:					
14	Non Patent Literature	0083_response_05_20_11.pdf	85398 b65decc781c4373fc55a03a44cb632786fbee4c4	no	14
Warnings:					
Information:					
15	Non Patent Literature	0084_3338005us3_aarn_071510.pdf	1248816 806d5e83a197ff7bb67ddee90e969225b2f315d	no	22
Warnings:					
Information:					

16	Non Patent Literature	0085_3338005us3_aarn_102711.pdf	133823 9e5203cad352035607ca52302e2edabd77ca5ada	no	12
Warnings:					
Information:					
17	Non Patent Literature	0086_5_4820007us1_adar_052912.pdf	175197 5a145d420d4cf1f12d0821e49b972224a69f3ec8	no	3
Warnings:					
Information:					
18	Non Patent Literature	0087_11_4820007us1_xpqa_021413.pdf	227881 ec56c5bc2d92d3a5955636bdd6777192e6f795b1	no	7
Warnings:					
Information:					
19	Non Patent Literature	0088_9_4820007us1_exir_122812.pdf	184679 0724962bddd26c0bfaff10cb50cc312cfe1dfed1	no	4
Warnings:					
Information:					
20	Non Patent Literature	0089_8_4820007us1_foar_103112.pdf	768622 e38af293849b00d1248cc870220bed7640ac32ae	no	21
Warnings:					
Information:					
21	Non Patent Literature	0090_3_4820007us1_foar_122011.pdf	731086 6ab4e6bde9b0108c0f258103bf3b5a67b1e39e91	no	21
Warnings:					
Information:					
22	Non Patent Literature	0091_6_4820007us1_oarn_061112.pdf	689805 06fb229b248ed1fc6e8dd634fc7ad7d67bb1cc95	no	18
Warnings:					
Information:					

23	Non Patent Literature	0092_1_4820007us1_oarn_071911.pdf	738159 d86956a17e55320016d34d7dbc46823ec2d4e7ef	no	20
Warnings:					
Information:					
24	Non Patent Literature	0093_14_4820007us1_noar_011614.pdf	181773 e695a030bae87c842bbdcc83886a541f4d7c68a9	no	5
Warnings:					
Information:					
25	Non Patent Literature	0094_13_4820007us1_noar_091113.pdf	481565 b23cbc65b96ad1125f266c9e2a213740380cba63	no	11
Warnings:					
Information:					
26	Non Patent Literature	0095_10_4820007us1_aarf_013113.pdf	877608 d720648f961fd7c5fd1fc8e628c510a87883704f	no	19
Warnings:					
Information:					
27	Non Patent Literature	0096_12_4820007us1_xpqre_030713.pdf	262683 a985370c5e8d9b389bfcf015833f15fc4b2bd148	no	7
Warnings:					
Information:					
28	Non Patent Literature	0097_4_4820007us1_aarf_051112.pdf	456090 b56bb02739cf7856485f92c6b14f93bdb25e0f5	no	11
Warnings:					
Information:					
29	Non Patent Literature	0098_7_4820007us1_aarn_091112.pdf	748680 81fd191ca3f6cfc76a2a0286d0084c334e1c964d	no	16
Warnings:					
Information:					

30	Non Patent Literature	0099_2_4820007us1_aarn_101811.pdf	771121 f31a7dadfb4a83d9223e107bff5f7051d71b5100	no	17
Warnings:					
Information:					
31	Non Patent Literature	0101_final_oa_08_03_12.pdf	1944595 f2cf3d46ead1b0c69c03d14a1493262af9c99dd7	no	12
Warnings:					
Information:					
32	Non Patent Literature	0102_3338005us4_noar_041613.pdf	386802 d25790931c24b71e4d5b80fd85b83e79796a375c	no	8
Warnings:					
Information:					
33	Non Patent Literature	0103_3338005us4_aarn_032113.pdf	213214 414325a0c09c48c7c77841e0e4360fd487fbb7a7	no	20
Warnings:					
Information:					
34	Non Patent Literature	0104_response_10_10_12.pdf	127180 900755ce923b6afe7a03a23642935071bd41ad65	no	15
Warnings:					
Information:					
35	Non Patent Literature	0105_03338005us4_pamd_032212.pdf	54284 a0e050ba6692e25863335033a5585694f758a522	no	3
Warnings:					
Information:					
36	Non Patent Literature	0106_advisory_action.pdf	720172 92c2670cdda82ca1f966f5f530ce6fa1b88e26a8	no	3
Warnings:					
Information:					

37	Non Patent Literature	0107_final_oa_10_16_2014.pdf	785112 957ea38cc0d86194f919d2ca0ae2b13106ac6d3b	no	4
Warnings:					
Information:					
38	Non Patent Literature	0108_nonfinal_oa_05_30_14.pdf	1147067 14a7e819c6b87d2fe549a8c9fc04820c8eb093f1	no	6
Warnings:					
Information:					
39	Non Patent Literature	0109_noa_01_05_15.pdf	1592075 d1241165dfd016beda2df33a72f5ac5836a1a3ed	no	5
Warnings:					
Information:					
40	Non Patent Literature	0110_response_9_2_2014.pdf	163527 30502decc3905a02ac35b059d1513369342c146a	no	13
Warnings:					
Information:					
41	Non Patent Literature	0111_amend_response_110614.pdf	117087 94dd81ad3899380ccedc57e2e166795f5e5e1f32	no	7
Warnings:					
Information:					
42	Non Patent Literature	0112_response_12_9_2014.pdf	106545 25c388f17597c22640e473549d3e61a4eaf916bf	no	6
Warnings:					
Information:					
43	Non Patent Literature	0113_nonfinal_oa_12_06_13.pdf	5611782 392268970e97efe6d8118dc8432d2b10104c5199	no	7
Warnings:					
Information:					

44	Non Patent Literature	0114_noa_08_01_2014.pdf	5287665 93feb3124425c7d4bf8d087fa06d5d06ff08cd3a	no	6
Warnings:					
Information:					
45	Non Patent Literature	0115_noa_4_18_2014.pdf	1746637 7861453bae3ff4914aa2168f74d41b1cf77972d7	no	7
Warnings:					
Information:					
46	Non Patent Literature	0116_prel_amend_08_14_13.pdf	272047 999dccf650da4cccc5fadf78e6a83dc8b91f96bd	no	3
Warnings:					
Information:					
47	Non Patent Literature	0117_response_3_6_2014.pdf	104141 7b6c22193b2d70598128e2734f5795a3215ece17	no	6
Warnings:					
Information:					
48	Non Patent Literature	0118_supp_prel_amend_08_15_13.pdf	599674 c98429f302170e2ec6e4a4c71da3991d22a076f5	no	6
Warnings:					
Information:					
49	Non Patent Literature	0119_4820007us2_adar_121615.pdf	141988 6a9fdb5d66eb2c883c74b1fa15fd72e40eff9884	no	3
Warnings:					
Information:					
50	Non Patent Literature	0121_4820007us2_oarn_032315.pdf	466756 cf56621fa961bd88b19bb11a5d99b4a9e626af4a	no	13
Warnings:					
Information:					

51	Non Patent Literature	0122_4820007us2_noar_061016.pdf	403252 97f20e535e47cb121a1674766cc3c18ba63228a3	no	7
Warnings:					
Information:					
52	Non Patent Literature	0123_4820007us2_adaf_012216.pdf	532379 dbaa0b8bc7199048383de686f1ff2b814511195e	no	11
Warnings:					
Information:					
53	Non Patent Literature	0124_4820007us2_aarn_062215.pdf	439275 65eb6cc23cc51c3655e7b3f41c7327a6ded00ebb	no	10
Warnings:					
Information:					
54	Non Patent Literature	0125_4820007us2_aarf_112415.pdf	253871 93095bdb4db1ee38b842a950088c992c121d5afc	no	5
Warnings:					
Information:					
55	Non Patent Literature	0128_3338021us1_foar_031816.pdf	597264 37b758335ed573c61489f06bff0c56da30a28e6c	no	18
Warnings:					
Information:					
56	Non Patent Literature	0129_3338021us1_foar_112216.pdf	223016 f1bcf00faebc9075e308a790c6f4738803853 4ff	no	7
Warnings:					
Information:					
57	Non Patent Literature	0131_3338021us1_oarn_062016.pdf	373862 c2ae96927253c4cc2422947d111b3edb96500480	no	11
Warnings:					
Information:					

58	Non Patent Literature	0132_3338021us1_oarn_112415.pdf	620829 9dc97ce6d39e10ed613cf8349e7dbf5a55776ad4	no	19
Warnings:					
Information:					
59	Non Patent Literature	0133_3338021us1_noar_020717.pdf	351877 b1e11236d02d35e31a78b85536b877bc5b9dc5bd	no	5
Warnings:					
Information:					
60	Non Patent Literature	0134_3338021us1_aarf_011817.pdf	62577 751af160d8c046593b58e09398bcfd92782c301c	no	7
Warnings:					
Information:					
		Total Files Size (in bytes):	56094380		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/12828

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B01J 20/34, 38/48, 38/60, 38/62

US CL : 502/22, 27, 28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/22, 27, 28

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

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P --- Y,P	US 6,579,507 B2 (PAHLMAN et al) 17 June 2003 (17.06.2003), column 10, lines 39-67; column 40, lines 32-67.	1-3,11-14,17-22,26-32,36-38,42-48,55-58, and 62-69 --- 4-10,15,16,23-25,33-35,39-41,49-51, and 59-61
X	US 6,475,451 B1 (LEPPIN et al) 05 November 2002 (05.11.2002), see abstract.	43-48
A	US 5,827,352 (ALTMAN et al) 27 October 1998 (27.10.1998), see abstract and entire patent.	1-69
Y	US 5,480,619 (JOHNSON et al) 02 January 1996 (02.01.1996), see abstract, col . 4, lines 30-35.	7-10, 15,16,23-25,33-35,39-41,49-51 and 59-61
Y	US 4,196,173 (deJong et al.) 01 April 1980 (01.04.1980), see abstract.	4-6

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 September 2004 (22.09.2004)	22 OCT 2004
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner of Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Jonas N. Strickland Telephone No. 571-272-1700

Form PCT/ISA/210 (second sheet) (July 1998)

Continuation of B. FIELDS SEARCHED Item 3:
EAST, WEST search terms: sorbent, regeneration, mercury, acid, water, solvent, solution, liquid, reactivation

[19] 中华人民共和国国家知识产权局

[51] Int. Cl.
B01D 53/02 (2006.01)

[12] 发明专利申请公布说明书

[21] 申请号 200580037037.0

[43] 公开日 2007 年 10 月 3 日

[11] 公开号 CN 101048218A

[22] 申请日 2005.8.23
[21] 申请号 200580037037.0
[30] 优先权
[32] 2004.8.30 [33] US [31] 60/605,640
[32] 2005.8.22 [33] US [31] 11/209,163
[86] 国际申请 PCT/US2005/030018 2005.8.23
[87] 国际公布 WO2006/039007 英 2006.4.13
[85] 进入国家阶段日期 2007.4.27
[71] 申请人 能源与环境研究中心财团
地址 美国北达科他
[72] 发明人 爱德温·S·奥尔森
迈克尔·J·霍姆斯
约翰·H·帕夫利施
[74] 专利代理机构 中原信达知识产权代理有限责任公司
代理人 王海川 樊卫民

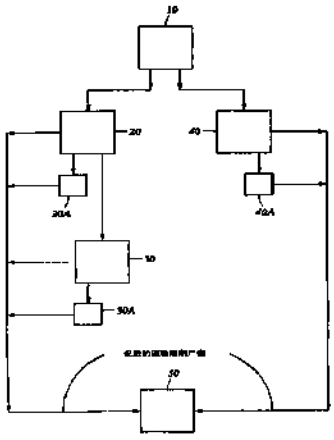
权利要求书 6 页 说明书 32 页 附图 7 页

[54] 发明名称

用于汞的氧化及清除的吸附剂

[57] 摘要

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



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

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

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

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

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

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

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

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

9. 权利要求 8 的促进的碳吸附剂，其中与基体活性碳结合时的促

PAC ET AL. EXHIBIT 1019
Page 1708

进剂基本上是蒸汽形式的。

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1709

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

20. 权利要求 19 的方法，其中促进剂与活性碳接触时是在气相中。

21. 权利要求 19 的方法，其中促进剂在接触活性碳时在有机溶剂中。

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

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

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

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

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

27. 权利要求 24 的方法，其中任选的次级组分包括 I_2 或 HI。

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

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

PAC ET AL. EXHIBIT 1019
Page 1710

SeO_2、CS_2、P_2S_5及其组合的汞稳定剂。

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

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

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

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

34. 权利要求33的方法，其中促进剂选自分子态卤素、卤化物及其组合。

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

36. 权利要求35的方法，其中促进剂在气相中或以蒸汽形式进行反应。

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

38. 权利要求37的方法，其中通过在气动运输管线内使活性碳、

PAC ET AL. EXHIBIT 1019
Page 1711

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

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

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1712

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

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1713

用于汞的氧化及清除的吸附剂

联邦政府资助的研究或开发声明

本发明是在美国政府支持下做出的，美国环境保护署的批准号为R 827649-01 和 CR 830929-01。美国政府拥有本发明的某些权利。

发明背景

发明技术领域

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

发明背景

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

汞吸附剂技术

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

PAC ET AL. EXHIBIT 1019
Page 1714

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

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

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

发明概述

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

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

PAC ET AL. EXHIBIT 1019
Page 1715

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1716

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1717

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1718

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

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

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

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

为了可以更好地理解随后对本发明的详细描述，前述内容已经相

PAC ET AL. EXHIBIT 1019
Page 1719

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

附图说明

本发明优选实施方案的更详细描述可参考所给出的附图。

图 1 示意性地例示根据本发明的促进的碳吸附剂的制备方法。

图 2 例示了提出的导致汞氧化及捕集的化学反应的机理模型。

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

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

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

图 6 为例示中试规模汞清除结果的条形图表，包括大尺寸吸附剂的结果。

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

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

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

图 10 为具有和不具有共注入的碱性物质时的汞清除对碳注入速率的图示。

优选实施方案的详细描述

PAC ET AL. EXHIBIT 1019
Page 1720

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1721

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1722

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1723

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1724

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1725

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1726

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1727

H_2Se、SeO_2、CS_2、P_2S_5以及它们的组合。

汞的捕集中的卤素

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

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

卤素促进的吸附剂特性

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

PAC ET AL. EXHIBIT 1019
Page 1728

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

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

任选的次级组分

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

任选的碱性组分

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

PAC ET AL. EXHIBIT 1019
Page 1729

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

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

“动态的”吸附剂制备

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

原位制备的优点

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

PAC ET AL. EXHIBIT 1019
Page 1730

●排除了处理设施的投资设备成本

●排除了操作处理设施的的成本

●没有关于将碳和添加剂运输到处理设施的成本

●本发明方法使用现有的硬件及操作步骤

●本发明技术确保吸附剂始终是新的，因此更具有活性

●没有引入新的处理方面的问题

●没有从处理系统中清除碳的成本

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

●本发明技术使需处理的用过的吸附剂量减少

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

吸附剂注入位置

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

吸附剂再生

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

PAC ET AL. EXHIBIT 1019
Page 1731

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

吸附剂注入控制方案

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

促进的碳吸附剂

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

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

实施例

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

PAC ET AL. EXHIBIT 1019
Page 1732

的限制。

实施例 1-制备及测试卤化的碳(及比较例)

气相卤化

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

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

汞的氧化及捕集效率的实验室规模测试

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

PAC ET AL. EXHIBIT 1019
Page 1733

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

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

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

实施例 2 -流态化碳的气相卤化

PAC ET AL. EXHIBIT 1019
Page 1734

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

实施例 3 -液相(水)卤化

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

实施例 4 -任选次级卤化物组分的加入

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

实施例 5-液相磷卤化

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

实施例 6-更大粒子碳的制备及其上的吸附

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

PAC ET AL. EXHIBIT 1019
Page 1735

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

处理-气相卤化

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

PTC 装置

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

PAC ET AL. EXHIBIT 1019
Page 1736

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

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

PTC 步骤

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1737

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

PTC 结果

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

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

实施例 7-液相(有机溶剂)卤化

将 50 g 溴小心地加入到 1 升冷的轻石油中，制备溴在轻石油中的

PAC ET AL. EXHIBIT 1019
Page 1738

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

实施例 8-促进的活性碳吸附剂

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

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

PAC ET AL. EXHIBIT 1019
Page 1739

实施例 9-流化/沸腾床制备

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

实施例 10-大规模测试

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

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

实施例 11A-任选的碱性组分的加入—实验室规模

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

制备由 37 mg 溴化的活性碳与 113 mg 氧化钙混合组成的过滤器，

PAC ET AL. EXHIBIT 1019
Page 1740

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

实施例 11B-任选的碱性组分的加入—中试规模

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

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

PAC ET AL. EXHIBIT 1019
Page 1741

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

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

5% Br2D-AC 的制备

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

5% PBr3-AC 的制备

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

氢气氛下的测试—步骤

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

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

PAC ET AL. EXHIBIT 1019
Page 1742

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

结果

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

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

PAC ET AL. EXHIBIT 1019
Page 1743

表 1

50%穿透的时间

观察到的吸附剂最大 Hg 浓度

(10% 氢流)

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1744

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1745

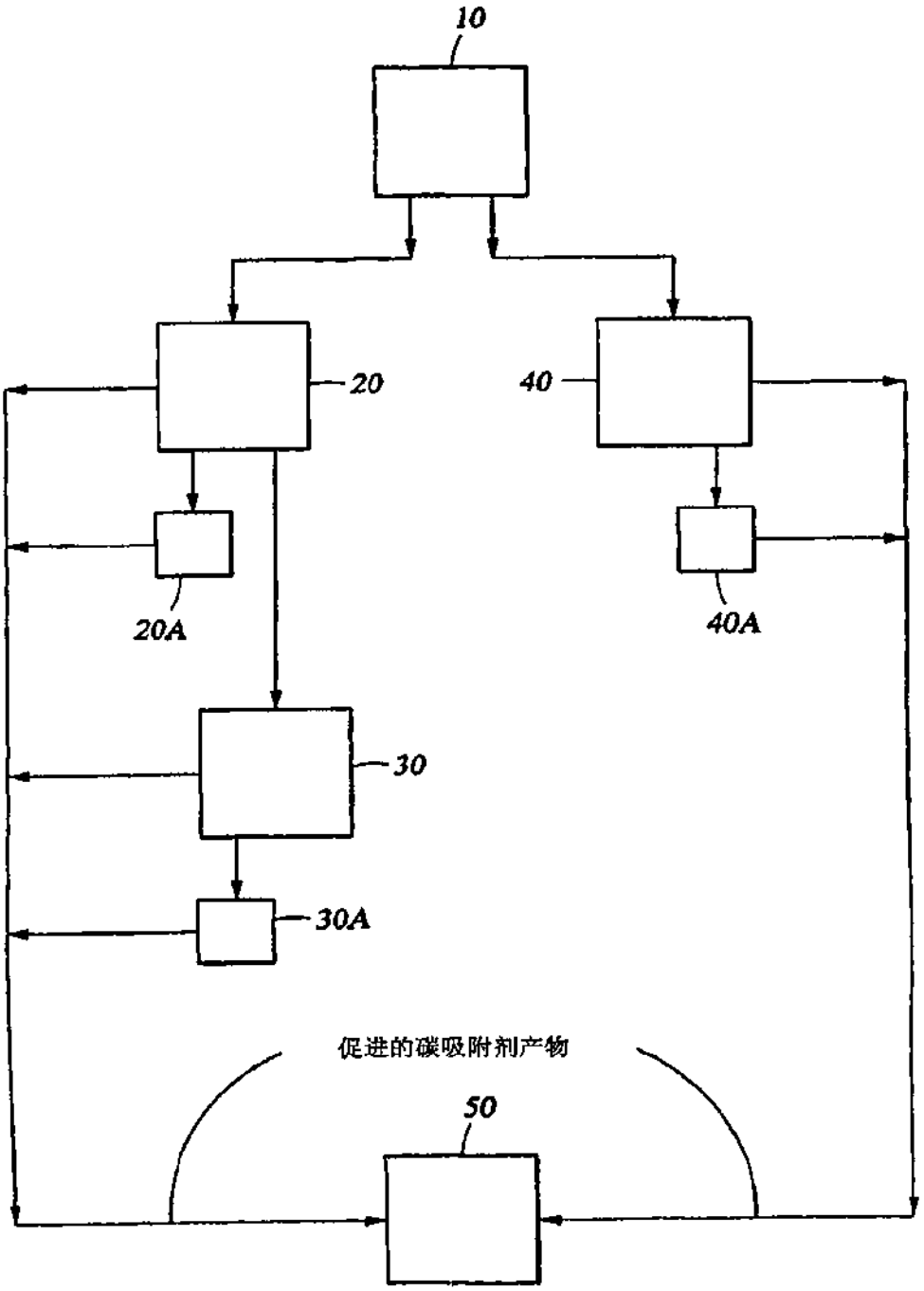


图1

PAC ET AL. EXHIBIT 1019
Page 1746

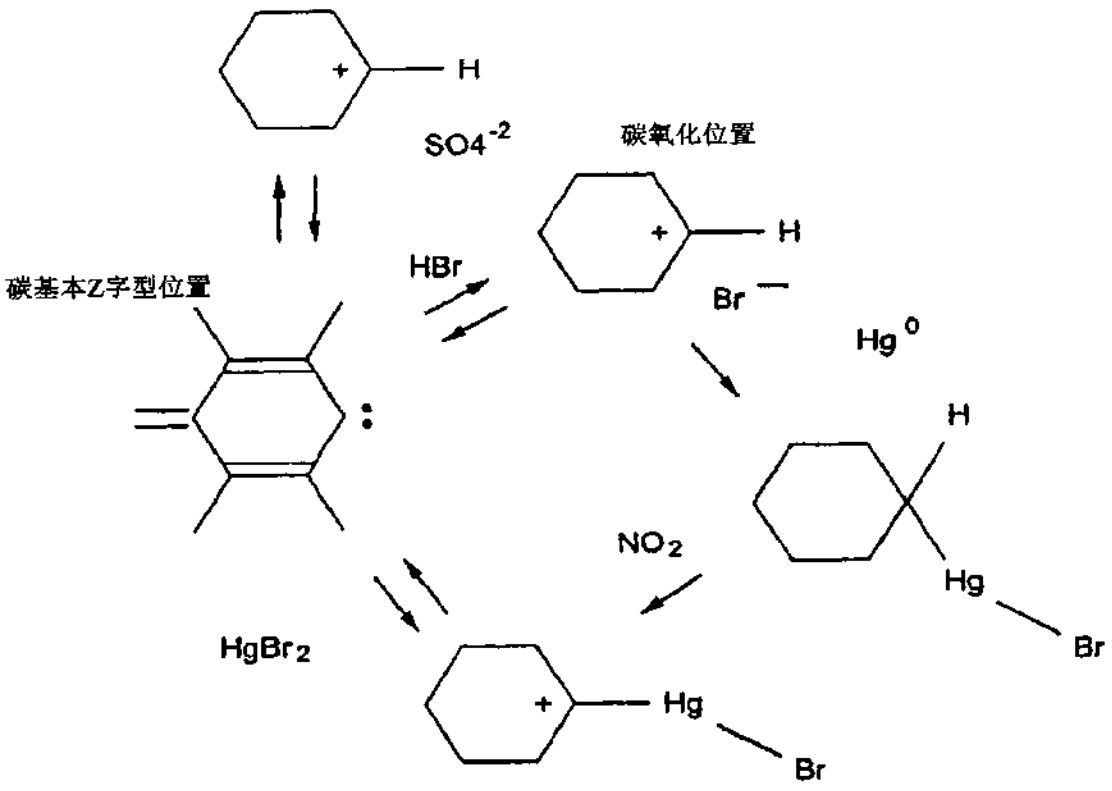


图2

PAC ET AL. EXHIBIT 1019
Page 1747

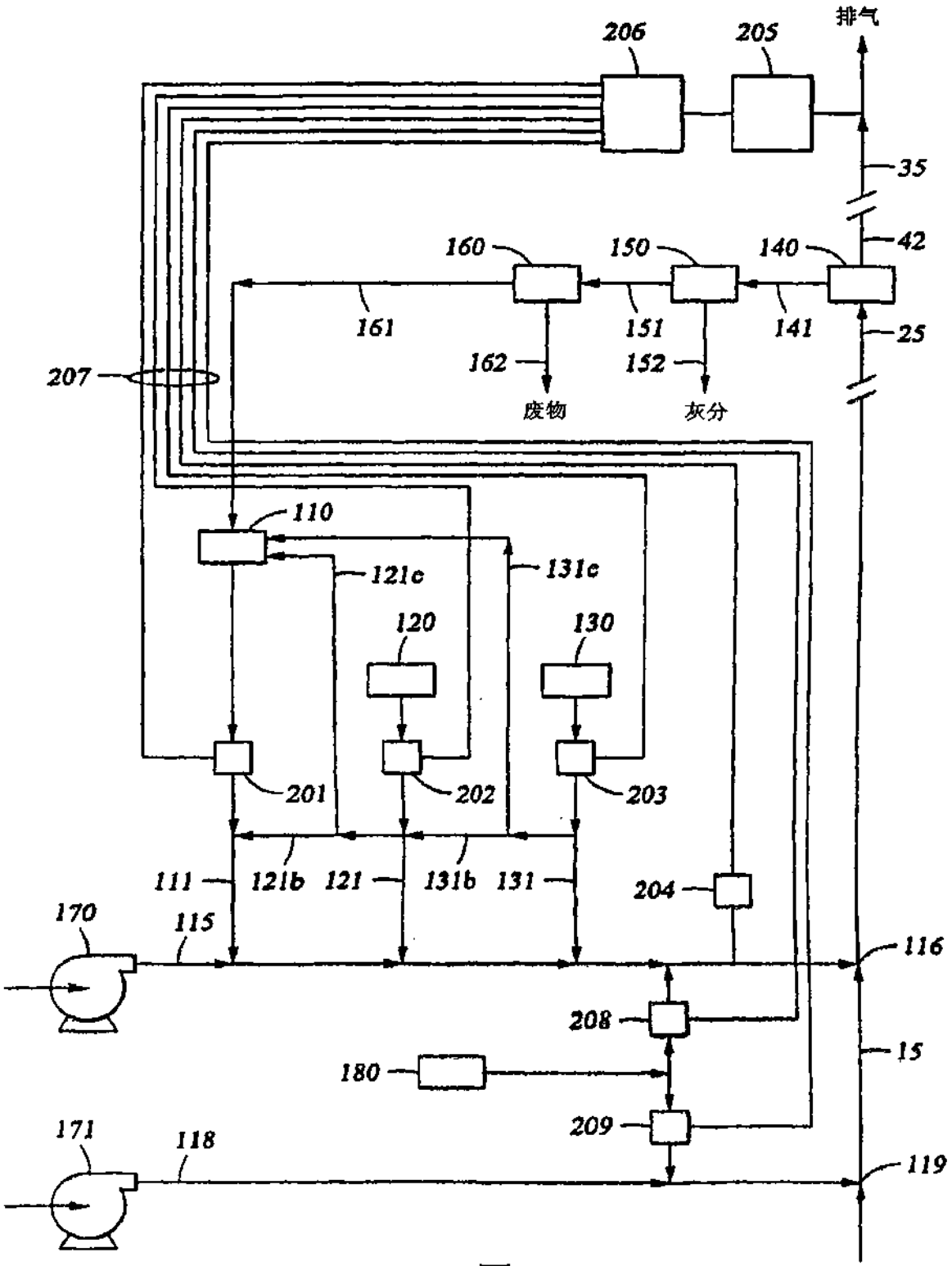


图3

PAC ET AL. EXHIBIT 1019
Page 1748

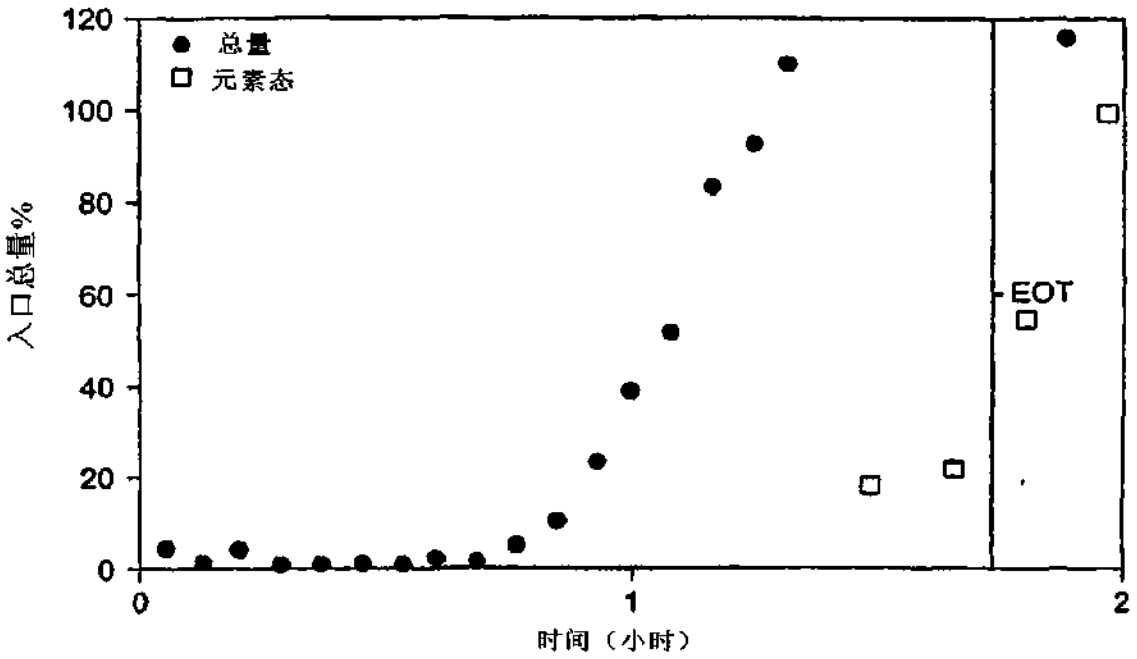


图4

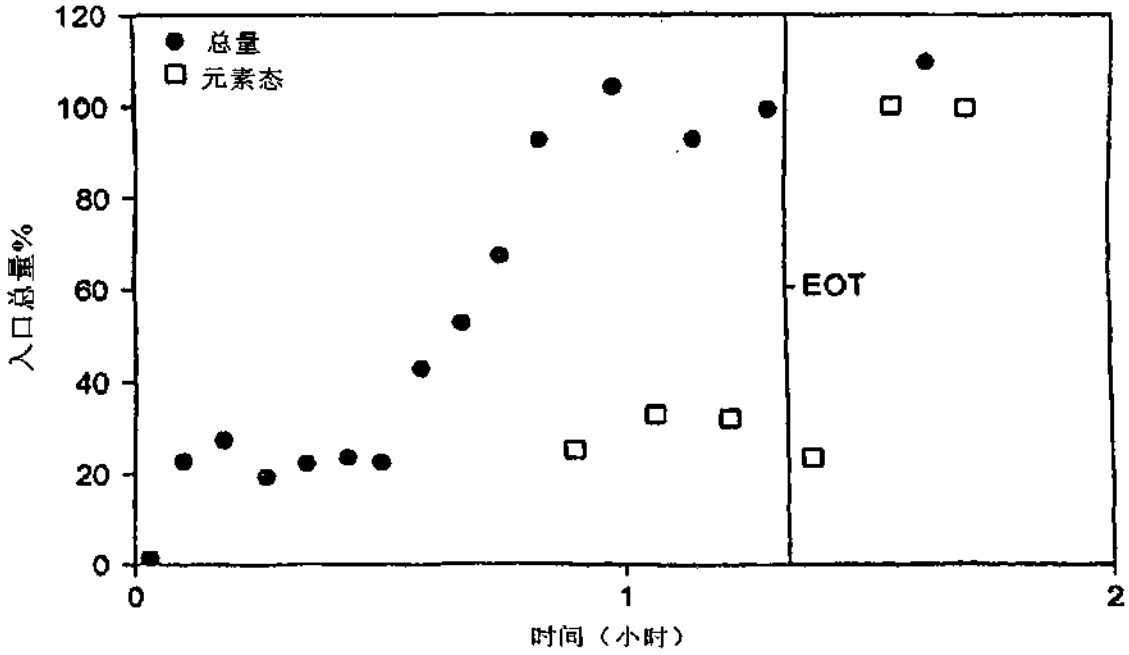


图5

PAC ET AL. EXHIBIT 1019
Page 1749

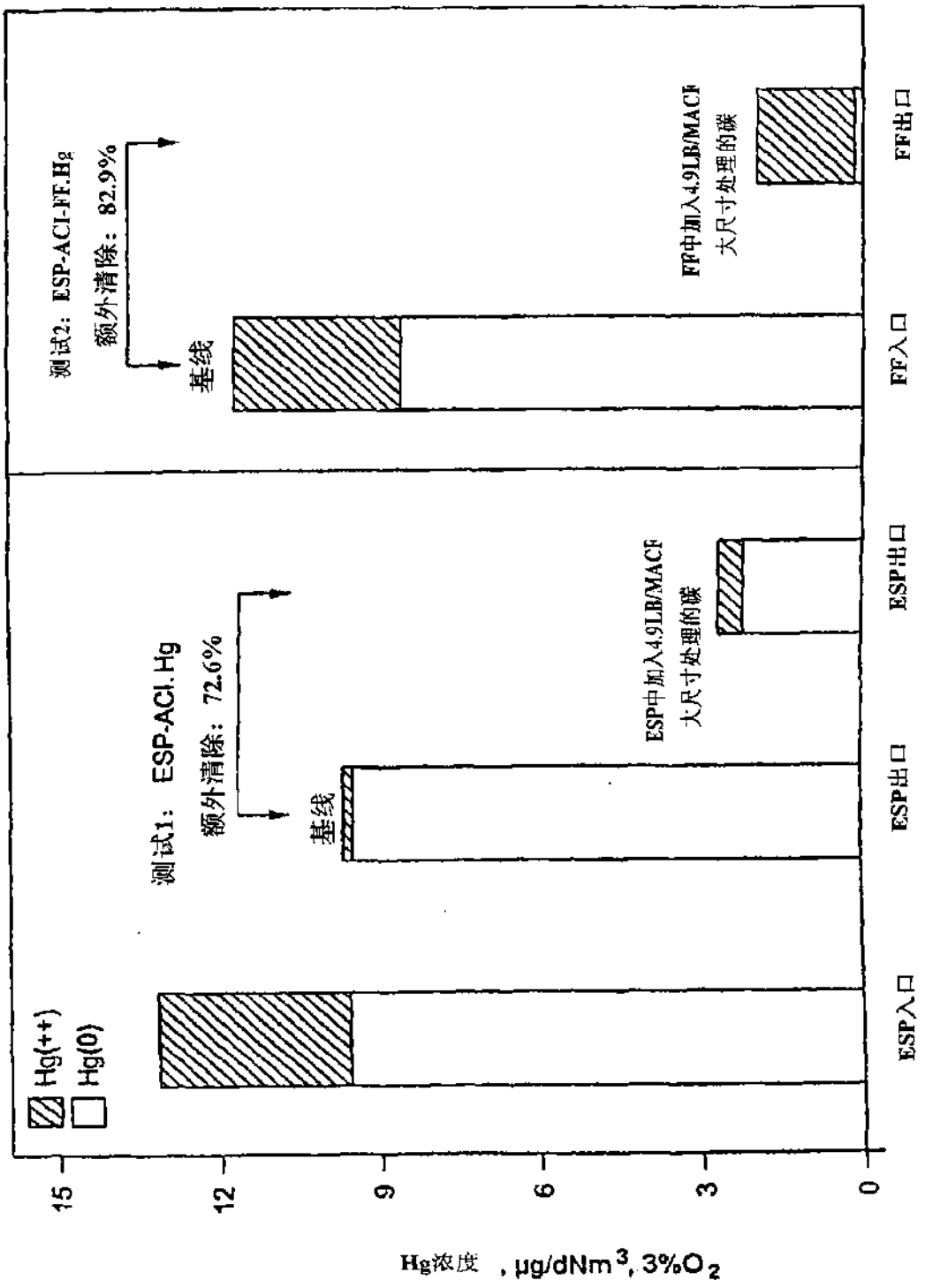


图6

PAC ET AL. EXHIBIT 1019
Page 1750

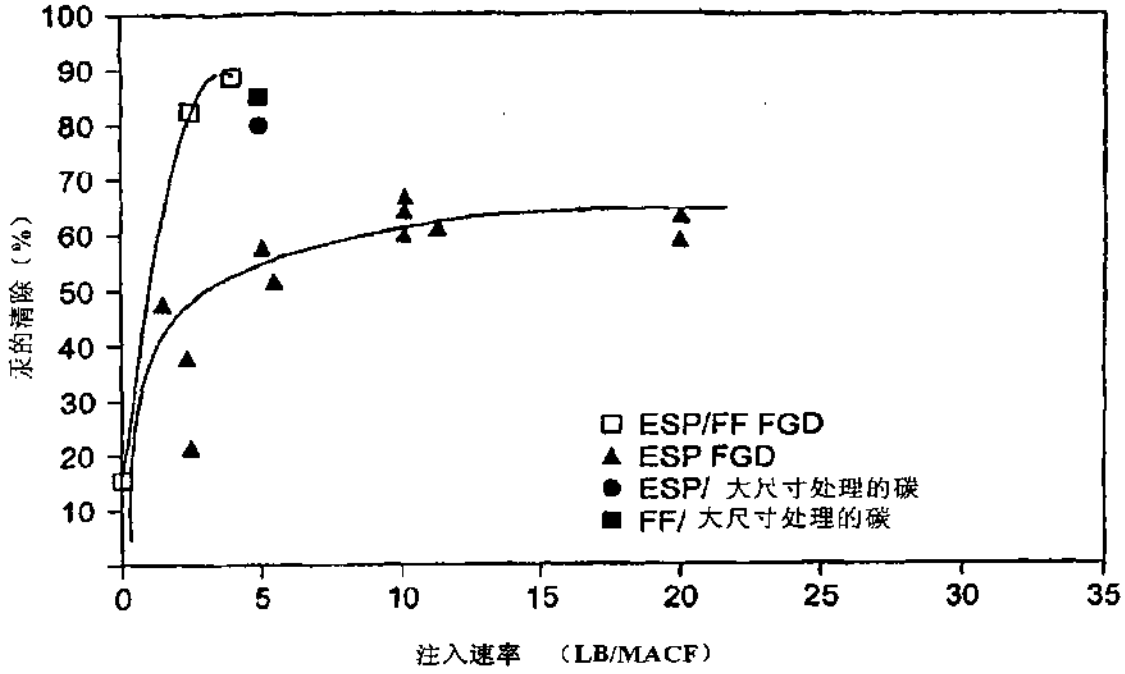


图7

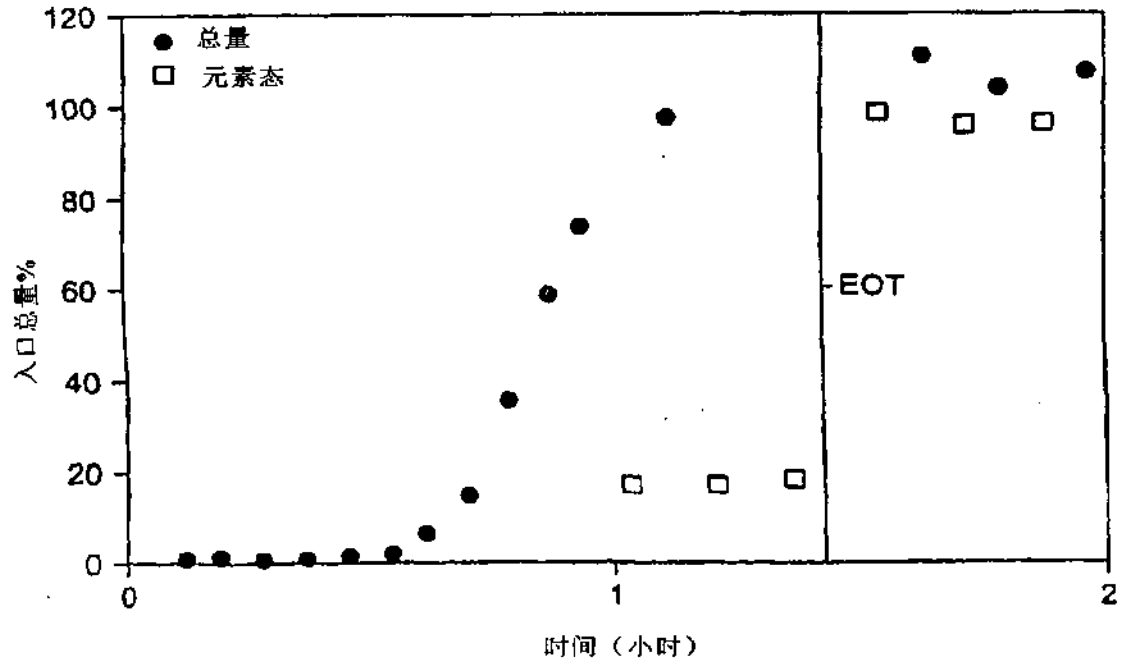


图8

PAC ET AL. EXHIBIT 1019
Page 1751

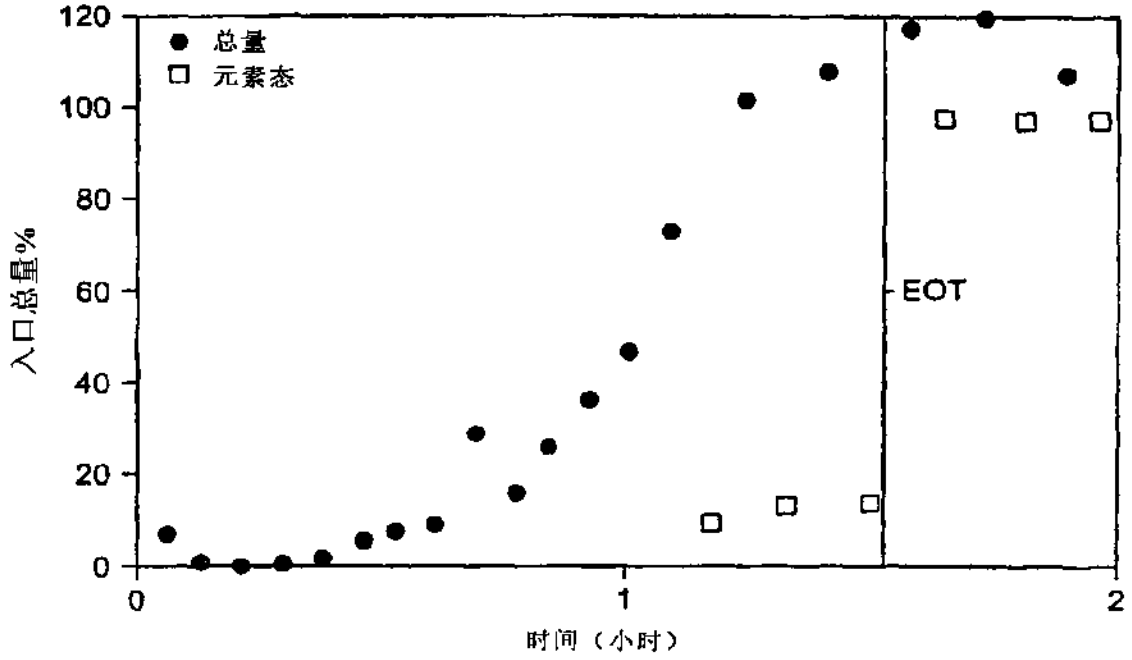


图9

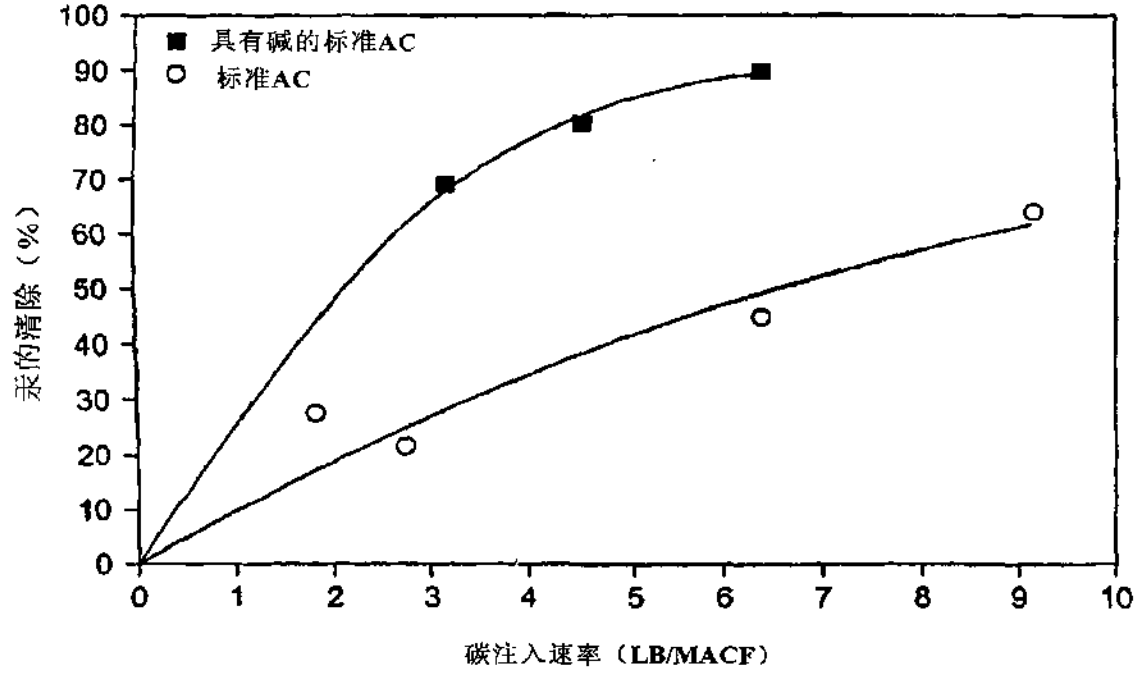


图10

PAC ET AL. EXHIBIT 1019
Page 1752

Electronic Acknowledgement Receipt

EFS ID:	32666563
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
Filer Authorized By:	Jordan Rivard Golomb
Attorney Docket Number:	4820.001US9
Receipt Date:	18-MAY-2018
Filing Date:	
Time Stamp:	16:05:25
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Non Patent Literature	0135_3338021us1_aarn_022216.pdf	289688 dd3eb3360dab3b1bc367f53e7cd1f97c6f9e3e62d	no	21

Warnings:

Information:					
2	Non Patent Literature	0136_3338021us1_aarf_051716.pdf	1125519 bf57ec7b4a5c5116bbfe384e8d271785745 9cc0c	no	15
Warnings:					
Information:					
3	Non Patent Literature	0139_3338005us6_foar_112516.pdf	984608 44387fb75a206ed594f5eb2ee5e5759ac4f4 f9c4	no	25
Warnings:					
Information:					
4	Non Patent Literature	0142_3338005us6_aarf_012517.pdf	107620 abf655cc23807116 3d48dd4b173011e5442 6ae3c	no	14
Warnings:					
Information:					
5	Non Patent Literature	0143_3338005us6_adaf_022717.pdf	100183 53dccaae95ffc8ffb3c6324b393c81553ce44 2e1	no	15
Warnings:					
Information:					
6	Non Patent Literature	0144_3338005us6_rrr1mo_030216.pdf	178234 39bc7f85a32042872 1f134b6d341535b34cf d252	no	9
Warnings:					
Information:					
7	Non Patent Literature	0145_3338005us6_aarn_082216.pdf	110525 ce26f565d7c837c9bec1644177619c42ddfa cd97	no	14
Warnings:					
Information:					
8	Non Patent Literature	0146_3338005us6_rerr_011416.pdf	304284 6a4bfad9c73b07da4d4d2ad82d1f585436f 1f00d	no	8
Warnings:					
Information:					

9	Non Patent Literature	0150_3338016us2_pamd_121014.pdf	108071 0eace732e44127941797b4a09a331514759 5b6e1	no	6
Warnings:					
Information:					
10	Non Patent Literature	0151_3338016us2_rrr1mo_050616.pdf	119566 3e23ec0db1430f922dc01ca416d38f3170f4 0bac	no	9
Warnings:					
Information:					
11	Non Patent Literature	0152_3338016us2_aarn_100316.pdf	422975 a890ad357636578aa4332f4ebd32fc24b28 35caf	no	11
Warnings:					
Information:					
12	Non Patent Literature	0158_4820001us7_aarf_012318.pdf	778557 e7725b326c5090ef9445da6db672d08e689 993df	no	13
Warnings:					
Information:					
13	Non Patent Literature	0159_4820001us7_aarf_040218.pdf	101248 d5bf171dcbe72ebbf892025805c525ca76b a1897	no	7
Warnings:					
Information:					
14	Non Patent Literature	0161_4820001us7_supamd_05152018.pdf	110670 5881a25b707d8d4ef65a362e9231722b7c2 4b6cc	no	6
Warnings:					
Information:					
15	Non Patent Literature	0162_4820001us7_pamd2_051515.pdf	154717 49b1fefc8f9c1f38c18dc81d7851267cc937e 58c	no	6
Warnings:					
Information:					

16	Non Patent Literature	0163_4820007us3_pamd_012617.pdf	253354 ac684a007d2e49628b63106c1bd1c3e66bd91fe2	no	8
Warnings:					
Information:					
17	Non Patent Literature	0164_4820007us3_pamd_061317.pdf	60068 a1b3645ce6a66fee5d563980e29b76d8b74f3719	no	7
Warnings:					
Information:					
18	Non Patent Literature	0165_3338031us1_pamd_040417.pdf	44929 765be4dce35df5b3d939861cd85c0199fca9aad2	no	3
Warnings:					
Information:					
19	Non Patent Literature	0169_4820005us1_aarn_011618.pdf	129915 e0dd972f2f2ac807426ed94b3ebe55f4d1534241	no	16
Warnings:					
Information:					
20	Non Patent Literature	0170_4820005us1_aarf_051418.pdf	168019 759fd6adbe7202d7d2b8a4973829e4d04af78530	no	13
Warnings:					
Information:					
21	Non Patent Literature	0171_4820005us1_aarf_040618.pdf	167892 91c6287f71a623f75071d57794aa094bf5ef7c27	no	13
Warnings:					
Information:					
22	Non Patent Literature	0172_3338016us3_pamd_030817.pdf	44311 54ec478c60506c0c2d3b364b086e66132f9a865c	no	3
Warnings:					
Information:					

23	Non Patent Literature	0174_4820003us2_pamd_010318.pdf	55143 c7ab10bdc2aa55901fae60add6bff2c7881c2b9a	no	6
Warnings:					
Information:					
24	Non Patent Literature	0175_3338013wo1.pdf	77322 d7f53505b268027837a7ff7ddee7abdfc06064f1	no	2
Warnings:					
Information:					
25	Non Patent Literature	0177_3338021us1_aarn_091616.pdf	95988 41ab3663331891cc309efed4ba6442d0a84e118f	no	12
Warnings:					
Information:					
26	Non Patent Literature	0178_bromine_and_its_compounds.pdf	1412781 3e7afd29f30576a129c22a411c2c5ed9f928d13d	no	4
Warnings:					
Information:					
27	Non Patent Literature	0179_ca_oa_7_18_11.pdf	278128 c88f8873a4cfa5611fa61fa1e20d15b338e3c40c	no	3
Warnings:					
Information:					
28	Non Patent Literature	0181_ca_office_action_03_03_09.pdf	723891 72541ee9220334b3b75b1faa63736aaa72f49aea	no	4
Warnings:					
Information:					
29	Non Patent Literature	0182_4820001ca1_oarmisc_120709.pdf	53920 2f6d2e9adfc6ec8606da8d3c117ca9ff67d6c116	no	2
Warnings:					
Information:					

30	Non Patent Literature	0183_4820001ca1_aarmisc_031910.pdf	273013 83c6a547e6c1eff8b252f4032043f42917ccca06	no	8
Warnings:					
Information:					
31	Non Patent Literature	0184_4820001ca1_aarmisc_090209.pdf	666230 fdcf820c8f919867a1e91e60a2bbb5e17b660d08	no	21
Warnings:					
Information:					
32	Non Patent Literature	0185_3338002ca1.pdf	96840 7ff822d2fcf6d5ba1ebe3ea9f78791a13de5e127	no	2
Warnings:					
Information:					
33	Non Patent Literature	0186_4820007ca1_oarmisc_120715.pdf	245718 8ddfbbfe2e5e47703e9cc6b3be8d36a9ab584e88	no	3
Warnings:					
Information:					
34	Non Patent Literature	0187_4820007ca1_aarmisc_060616.pdf	498287 d04ab4cf2b9b32c50f1d1a48a64fb9bc8fd1f24e	no	13
Warnings:					
Information:					
35	Non Patent Literature	0188_4820007ca1_vamd_013015.pdf	1206808 3ae16285c37fe6641199d9c46f838ccb68c58032	no	27
Warnings:					
Information:					
36	Non Patent Literature	0189_ca_response_02_26_16.pdf	676384 9a12db0bf2190123497d4b31061d27a3971a723f	no	13
Warnings:					
Information:					

37	Non Patent Literature	0190_ca_office_action_04_02_15.pdf	931853 0025cfbb4a20f69c9283f6288ac0fee62c14dde2	no	5
Warnings:					
Information:					
38	Non Patent Literature	0192_ca_office_action_09_09_15.pdf	799688 73c42aac682dd8fede18676313e55722945 65a01	no	3
Warnings:					
Information:					
39	Non Patent Literature	0196_ca_response_08_28_15.pdf	1337484 2b223f5ff693100ac95de157dae70e2126e0 9c6d	no	22
Warnings:					
Information:					
40	Non Patent Literature	0197_cn_notice_12_8_11.pdf	227226 1d83c587ba76485cbfadb4b7eab879144f2 6d9bb	no	6
Warnings:					
Information:					
41	Non Patent Literature	0199_200580037037.pdf	1980964 669dbbc8c685dcf92affcf4558e7402146f81 380	no	46
Warnings:					
Information:					
42	Non Patent Literature	0201_3338016cn1_aarmisc_01 1416.pdf	273322 874255688f17f6932a5d3e59656eeaddcd7 70030	no	7
Warnings:					
Information:					
43	Non Patent Literature	0202_4820003cn1_oarmisc_01 1618.pdf	432179 780cf305cd2ecfc651a1f0a92f3368b0feed2 b47	no	8
Warnings:					
Information:					

44	Non Patent Literature	0204_3338021cn1_oarmisc_072516.pdf	345880 b2ce0b803ebd3b3e79c6679c7be5f190b201a7cd	no	4
Warnings:					
Information:					
45	Non Patent Literature	0206_pages_from_20148002570 19aarmiscsolidated_correspondence_041217_137201704112.pdf	720660 0e070ef500f60bb727291b371835c0b4bba06220	no	24
Warnings:					
Information:					
46	Non Patent Literature	0207_4820003cn1aarn20180327.pdf	611918 e803c758fbd8b9d586d79b3ae62977a6c3aad3ce	no	20
Warnings:					
Information:					
47	Non Patent Literature	0208_20148002570 19aarmisc_092017_20170915.pdf	600891 3ebe5dd751017f6011b8a32213e6529c7ed3c120	no	21
Warnings:					
Information:					
48	Non Patent Literature	0210_jp_49_53593.pdf	657268 e6e97b39c148c684d96c5ff339bba4a615b6796e	no	4
Warnings:					
Information:					
49	Non Patent Literature	0211_ep_reply_09_09_11.pdf	2778099 2e070d272b02df4059b86a8dd30f45f07fcc56a4	no	20
Warnings:					
Information:					
50	Non Patent Literature	0212_4820001ep1_e2001_110509.pdf	136314 5114c15c37cb54199c5527df0f34b19d8a9a49b0	no	4
Warnings:					
Information:					

51	Non Patent Literature	0213_4820001ep1_decisiontogrant_060812.pdf	98488 79c610e840b0fb569a528eb3aa7ede5a9e8537cc	no	2
Warnings:					
Information:					
52	Non Patent Literature	0214_4820001ep1_eesr_041409.pdf	451109 a5a2f9925ccf2768e03444980 7fe6235e126f286	no	13
Warnings:					
Information:					
53	Non Patent Literature	0215_ep_oa_01_25_08.pdf	210808 603fffb3545fbcaacada93593664b76f1a7dd698	no	2
Warnings:					
Information:					
54	Non Patent Literature	0216_4820001ep1_e2001_013112.pdf	121685 bb82c8e4ef222925f7e31a97d1cb26f24b781ec1	no	4
Warnings:					
Information:					
55	Non Patent Literature	0217_4820001ep1_oarmisc_042712.pdf	218880 1ea6a2d0c0cf1a7f216c9f1681ba2f1a84ac9e38	no	6
Warnings:					
Information:					
56	Non Patent Literature	0218_ep_oa_11_05_09.pdf	579093 c7b60379d9c43f597a2205444fe986b5bf94cc64	no	4
Warnings:					
Information:					
57	Non Patent Literature	0219_ep_search_report_04_14_09.pdf	1932984 0d6ba60310dd1b100264f89e06d9167e7e5f89dc	no	13
Warnings:					
Information:					

58	Non Patent Literature	0220_4820001ep1_e2001ar_022812.pdf	1645796 923349db147a064b8767d40176a903c8b66ce84a	no	30
Warnings:					
Information:					
			Total Files Size (in bytes):	29317995	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
2380-01102		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2008/071986	**01 AUGUST 2008 (01.08.2008)**	01 AUGUST 2007 (01.08.2007)

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER et al

This International search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of :
      ☒ the international application in the language in which it was filed
      ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.
2. ☐ **Certain claims were found unsearchable** (See Box No. II)
3. ☐ **Unity of invention is lacking** (See Box No. III)
4. With regard to the **title**,
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established by this Authority to read as follows:
5. With regard to the **abstract**,
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. With regard to the drawings,
   a. the figure of the **drawings** to be published with the abstract is Figure No. 1
      ☒ as suggested by the applicant.
      ☐ because the applicant failed to suggest a figure.
      ☐ because this figure better characterizes the invention.
   b. ☐ none of the figure is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/071986

A. CLASSIFICATION OF SUBJECT MATTER

F17C 5/00(2006.01)i, B01D 53/00(2006.01)i, F02C 6/14(2006.01)i, E21B 21/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: F17C, F02C, C10G

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

Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS (KIPO internal) & keywords: "gas compressor", "gas turbine", "sulfur", "water" and "separate"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 09-256812 A (TOSHIBA CORP.) 30 September 1997 See the abstract and Claim 1.	1, 10
A	US 4,342,192 (KLAUS HEYN et al.) 3 August 1982 See the abstract and Fig. 1.	1, 10
A	US 7,017,330 B2 (JAMES C. BELLOWS) 28 March 2006 See the abstract and Fig. 1.	1, 10
A	KR 10-2002-0052209 A (JGC CORPORATION) 2 July 2002 See page 2, line 31 - page 6, line 1 and Fig. 3.	1, 10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 JANUARY 2009 (30.01.2009)	**30 JANUARY 2009 (30.01.2009)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea	HAN, JAE SEOB
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-5439

Form PCT/ISA/210 (second sheet) (July 2008)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2008/071986

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 09-256812 A	30.09.1997	NONE	
US 4342192	03.08.1982	CA 1134219 A1	26.10.1982
		DE 2850005 A1	29.05.1980
		DE 2931427 A1	19.02.1981
US 7017330 B2	28.03.2006	US 6804964	19.10.2004
		US 7431757	07.10.2008
		US 2004-0055309 A1	25.03.2004
		US 2005-039462 A1	24.02.2005
		US 6804964 B2	19.10.2004
KR 10-2002-0052209 A	02.07.2002	DE 60002602 D1	12.06.2003
		DE 60002602 T2	19.02.2004
		EP 1230323 B1	07.05.2003
		EP 1230323 A1	14.08.2002
		ES 2195942 T3	16.12.2003
		JP 2001-140656 A	22.05.2001
		TW 477812 B	01.03.2002
		TW 477812 A	01.03.2002
		US 6786050 B1	07.09.2004
		WO 01-36566 A1	25.05.2001

PATENT COOPERATION TREATY

PCT

REC'D 29 JAN 2007
WIPO PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2380-00201	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/US05/30018	International filing date *(day/month/year)* 23 August 2005 (23.08.2005)	Priority date *(day/month/year)* 30 August 2004 (30.08.2004)

International Patent Classification (IPC) or national classification and IPC

IPC: **B01D 53/02**(2006.01)
USPC: 95/13,107,134

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 3 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 5 sheets, as follows:
      ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) _____ , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).
4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
25 October 2006 (25.10.2006)	27 December 2006 (27.12.2006)
Name and mailing address of the IPEA/ US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (571) 273-3201	Authorized officer Robert A. Hopkins Telephone No. 571-272-1700

DEBORAH A. THOMAS
PARALEGAL SPECIALIST

Form PCT/IPEA/409 (cover sheet)(April 2005)

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US05/30018

Box No. I Basis of the report

1. With regard to the **language**, this report is based on:
   - ☒ the international application in the language in which it was filed.
   - ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of:
     - ☐ international search (under Rules 12.3 and 23.1(b))
     - ☐ publication of the international application (under Rule 12.4(a))
     - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:
   - ☐ the international application as originally filed/furnished
   - ☒ the description:
     pages 1-28 as originally filed/furnished
     pages* NONE received by this Authority on _____
     pages* NONE received by this Authority on _____
   - ☒ the claims:
     pages NONE as originally filed/furnished
     pages* NONE as amended (together with any statement) under Article 19
     pages* 29-33 received by this Authority on 25 October 2006 (25.10.2006)
     pages* NONE received by this Authority on _____
   - ☒ the drawings:
     pages 1-7 as originally filed/furnished
     pages* NONE received by this Authority on _____
     pages* NONE received by this Authority on _____
   - ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☒ The amendments have resulted in the cancellation of:
   - ☒ the description, pages NONE
   - ☒ the claims, Nos. 48-54
   - ☒ the drawings, sheets/figs NONE
   - ☐ the sequence listing (*specify*): _____
   - ☐ any table(s) related to the sequence listing (*specify*): _____

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages _____
   - ☐ the claims, Nos. _____
   - ☐ the drawings, sheets/figs _____
   - ☐ the sequence listing (*specify*): _____
   - ☐ any table(s) related to the sequence listing (*specify*): _____

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US05/30018

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 34-47	YES
	Claims 1-33	NO
Inventive Step (IS)	Claims 34-47	YES
	Claims 1-33	NO
Industrial Applicability (IA)	Claims 1-47	YES
	Claims NONE	NO

2. Citations and Explanations (Rule 70.7)

Claims 1-33 lack novelty under PCT Article 33(2) as being anticipated by NISHINO ET AL. Note the base activated carbon and impregnated halide or halogen. Note also the optional secondary component including an alkaline earty salt. Note also the use of an organic solvent(ethanol). Note also the activated carbon with promoter is used for removal of mercury vapor. Note also the sorbent is either a fixed bed, moving bed, or fluidized bed sorbent. Note also the mercury content of the flue gas is monitored, and the sorbetn is recovered from the clean gas. Examiner also notes that the amendment "wherein the composition of the promoted carbon sorbent is controlled by the mercury content of the cleaned gas stream" does not have patentable weight upon a product claim(claim 1) and a method of making a product claim(claim 17)

Claims 1 and 17 lack novelty under PCT Article 33(2) as being anticipated by REVOIR ET AL. REVOIR ET AL teaches a base activated carbon and impregnated halide or halogen. Examiner also notes that the amendment "wherein the composition of the promoted carbon sorbent is controlled by the mercury content of the cleaned gas stream" does not have patentable weight upon a product claim(claim 1) and a method of making a product claim(claim 17).

Claims 1-47 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

Claims 34-47 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest a step of preparing the sorbent by in-flight reaction of the base activated carbon with the at least one component within a transport line from which the reaction product is injected into the mercury containing gas stream.

---------- NEW CITATIONS ----------

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US05/30018

A. CLASSIFICATION OF SUBJECT MATTER
IPC: **B01D 53/02**(2006.01)

USPC: 95/13,107,134
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 95/13,107,134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,500,327 A (NISHINO et al) 19 February 1985, column 1 lines 66-68, column 2 lines 9-17, column 2 lines 34-38.	1-54
X	US 3,662,523A (REVOIR et al) 16 May 1972, column 1 lines 5-10, lines 62-69, column 2 lines 1-11.	1,16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search
12 June 2006 (12.06.2006)

Date of mailing of the international search report
25 JUL 2006

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
Facsimile No. (571) 273-3201

Authorized officer
Robert A. Hopkins
Telephone No. 703-872-9306

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

Continuation of B. FIELDS SEARCHED Item 3:
EAST

search terms: activated adj carbon, halide, halogen, mercury, sorbent, adsorption , adsorb

PATENT COOPERATION TREATY

REC'D 28 JUL 2006
PCT

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
TIMOTHY S. WESTBY
CONLEY ROSE, P.C.
P.O. BOX 3267
HOUSTON, TX 77253-3267

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing (*day/month/year*)	25 JUL 2006
Applicant's or agent's file reference 2380-00201	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date (*day/month/year*)	Priority date (*day/month/year*)
PCT/US05/30018	23 August 2005 (23.08.2005)	30 August 2004 (30.08.2004)

International Patent Classification (IPC) or both national classification and IPC

IPC: **B01D 53/02**(2006.01)
USPC: 95/13,107,134

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

1. This opinion contains indications relating to the following items:

- [X] Box No. I — Basis of the opinion
- [ ] Box No. II — Priority
- [ ] Box No. III — Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- [ ] Box No. IV — Lack of unity of invention
- [X] Box No. V — Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- [ ] Box No. VI — Certain documents cited
- [ ] Box No. VII — Certain defects in the international application
- [ ] Box No. VIII — Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(*b*) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA/ US	Date of completion of this opinion	Authorized officer
Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (571) 273-3201	12 June 2006 (12.06.2006)	Robert A. Hopkins Telephone No. 703-872-9306

Form PCT/ISA/237 (cover sheet) (April 2005)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US05/30018

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:

☒ the international application in the language in which it was filed

☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:

a. type of material

☐ a sequence listing

☐ table(s) related to the sequence listing

b. format of material

☐ on paper

☐ in electronic form

c. time of filing/furnishing

☐ contained in the international application as filed.

☐ filed together with the international application in electronic form.

☐ furnished subsequently to this Authority for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table(s) relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US05/30018

Box No. V Reasoned statement under Rule 43 *bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims NONE	YES
	Claims 1-54	NO
Inventive step (IS)	Claims NONE	YES
	Claims 1-54	NO
Industrial applicability (IA)	Claims 1-54	YES
	Claims NONE	NO

2. Citations and explanations:

Claims 1-54 are novelty under PCT Article 33(2) as being anticipated by NISHINO ET AL. Note the base activated carbon and impregnated halide or halogen. Note also the optional secondary component including an alkaline earty salt. Note also the use of an organic solvent(ethanol). Note also the activated carbon with promoter is used for removal of mercury vapor. Note also the sorbent is either a fixed bed, moving bed, or fluidized bed sorbent. Note also the mercury content of the flue gas is monitored, and the sorbetn is recovered from the clean gas.

Claims 1 and 16 lack novelty under PCT Article 33(2) as being anticipated by REVOIR ET AL. REVOIR ET AL teaches a base activated carbon and impregnated halide or halogen.

Claims 1-54 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING TRANSMITTAL OF COPY OF INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (CHAPTER I OF THE PATENT COOPERATION TREATY)
(PCT Rule 44bis.1(c))

To:

KOWALCHYK, Katherine, M.
Merchant & Gould P.C.
P.O. Box 2903
Minneapolis, MN 55402-0903
ETATS-UNIS D'AMERIQUE

Date of mailing *(day/month/year)*
03 November 2011 (03.11.2011)

Applicant's or agent's file reference
16291.3WOI1

IMPORTANT NOTICE

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2010/022807	02 February 2010 (02.02.2010)	23 April 2009 (23.04.2009)

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION et al

The International Bureau transmits herewith a copy of the international preliminary report on patentability (Chapter I of the Patent Cooperation Treaty)

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. +41 22 338 82 70

Authorized officer
Lingfei Bai

e-mail: pt02.pct@wipo.int

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference 16291.3WOI1	**FOR FURTHER ACTION**	See item 4 below
International application No. PCT/US2010/022807	International filing date *(day/month/year)* 02 February 2010 (02.02.2010)	Priority date *(day/month/year)* 23 April 2009 (23.04.2009)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 *bis*.1(a).

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44*bis*.3(c) and 93*bis*.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44*bis* .2).

	Date of issuance of this report 25 October 2011 (25.10.2011)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. +41 22 338 82 70	Authorized officer Lingfei Bai e-mail: pt02.pct@wipo.int

Form PCT/IB/373 (January 2004)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
KOWALCHYK KATHERINE M.

MERCHANT & GOULD P.C. P.O. BOX 2903
MINNEAPOLIS MN 55402-0903 USA

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Date of mailing *(day/month/year)*	**13 SEPTEMBER 2010 (13.09.2010)**
Applicant's or agent's file reference 16291.3WO01	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2010/022807	**02 FEBRUARY 2010 (02.02.2010)**	23 APRIL 2009 (23.04.2009)

International Patent Classification (IPC) or both national classification and IPC

B01D 53/02(2006.01)i, B01D 53/64(2006.01)i, F23J 15/00(2006.01)i

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION et al

1. This opinion contains indications relating to the following items:

- [x] Box No. I Basis of the opinion
- [ ] Box No. II Priority
- [ ] Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- [ ] Box No. IV Lack of unity of invention
- [x] Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement
- [ ] Box No. VI Certain documents cited
- [ ] Box No. VII Certain defects in the international application
- [ ] Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.
For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA/KR	Date of completion of this opinion	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302 -701, Republic of Korea Facsimile No. 82-42-472-7140	13 SEPTEMBER 2010 (13.09.2010)	JO Soo Ik Telephone No.82-42-481-5893

Form PCT/ISA/237 (cover sheet) (July 2009)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2010/022807

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of :

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into _____ , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of:

   a. a sequence listing filed or furnished
      ☐ on paper
      ☐ in electronic form

   b. time of filing or furnishing
      ☐ contained in the international application as filed.
      ☐ filed together with the international application in electronic form.
      ☐ furnished subsequently to this Authority for the purposes of search.

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additioanl copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2010/022807

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	NONE	YES
	Claims	1-35	NO
Inventive step (IS)	Claims	NONE	YES
	Claims	1-35	NO
Industrial applicability (IA)	Claims	1-35	YES
	Claims	NONE	NO

2. Citations and explanations :

Reference is made to the following documents:

D1: US 2009-0062119 A1 (OLSON EDWIN S. et al.) 05 March 2009
D2: US 2006-0204418 A1 (CHIEN-CHUNG CHAO et al.) 14 September 2006
D3: US 2007-0234902 A1 (DAVID FAIR et al.) 11 October 2007

1. Novelty & Inventive Step

Claims [1-35] relate to a method for separating mercury from mercury containg gas.

D1 discloses 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.(See the abstract, fig. 1~10, Paragraph [10] ~ Paragraph [134], whole claims)

D2 discloses a catalytic adsorbents for use in the removal of mercury from flue gas streams and methods of manufacturing such catalytic adsorbents.(See the abstract, Paragraph [33] ~ Paragraph [101])

D3 discloses a method for removing mercury from a flue gas stream of the present invention is comprised of first treating a sorbent with a metal halide, and then contacting a sufficient amount of the sorbent with a gas stream for a sufficient amount of time to bind with a desired amount of the mercury in said gas stream.(See the whole document).

1.1 Claims [1-35]

1.1.1 Concerning Claim [1]

Document D1 which is considered to represent the most relevant state of the art, disclose a method of using a sorbent, a halogen promoter, a reaction process for promted halogen sorbent, a separation process.

As all of the features of claim [1] are disclosed in D1 this claim is anticipated by D1. Therefore, claim [1] lacks novelty under PCT Article 33(2).

1.1.2 Concerning Claims [2-11]

The additional feature of claims [2-11] dependent on claim [1] such as a injection and introduction of sorbent, promoter, a rate control are disclosed in D1, this claim is anticipated by D1. Therefore, claims [2-11] lack novelty under PCT Article 33(2).

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of :

Box V

1.1.3 Concerning Claims [12-22]

The additional feature of claims [12-22] dependent on claim [1] such as a activated carbon sorbent, non carbon based sorbents, lewis base, acid group, alkaline, inorganic, sobents are disclosed in D1, this claim is anticipated by D1. Therefore, claims [12-22] lack novelty under PCT Article 33(2).

1.1.4 Concerning Claims [23-28]

The additional feature of claims [23-28] dependent on claim [1] such as carbon and non carbon promoters, a reaction process with noncarbon lewis base, acid group, alkaline, inorganic, promoted sorbent are disclosed in D1, this claim is anticipated by D1. Therefore, claims [23-28] lack novelty under PCT Article 33(2).

1.1.5 Concerning Claims [29-32]

The additional feature of claims [29-32] dependent on claim [1] such as vacuum, chmical, alkaline pretreatment process and alkaline introduction are disclosed in D1, this claim is anticipated by D1. Therefore, claims [29-32] lack novelty under PCT Article 33(2).

1.1.6 Concerning Claims [33-35]

The additional feature of claims [33-35] dependent on claim [1] such as a promoted carbon sorbent and mercury level control are disclosed in D1, this claim is anticipated by D1. Therefore, claims [33-35] lack novelty under PCT Article 33(2).

2. Industrial Applicability

The subject matter of claims [1-35] are considered to be industrially applicable under PCT Article 33(4).

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
16291.3WO11		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2010/022807	**02 FEBRUARY 2010 (02.02.2010)**	23 APRIL 2009 (23.04.2009)

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION et al

This International search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of **3** sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of :
      ☒ the international application in the language in which it was filed
      ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.
2. ☐ **Certain claims were found unsearchable** (See Box No. II)
3. ☐ **Unity of invention is lacking** (See Box No. III)
4. With regard to the **title,**
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established by this Authority to read as follows:
5. With regard to the **abstract,**
   ☒ the text is approved as submitted by the applicant.
   ☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. With regard to the drawings,
   a. the figure of the **drawings** to be published with the abstract is Figure No. **3**
      ☐ as suggested by the applicant.
      ☒ as selected by this Authority, because the applicant failed to suggest a figure.
      ☐ as selected by this Authority, because this figure better characterizes the invention.
   b. ☐ none of the figure is to be published with the abstract.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/022807

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/02(2006.01)i, B01D 53/64(2006.01)i, F23J 15/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D 53/02; C01B 31/08; B01J 8/00; B01J 20/00

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: sorbent, mercury, flue gas, halogen promoter

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009-0062119 A1 (OLSON EDWIN S. et al.) 05 March 2009 See the abstract, fig. 1-10, Paragraph [101] - Paragraph [134], whole claims	1-35
A	US 2006-0204418 A1 (CHIEN-CHUNG CHAO et al.) 14 September 2006 See the abstract, Paragraph [38] - Paragraph [101]	1-35
A	US 2007-0234902 A1 (DAVID FAIR et al.) 11 October 2007 See the whole document	1-35

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 SEPTEMBER 2010 (13.09.2010)	**13 SEPTEMBER 2010 (13.09.2010)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	JO Soo Ik Telephone No. 82-42-481-5893

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2010/022807

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009-0062119 A1	05.03.2009	None	
US 2006-0204418 A1	14.09.2006	CA 2600876-A1	21.09.2006
		CN 101175692 A0	07.05.2008
		EP 1866245 A2	19.12.2007
		KR 10-2007-0113287 A	28.11.2007
		MX 2007011233 A	08.11.2007
		US 2006-0205592 A1	14.09.2006
		WO 2006-099291 A2	21.09.2006
		WO 2006-099291 A3	21.09.2006
US 2007-0234902 A1	11.10.2007	WO 2007-112248 A2	04.10.2007
		WO 2007-112248 A3	13.12.2007
		WO 2007-112248 A3	04.10.2007

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:
KOWALCHYK KATHERINE M.

MERCHANT & GOULD P.C. P.O. BOX 2903
MINNEAPOLIS MN 55402-0903 USA

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

Date of mailing *(day/month/year)*	**13 SEPTEMBER 2010 (13.09.2010)**
Applicant's or agent's file reference 16291.3WO01	**FOR FURTHER ACTION** See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2010/022807	**02 FEBRUARY 2010 (02.02.2010)**	23 APRIL 2009 (23.04.2009)

International Patent Classification (IPC) or both national classification and IPC

B01D 53/02(2006.01)i, B01D 53/64(2006.01)i, F23J 15/00(2006.01)i

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION et al

1. This opinion contains indications relating to the following items:

- [x] Box No. I Basis of the opinion
- [ ] Box No. II Priority
- [ ] Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- [ ] Box No. IV Lack of unity of invention
- [x] Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement
- [ ] Box No. VI Certain documents cited
- [ ] Box No. VII Certain defects in the international application
- [ ] Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.
For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA/KR	Date of completion of this opinion	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302 -701, Republic of Korea Facsimile No. 82-42-472-7140	13 SEPTEMBER 2010 (13.09.2010)	JO Soo Ik Telephone No.82-42-481-5893

Form PCT/ISA/237 (cover sheet) (July 2009)

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2010/022807

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of :

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into _____ , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43*bis*.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of:

   a. a sequence listing filed or furnished
      ☐ on paper
      ☐ in electronic form

   b. time of filing or furnishing
      ☐ contained in the international application as filed.
      ☐ filed together with the international application in electronic form.
      ☐ furnished subsequently to this Authority for the purposes of search.

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additioanl copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/US2010/022807

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	NONE	YES
	Claims	1-35	NO
Inventive step (IS)	Claims	NONE	YES
	Claims	1-35	NO
Industrial applicability (IA)	Claims	1-35	YES
	Claims	NONE	NO

2. Citations and explanations :

Reference is made to the following documents:

D1: US 2009-0062119 A1 (OLSON EDWIN S. et al.) 05 March 2009
D2: US 2006-0204418 A1 (CHIEN-CHUNG CHAO et al.) 14 September 2006
D3: US 2007-0234902 A1 (DAVID FAIR et al.) 11 October 2007

1. Novelty & Inventive Step

Claims [1-35] relate to a method for separating mercury from mercury containg gas.

D1 discloses 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.(See the abstract, fig. 1~10, Paragraph [10] ~ Paragraph [134], whole claims)

D2 discloses a catalytic adsorbents for use in the removal of mercury from flue gas streams and methods of manufacturing such catalytic adsorbents.(See the abstract, Paragraph [33] ~ Paragraph [101])

D3 discloses a method for removing mercury from a flue gas stream of the present invention is comprised of first treating a sorbent with a metal halide, and then contacting a sufficient amount of the sorbent with a gas stream for a sufficient amount of time to bind with a desired amount of the mercury in said gas stream.(See the whole document).

1.1 Claims [1-35]

1.1.1 Concerning Claim [1]

Document D1 which is considered to represent the most relevant state of the art, disclose a method of using a sorbent, a halogen promoter, a reaction process for promted halogen sorbent, a separation process.

As all of the features of claim [1] are disclosed in D1 this claim is anticipated by D1. Therefore, claim [1] lacks novelty under PCT Article 33(2).

1.1.2 Concerning Claims [2-11]

The additional feature of claims [2-11] dependent on claim [1] such as a injection and introduction of sorbent, promoter, a rate control are disclosed in D1, this claim is anticipated by D1. Therefore, claims [2-11] lack novelty under PCT Article 33(2).

Supplemental Box

In case the space in any of the preceding boxes is not sufficient.
Continuation of :

Box V

1.1.3 Concerning Claims [12-22]

The additional feature of claims [12-22] dependent on claim [1] such as a activated carbon sorbent, non carbon based sorbents, lewis base, acid group, alkaline, inorganic, sobents are disclosed in D1, this claim is anticipated by D1. Therefore, claims [12-22] lack novelty under PCT Article 33(2).

1.1.4 Concerning Claims [23-28]

The additional feature of claims [23-28] dependent on claim [1] such as carbon and non carbon promoters, a reaction process with noncarbon lewis base, acid group, alkaline, inorganic, promoted sorbent are disclosed in D1, this claim is anticipated by D1. Therefore, claims [23-28] lack novelty under PCT Article 33(2).

1.1.5 Concerning Claims [29-32]

The additional feature of claims [29-32] dependent on claim [1] such as vacuum, chmical, alkaline pretreatment process and alkaline introduction are disclosed in D1, this claim is anticipated by D1. Therefore, claims [29-32] lack novelty under PCT Article 33(2).

1.1.6 Concerning Claims [33-35]

The additional feature of claims [33-35] dependent on claim [1] such as a promoted carbon sorbent and mercury level control are disclosed in D1, this claim is anticipated by D1. Therefore, claims [33-35] lack novelty under PCT Article 33(2).

2. Industrial Applicability

The subject matter of claims [1-35] are considered to be industrially applicable under PCT Article 33(4).

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
3338021WO1		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2014/019916	3 March 2014 (03-03-2014)	6 March 2013 (06-03-2013)

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 8 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the language, the international search was carried out on the basis of:
      ☒ the international application in the language in which it was filed
      ☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))
   b. ☐ This international search report has been established taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).
   c. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box No. II)

3. ☒ **Unity of invention is lacking** (see Box No III)

4. With regard to the title,
   ☒ the text is approved as submitted by the applicant
   ☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,
   ☒ the text is approved as submitted by the applicant
   ☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the drawings,
   a. the figure of the drawings to be published with the abstract is Figure No. _____
      ☐ as suggested by the applicant
      ☐ as selected by this Authority, because the applicant failed to suggest a figure
      ☐ as selected by this Authority, because this figure better characterizes the invention
   b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/019916

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

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

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

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

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

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

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

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

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

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

1-49(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/019916

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/20 B01D53/02 B01D53/10 B01J20/32 C01B31/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C01B B01D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YUANJING ZHENG ET AL: "Review of technologies for mercury removal from flue gas from cement production processes", PROGRESS IN ENERGY AND COMBUSTION SCIENCE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 38, no. 5, 26 April 2012 (2012-04-26), pages 599-629, XP028415255, ISSN: 0360-1285, DOI: 10.1016/J.PECS.2012.05.001 [retrieved on 2012-05-25]	1-9, 16-25, 38,39, 48,49
Y	page 600, paragraph 1 page 615, paragraph 4.2.5.1 page 615, right-hand column, line 1 - line 4 "...by impregnation of nitrogen-containing polymers or pitches ..."; page 616, left-hand column 2nd paragraph; -/--	5-9, 16-25, 38,39, 48,49

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 May 2014	13/10/2014

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

4

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

PACT ET AL. EXHIBIT 1019
Page 1789

(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	page 616, right-hand column page 622; figure 20 paragraph before 4.2.23; page 612, left-hand column	
X	DE 20 2012 003747 U1 (BLUECHER GMBH [DE]) 15 November 2012 (2012-11-15)	1-4
Y	claims 1, 25 paragraphs [0106], [0142], [0143]	5-9, 16-25, 38,39, 48,49

PACCAR EXHIBIT 1019
Page 1790

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/019916

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 202012003747 U1	15-11-2012	DE 102012007392 A1	08-05-2013
		DE 202012003747 U1	15-11-2012
		EP 2776153 A1	17-09-2014
		WO 2013068060 A1	16-05-2013

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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

1. claims: 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and applying the method for gases with a sulfur(VI) concentration of more than 3 ppm by mole

---

2. claims: 50-67(completely); 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and obtaining or providing the activated carbon sorbent comprises promoting an unpromoted carbon sorbent and/or obtaining the unpromoted carbon sorbent from a carbon precursor comprising nitrogen and/or the activated carbon sorbent comprising a stabilizing agent

---

3. claims: 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and adding an alkaline component into the pollutant containing gas

---

4. claims: 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and regenerating the activated carbon sorbent

---

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2014/019916	03.09.2014	06.03.2013

International Patent Classification (IPC) or both national classification and IPC
INV. B01J20/20 B01D53/02 B01D63/10 B01J20/32 C01B31/08

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	see form PCT/ISA/210	Pöhlmann, Robert Telephone No. +49 89 2399-2059

Form PCT/ISA/237 (Cover Sheet) (July 2009)

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:

   a. (means)

      ☐ on paper

      ☐ in electronic form

   b. (time)

      ☐ in the international application as filed

      ☐ together with the international application in electronic form

      ☐ subsequently to this Authority for the purposes of search

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

☐ the entire international application

☒ claims Nos. 50-67(completely); 1-49(partially)

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search *(specify)*:

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no international search report has been established for the whole application or for said claims Nos. 50-67(completely); 1-49(partially)

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

- ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b).

☐ See Supplemental Box for further details

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has, within the applicable time limit:

   ☐ paid additional fees

   ☐ paid additional fees under protest and, where applicable, the protest fee

   ☐ paid additional fees under protest but the applicable protest fee was not paid

   ☒ not paid additional fees

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

   ☐ complied with

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

   ☐ all parts.

   ☒ the parts relating to claims Nos. 1-49(partially)

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	5-49(partially)
	No:	Claims	1-4(partially)
Inventive step (IS)	Yes:	Claims	10-15, 26-37, 40-47(all partially)
	No:	Claims	1-9, 16-25, 38, 39, 48, 49(all partially)
Industrial applicability (IA)	Yes:	Claims	1-49(partially)
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item VIII

Certain observations on the international application

1 Clarity, Article 6 PCT)

1.1 General

The terms "about" (used in claims 4-6, 18-24, 34, 50, 58, 64), "substantially" (used in claims 5, 7-9, 50, 61-64, 67) and "core" (used in claims 3, 7, 18, 19, 51, 56, 61) are vague and unclear and leave the reader in doubt as to the meaning of the technical features to which they refer, thereby rendering the definition of the subject-matter of said claims unclear, Art. 6 PCT.

1.2 Claim 4

Claim 4 does not meet the requirements of Article 6 PCT because the matter for which protection is sought is not clearly defined. The claim attempts to define the subject-matter in terms of the result to be achieved (combines with at least 70 wt%), which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result (like but not limited to volume flows, distribution of sorbent, injection of sorbent, contact times, temperatures, other components in the mercury-containing gas).

1.3 Claim 7

It is unclear (Art. 6 PCT) how the nitrogen can be homogeneously distributed in the core of the particles and how at the same time there can be a concentration profile from the surface to the core (when referring to claim 3).

1.4 Claims 8, 9

Claims 8 and 9 do not meet the requirements of Art. 6 PCT because the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

1.5 Claim 18

It is unclear in claim 18 how a core of an activated carbon sorbent particle can comprise 99 wt% nitrogen (Art. 6 PCT). The core practically would consist of nitrogen only in this case.

1.6 Claim 20

It is unclear in claim 20 how a surface layer of an activated carbon sorbent particle can comprise 99 wt% nitrogen (Art. 6 PCT). The surface would consist of nitrogen only in this cas. Also it is unclear if the technical effect related to nitrogen being present at 0.001 wt% in the surface layer is still existing (Art.6 PCT).

1.7 Claim 22

The definition of the surface layer is unclear as a thickness of 99% of the radius of the particles is in fact the complete particle and not only a "surface layer" (Art. 6 PCT).

Re Item IV

2 **Lack of unity of invention**

Notwithstanding the objections under Article 6 PCT above, the application lacks unity within the meaning of Rule 13.1 PCT.

2.1 Reference is made to the following document:

D1 YUANJING ZHENG ET AL: "Review of technologies for mercury removal from flue gas from cement production processes",PROGRESS IN ENERGY AND COMBUSTION SCIENCE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL,vol. 38, no. 5, 26 April 2012 (2012-04-26), pages 599-629, XP028415255,ISSN: 0360-1285, DOI: 10.1016/J.PECS.2012.05.001[retrieved on 2012-05-25]

D2 DE 20 2012 003747 U1 (BLUECHER GMBH [DE]) 15 November 2012 (2012-11-15)

2.2 **There are several groups of claims:**

- Group 1: Claims 1-49 (partially), in particular claims 2-9, 16-25, 38, 39, 48, 49
- Group 2: Claims 1-49 (partially), in particular claims 10-15, 26-37, 40, 41, 44, 45, claims 50-67 (completely)
- Group 3: Claims 1-49 (partially), in particular claims 42, 43
- Group 4: Claims 1-49 (partially), in particular claims claims 46, 47

2.3 **The common concept linking together the groups is the subject-matter of claim 1.** This common concept is not new over D1.

2.3.1 D1 discloses a method of reducing the mercury content in a mercury-containing gas (see page 600, para. 1.), the method comprising obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see page 615, para. 4.2.5.1 and page 616, left column, "...by impregnation of nitrogen-containing polymers or pitches ..."), contacting a pollutant-containing gas with the activated carbon sorbent to form a pollutant-sorbent composition (implicitly disclosed as for a sorbent based removal process the pollutant has to be contacted with the sorbent, the pollutant thereby always forms a pollutant-sorbent composition), and separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give a separated gas (see page 622, figure 20).

Hence, D1 discloses all the features of claim 1.

2.3.2 D1 further discloses

- claim 3: the concentration of nitrogen in the surface layer of the sorbent particles to be higher than in a core of the particles (see page 615, right column, lines 1-4, nitrogenated function introduced on carbon surface, therefrom following a lower nitrogenous concentration in the core of the particles)

- claim 5, 6: the mercury-containing gas to comprise a sulfur(VI) concentration, like SO_3 (see page 616, right column, 2nd paragraph)

2.4 **The differentiating features are**

- Group 1: applying the method for gases with a sulfur(VI) concentration of more than 3 ppm by mole
- Group 2: obtaining or providing the activated carbon sorbent comprises promoting an unpromoted carbon sorbent and/or providing or obtaining the unpromoted carbon sorbent from a carbon precursor comprising nitrogen and/or the activated carbon sorbent comprising a stabilizing agent
- Group 3: adding an alkaline component into the pollutant containing gas
- Group 4: regenerating the activated carbon sorbent

2.5 **with following resulting technical effects:**

- Group 1: no surprising and unexpected technical effect distinguishable

- Group 2: further enhancement of the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: reduction of sulfuric compounds in the pollutant containing gas
- Group 4: saving financial means for sorbent

2.6 **Thus the problems solved may be regarded as**

- Group 1: finding an alternative mercury containing gas for which the method can be applied.
- Group 2: how to modify the method of D1 in order to further enhance the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: how to modify the method of D1 in order to reduce the sulfuric compounds in the pollutant containing gas
- Group 4: how to modify the method of D1 in order to save financial means for sorbent

2.7 **The special technical features (R. 13.2 PCT) are**

- Group 1: no special technical feature A as the alternative gas is considered to be obvious for the skilled person.
- Group 2: differentiating feature = special technical feature B as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 3: differentiating feature = special technical feature C as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 4: no special technical feature D as the regeneration and reuse of the sorbent is disclosed by D1 (see page 612, left column, paragraph before 4.2.2.3).

2.8 **Groups of (alleged) inventions**

The groups of technical features do not solve any common technical problem. Thus the groups of claims are neither linked by the same nor by corresponding special technical features and define different inventions not linked by a single general inventive concept (Rule 13.1 and 13.2 PCT) and *therefore* **the requirement for unity of invention referred to in Rule 13 PCT is not fulfilled**.

2.9 **Consequence**

A search has been performed for the invention first mentioned in the claims, here the subject-matter of the claims forming group 1. Correspondingly, in the following this written opinion is restricted to group 1.

Group 1 : Claims 1-9, 16-25, 38, 39, 48, 49 (partially)

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

3 Novelty Claim 1

3.1 As already shown under point 2.3.1 above the subject-matter of claim 1 is not new (Article 33(2) PCT).

4 Inventive Step Claim 1

Besides D1, which is considered to be the closest prior art to the subject-matter of claim 1, also D2 could be regarded as the closest prior art the subject-matter of claim 1.

4.1.1 D2 discloses

A method of reducing the pollutant content in a pollutant-containing gas (see §0142 and 0143), the method comprising:

obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see claim 1);

4.1.2 The subject-matter of claim 1 therefore differs from this known D2 in that

a pollutant-containing gas is contacted with the activated carbon sorbent, to form a pollutant-sorbent composition; and in that at least some of the pollutant-sorbent composition is separated from the pollutant-containing gas, to give a separated gas.

4.1.3 There is no unexpected technical effect related to that difference.

4.1.4 The problem to be solved by the present invention may therefore be regarded as how to to apply the method of D2 for reducing the pollutant content in a pollutant-containing gas.

4.1.5 The solution proposed in claim 1 of the present application cannot be considered to involve an inventive step (Article 33(3) PCT) for the following reasons:

It is common general knowledge for the skilled person to contact the sorbent with the gas to form a pollutant-sorbent composition and to separate the pollutant-sorbent composition from the gas to give a separated gas. Also, amongst many other documents he finds in D1 an indication (see cited passages) with which he would contact the sorbent with the gas, thereby forming a pollutant sorbent composition and separate this composition from the gas to give a separated gas, thereby arriving at the subject-matter of claim 1 without being inventive.

5 Dependent claims

Dependent claims 2-9, 16-25, 38, 39, 48, 49 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step.

5.1 Claims 2, 3

The subject-matter of said claims is neither new (see points 2.3.1 and 2.3.2 above), nor inventive (see D2, claim 1 and §0143, mercury being an obvious toxic substance whose removal from gas streams with activated carbon is widely known in industry).

5.2 Claims 5, 6

D1 discloses a sulfur(VI) concentration in the mercury-containing gas (see 2.3.2 above) and the claimed ranges for said concentration are considered to be merely an arbitrary selection out of a variety of possible mercury containing gases without showing an unexpected technical effect. The properties of the activated carbon sorbent of D1 are considered to achieve the results claimed in claim 5 with regard to corresponding activated carbon sorbents.

5.3 Claims 16, 17, 38, 39, 48, 49

It is well-known in the art to add the sorbent into the mercury-containing gas and to remove it after a certain distance by various means like bag houses, electrostatic precipitators, cyclones or the like. As well, it is common general knowledge to contact the gas with the sorbent in a fixed bed, a dry or aqueous scrubber, a filter or a moving bed.

Claim 19, 21

D2 discloses a wide variety of possible nitrogen concentrations of the activated carbon (see claim 25), which is also considered to be applicable either to the surface and/or to the core of carbon particles. Therefore, the claimed ranges are not inventive.

Claim 24, 25

The claimed range of particle diameters is considered an arbitrary selection and activated carbon particles in this range are known to the skilled person (see for reference D2, §0106). Furthermore, every surface is considered to be continuous and therefore also a surface layer.

Re Item VII

Certain defects in the international application

6 The requirements of Rule 6.3(b) PCT (two-part form of independent claims) and Rule 5.1(a)(ii) and (iii) PCT (acknowledgement of prior art D1) are not met.

Electronic Acknowledgement Receipt

EFS ID:	32666807
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
Filer Authorized By:	Jordan Rivard Golomb
Attorney Docket Number:	4820.001US9
Receipt Date:	18-MAY-2018
Filing Date:	
Time Stamp:	16:16:40
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Non Patent Literature	0221_ep_response_04_18_08.pdf	1564401 f5c012dede340dcd216f09e59046dc2e811946ab	no	7

Warnings:

Information:					
2	Non Patent Literature	0222_4820001ep1_e2001ar_051110.pdf	333532 e7e1fc292905d5760a54a0ee5469e7126e7c73b9	no	11
Warnings:					
Information:					
3	Non Patent Literature	0223_ep_response_05_11_10.pdf	494091 aca9d76d09084359 8e2c22d9724c9367393e8328	no	11
Warnings:					
Information:					
4	Non Patent Literature	0224_4820001ep1_eesrr_090911.pdf	775159 fb64ee1962ab93cebe86b2dac95bf0eb40f5cb45	no	20
Warnings:					
Information:					
5	Non Patent Literature	0225_third_party_observations.pdf	442488 effb53e6dc8cd7e0911941b4d37ba62f65d35557	no	7
Warnings:					
Information:					
6	Non Patent Literature	0226_third_party_comment_12_04_07.pdf	812524 8473aa1c0f613a3edb809a75aeaa340482ac8de9	no	5
Warnings:					
Information:					
7	Non Patent Literature	0227_4820007ep1_decisiontograrant_041714.pdf	97620 07e704698ae098cc75f8d3c8c96ddbb2cd0ced3a	no	2
Warnings:					
Information:					
8	Non Patent Literature	0228_4820007ep1_eesr_120612.pdf	180666 85cd54f860002f3cb5d516c38055bc46f4a93034	no	5
Warnings:					
Information:					

9	Non Patent Literature	0229_4820007ep1_e2000c_031714.pdf	2610871 355584512 8ae0aa4f725bf57a434a73ab1992c49	no	44
Warnings:					
Information:					
10	Non Patent Literature	0230_4820007ep1_e2000c_093013.pdf	2685048 3d3cc80dd8336ca0b50ac3d67faba1cebeec55bc	no	44
Warnings:					
Information:					
11	Non Patent Literature	0231_4820007ep1_aarmisc_020314.pdf	417535 a04144e9a7f97a2cdcec80059a94df8b30d0daa7	no	11
Warnings:					
Information:					
12	Non Patent Literature	0232_4820007ep1_eesrr_062013.pdf	755172 002d2bb2de4e615acdd4d0f67b8698933e5f6607	no	18
Warnings:					
Information:					
13	Non Patent Literature	0233_3_4820001ep3_e2001_112612.pdf	116665 5e21e36a974630192d54be4cd79334c036e3b521	no	4
Warnings:					
Information:					
14	Non Patent Literature	0234_7_4820001ep3_decision_121913.pdf	478932 3dd56187e50cc04a11bb8df27b9b6a1ac7e1b08c	no	18
Warnings:					
Information:					
15	Non Patent Literature	0235_1_4820001ep3_eesr_020112.pdf	261647 5e5d38a83b911b70c57325056f020d8e909504e5	no	7
Warnings:					
Information:					

16	Non Patent Literature	0236_6_4820001ep3_oar_misc_110413.pdf	83017 e3695457a5471754886b7cdadc27e457f475bf42	no	4
Warnings:					
Information:					
17	Non Patent Literature	0237_4_4820001ep3_e2001r4_020413.pdf	302856 c0acab24403d76cc7a1393a5aab37b610fd0798e	no	9
Warnings:					
Information:					
18	Non Patent Literature	0238_2_4820001ep3_eesrr_082812.pdf	357100 6ede6faa477d50cea8087381200bca8a17d8a546	no	9
Warnings:					
Information:					
19	Non Patent Literature	0239_5_4820001ep3_oarmisc_041513.pdf	224389 8003bf4b699082e3c2c3477ed97aadae3cfd113c	no	7
Warnings:					
Information:					
20	Non Patent Literature	0240_4820001ep2_e2001_010913.pdf	129377 51212a09d6ebc8605bfd3646dc7c6760a951056c	no	4
Warnings:					
Information:					
21	Non Patent Literature	0241_4820001ep2_decisiontograntt_050214.pdf	98248 287bd001d1ca27ec9d22f62a181655f5c652822c	no	2
Warnings:					
Information:					
22	Non Patent Literature	0242_4820001ep2_eesr_012312.pdf	179244 036187455975bc3281dd077eeb5cdccc791c6dc0	no	6
Warnings:					
Information:					

23	Non Patent Literature	0243_4820001ep2_eesr_050912.pdf	422312 2dc6bf735e0383d48d4826e5deb2fd0d2423bae5	no	12
Warnings:					
Information:					
24	Non Patent Literature	0244_4820001ep2_e2001_103013.pdf	80112 46d589421efee22b6a2c072d896ff5abffd852cd	no	4
Warnings:					
Information:					
25	Non Patent Literature	0245_4820001ep2_oarmisc_121113.pdf	229813 ace4ddefd32b441886a08d33dd65ed410d8875ac	no	6
Warnings:					
Information:					
26	Non Patent Literature	0246_4820001ep2_e2001ar_021113.pdf	241870 8ecc38d759113f281117cdb15521fc37723471db	no	5
Warnings:					
Information:					
27	Non Patent Literature	0247_4820001ep2_aarmisc_101013.pdf	713659 a0744d524b62172258861265436e7059fa51a66e	no	18
Warnings:					
Information:					
28	Non Patent Literature	0248_4820001ep2_eesrr_112212.pdf	547968 bfc1dd5763f7ce8b435161ec1b74f0ee6d31ca18	no	13
Warnings:					
Information:					
29	Non Patent Literature	0249_4820001ep2_oarmisc_041513.pdf	215326 f3f147c0bb3b6010f80b417beaecade9f9c58172	no	6
Warnings:					
Information:					

30	Non Patent Literature	0252_ep_oa_12_19_2014.pdf	390998 72f17641c8420ced9d56f84ca2606959d86bcc17	no	2
Warnings:					
Information:					
31	Non Patent Literature	0253_ep_response_06_29_2015.pdf	3029253 a768f8da10ab7d166fbe20c12ad9fc330bcecc2e	no	19
Warnings:					
Information:					
32	Non Patent Literature	0255_147111066e2001r4_081717_20170222.pdf	132291 74fb5f3749ae44eedbccf1a83626950048b2c12b	no	10
Warnings:					
Information:					
33	Non Patent Literature	0256_2008071986_pct_13009.pdf	129607 c1e89271468f0a8281fb9dd52add8103b3fe0c5a	no	3
Warnings:					
Information:					
34	Non Patent Literature	0257_4820001wo1_p326_122706.pdf	165309 50f88745141c1b3a58f506a48cae8ce5cf3710f3	no	3
Warnings:					
Information:					
35	Non Patent Literature	0258_4820001wo1_p210_072506.pdf	61343 b84a36573f32ea25e9c1978d82d774b04e91f9db	no	2
Warnings:					
Information:					
36	Non Patent Literature	0259_4820001wo1_p237_072506.pdf	112196 9116ee956af820160ad8f3c52021daedce1cdc7b	no	3
Warnings:					
Information:					

37	Non Patent Literature	0260_4820007wo1_p326_110311.pdf	231100 7a031f5a65b3d2a4ee1a43b04c8b07fb907ef2a6	no	6
Warnings:					
Information:					
38	Non Patent Literature	0261_4820007wo1_p210_091310.pdf	127083 bcb289e98c2f44fd187be8f5418e2ae5ea028a6d	no	3
Warnings:					
Information:					
39	Non Patent Literature	0262_4820007wo1_p237_091310.pdf	167943 1c3b0791d78f1b27535b5118d2251a95b04a27b7	no	4
Warnings:					
Information:					
40	Non Patent Literature	0268_inter_sr_10_13_2014.pdf	1008812 8176f07b0a1bb208bc9bb1540b2638d011e9e26c	no	6
Warnings:					
Information:					
41	Non Patent Literature	0270_written_opinion_10_13_2014.pdf	2060724 25e5a5fedfcdcbe4c5c3a1d651cd0407fa6a7ce4	no	12
Warnings:					
Information:					
42	Non Patent Literature	0271_powdered_activated_carbon___cabot_corporation.pdf	455129 8d2e4e10581ffb9b313bcd21fca8e5f94ac3eb1a	no	3
Warnings:					
Information:					
43	Non Patent Literature	0272_137193389aarmisc_090517_201709042.pdf	85747 0a1ee377478eb8d04c9ee1b26b35e402bd810b55	no	7
Warnings:					
Information:					

44	Non Patent Literature	0273_14195360_co2_removal_potential_of_carbons_prepared.pdf	671720 a8cf88598473c41181727add218c64fbc8a2cb2f	no	9
Warnings:					
Information:					
45	Non Patent Literature	0274_bakandritos_2005.pdf	260838 c7fab0fe28c064feda0bcf87aa3132a64524f78a	no	7
Warnings:					
Information:					
46	Non Patent Literature	0276_141953602.pdf	618898 cd8db5b77f652a7504f2d0e698eb02eeb9eeb024	no	7
Warnings:					
Information:					
47	Non Patent Literature	0277_chang_2004.pdf	8513748 07b603e189e23ae10af13a6a650d9617eb49f3df	no	9
Warnings:					
Information:					
48	Non Patent Literature	0278_criswell.pdf	2769881 ab7d64cf4e35cfd7aee3d5bfe8ca4e3380cd5a87	no	23
Warnings:					
Information:					
49	Non Patent Literature	0279_darder_ruiz_hitzky_2005.pdf	1604278 9522fc9501f287e20d4a6426b9644809362faea1	no	6
Warnings:					
Information:					
50	Non Patent Literature	0280_14195360_sorption_of_mercury_by_activated_carbon.pdf	739167 3173f100570511e808e05062c7185101dbb908c0	no	6
Warnings:					
Information:					

51	Non Patent Literature	0281_dong_2009.pdf	1935893 fa7039d219469553c4e10b886a933206d6e12efd	no	6
Warnings:					
Information:					
52	Non Patent Literature	0282_dunham.pdf	1600971 0573e61e154188eda8a7f7c6259cb8c987db2657	no	6
Warnings:					
Information:					
53	Non Patent Literature	0283_eisazadeh_2007.pdf	300042 60c87c3b81cdda6269e0577597bb19c4921f7dd7	no	6
Warnings:					
Information:					
54	Non Patent Literature	0284_felsvang_etal_2001.pdf	3581959 38b18942a73c3cc89b52f74c63d505526bb9f12a	no	19
Warnings:					
Information:					
55	Non Patent Literature	0285_fernandez_saavedra_2008.pdf	2948163 3279ab9bc2182bb9a90d7b2f10b9713efb400762	no	10
Warnings:					
Information:					
56	Non Patent Literature	0286_ghorbani_2011.pdf	1199750 260bedb3c18e0ed7102c980e809288d6a5e6afa1	no	4
Warnings:					
Information:					
57	Non Patent Literature	0287_ghorishi_1998.pdf	3150707 a1e675f1add110e8dcc79be356f7bfa8b3175374	no	12
Warnings:					
Information:					

58	Non Patent Literature	0288_gomez_aviles_2006.pdf	228396 9cb14713716319e26451401b137cee04102adf50	no	3
Warnings:					
Information:					
59	Non Patent Literature	0289_gomez_aviles_darder_2010.pdf	3091287 79670af94643eb7e113ba526f84afb7751410443	no	13
Warnings:					
Information:					
60	Non Patent Literature	0292_14195360.pdf	375076 3bdf39999f038cdca10e9ac45314d83ac6b69727	no	4
Warnings:					
Information:					
		Total Files Size (in bytes):	57599951		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

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

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

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

New International Application Filed with the USPTO as a Receiving Office

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

Espacenet

Bibliographic data: CA2584327 (A1) — 2006-04-13

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

Inventor(s): PAVLISH JOHN H [US]; HOLMES MICHAEL J [US]; OLSON EDWIN S [US] ± (PAVLISH, JOHN H, ; HOLMES, MICHAEL J, ; OLSON, EDWIN S)

Applicant(s): ENERGY & ENVIRON RES CT FOUND [US] ± (ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION)

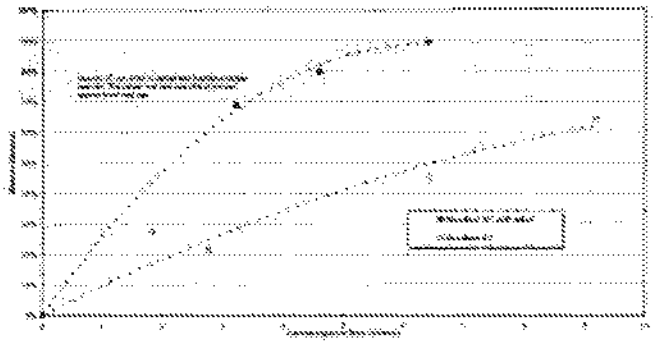
Classification: - international: ***B01D53/02***
- cooperative: **B01D53/10**; **B01D53/64**; **B01J20/20**; **B01J20/22**; B01D2253/102; B01D2257/602; Y10S95/901

Application number: CA20052584327 20050823

Priority number(s): US20040605640P 20040830 ; US20050209163 20050822 ; WO2005US30018 20050823

Also published as: CA2584327 (C) CN101048218 (A) CN101048218 (B) EP1796816 (A2) EP1796816 (A4) more

Abstract of CA2584327 (C)



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

gas stream are described.

(19) Canadian Intellectual Property Office
An Agency of Industry Canada

Office de la Proprit Intellectuelle du Canada
Un organisme d'Industrie Canada

(11) CA 2 584 327 (13) A1

(40) 13.04.2006
(43) 13.04.2006

(12)

(21) 2 584 327

(22) 23.08.2005

(51) Int. Cl.:
B01D 53/02 (2006.01)

(85) 22.02.2007

(86) PCT/US05/030018

(87) WO06/039007

(30) 60/605,640 US 30.08.2004
11/209,163 US 22.08.2005

(71) ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION,
P.O. Box 9018, GRAND FORKS, XX (US).

(72) HOLMES, MICHAEL J. (US).
PAVLISH, JOHN H. (US).
OLSON, EDWIN S. (US).

(74) RIDOUT & MAYBEE LLP

(54) SORBANTS POUR L'OXYDATION ET POUR LA SUPPRESSION DE MERCURE
(54) SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2584327 A1 2006/04/13

(21) 2 584 327

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

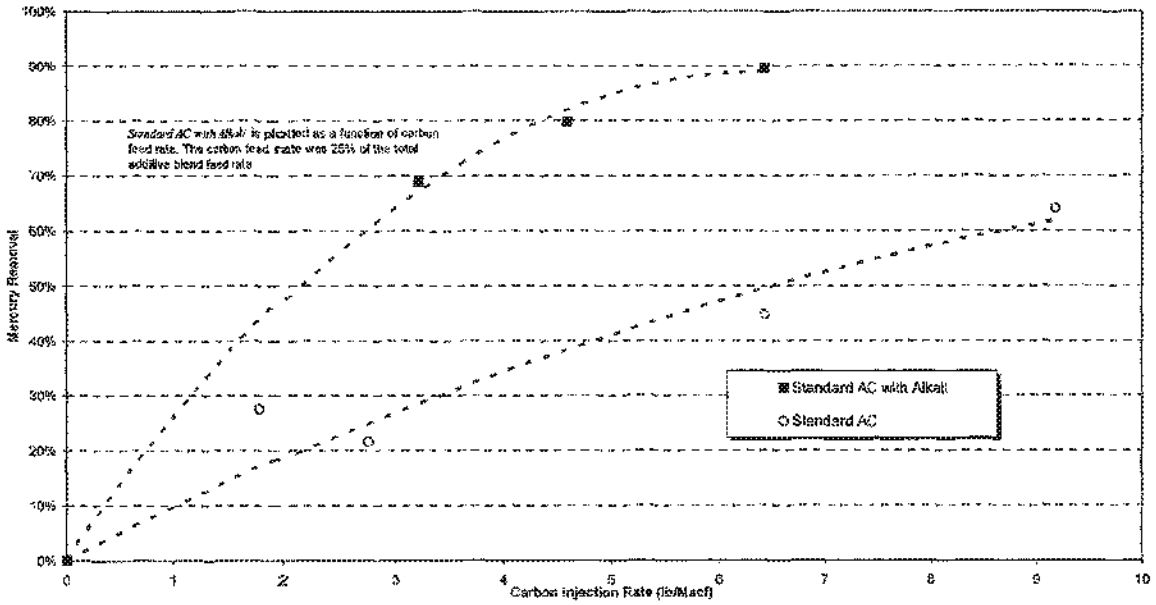
(86) Date de dépôt PCT/PCT Filing Date: 2005/08/23
(87) Date publication PCT/PCT Publication Date: 2006/04/13
(85) Entrée phase nationale/National Entry: 2007/02/22
(86) N° demande PCT/PCT Application No.: US 2005/030018
(87) N° publication PCT/PCT Publication No.: 2006/039007
(30) Priorités/Priorities: 2004/08/30 (US60/605,640); 2005/08/22 (US11/209,163)

(51) Cl.Int./Int.Cl. *B01D 53/02* (2006.01)
(71) Demandeur/Applicant:
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION, US

(72) Inventeurs/Inventors:
OLSON, EDWIN S., US;
HOLMES, MICHAEL J., US;
PAVLISH, JOHN H., US

(74) Agent: RIDOUT & MAYBEE LLP

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



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

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
13 April 2006 (13.04.2006)

(10) International Publication Number
WO 2006/039007 A2

(51) International Patent Classification:
B01D 53/02 (2006.01)

(21) International Application Number:
PCT/US2005/030018

(22) International Filing Date: 23 August 2005 (23.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/605,640	30 August 2004 (30.08.2004)	US
11/209,163	22 August 2005 (22.08.2005)	US

(71) Applicant *(for all designated States except US)*: **ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION** [US/US]; P.O. Box 9018, Grand Forks, North Dakota 58202-9018 (US).

(71) Applicants and
(72) Inventors: **OLSON, Edwin, S.** [US/US]; 223 Circle Hills Drive, Grand Forks, North Dakota 58201 (US). **HOLMES, Michael, J.** [US/US]; 614 6th Street, Thompson, ND 58278 (US). **PAVLISH, John, H.** [US/US]; 42204 210th Street Southwest, East Grand Forks, Minnesota 56721 (US).

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

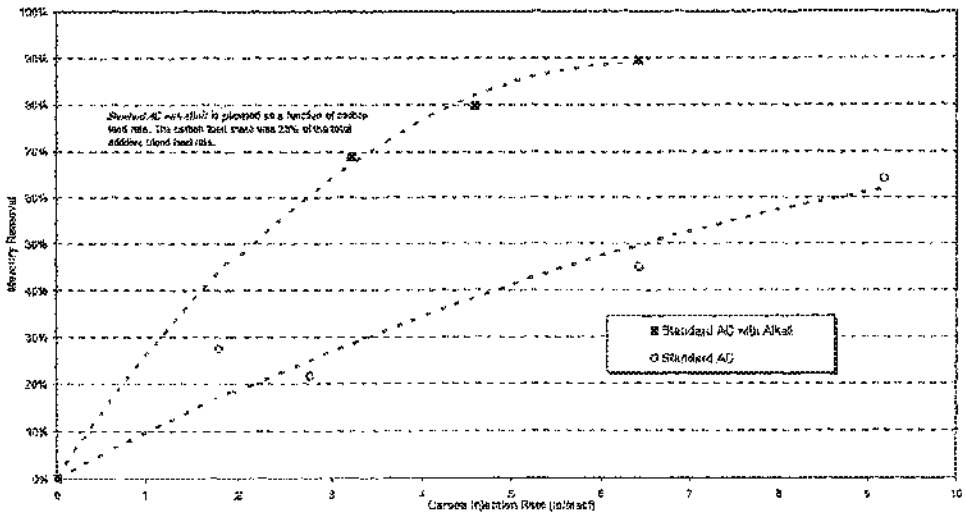
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK,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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

[Continued on next page]

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



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

WO 2006/039007 A2

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with United States Government support under the U.S. Environmental Protection Agency Grant Nos. R 827649-01 and CR 830929-01. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

Technical Field of the Invention

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

Background of the Invention

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

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic

silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

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

SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens,

PAC ET AL. EXHIBIT 1019
Page 1821

and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have an mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

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

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

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

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the

PAC ET AL. EXHIBIT 1019
Page 1822

reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

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

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury from a flue gas at lower removal rates with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

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

PAC ET AL. EXHIBIT 1019
Page 1823

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

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

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

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

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-

PAC ET AL. EXHIBIT 1019
Page 1824

containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

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

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

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

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

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

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

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

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

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

PAC ET AL. EXHIBIT 1019
Page 1825

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

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

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

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

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury *via* mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require *in situ* activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

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

Referring now to Figure 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas form a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base

PAC ET AL. EXHIBIT 1019
Page 1826

activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

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

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

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

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

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

PAC ET AL. EXHIBIT 1019
Page 1827

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

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

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

Referring now to Figure 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals

PAC ET AL. EXHIBIT 1019
Page 1828

of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to Figure 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional akali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

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

For clarity, single injection points 116 or 119 are shown in Figure 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device (s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at a location upstream and/or downstream of 140 when parallel, sequential, or combinations

PAC ET AL. EXHIBIT 1019
Page 1829

thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142, and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152, and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

An optional Continuous Emission Monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35, to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25, by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury "clean" flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, 209 can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

Referring still to Figure 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base activated carbon from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base activated carbon prior to injection point 116. This option is one form of what is referred to herein as "in-flight" preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with base activated carbon prior to entering

PAC ET AL. EXHIBIT 1019
Page 1830

transport line 115. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebullated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in Figure 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to Figure 1.

Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131b and 131c.

Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions..

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebullated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

PAC ET AL. EXHIBIT 1019
Page 1831

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the

PAC ET AL. EXHIBIT 1019
Page 1832

mercury on the sorbent and ash is very short – less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. In Addition to halide ions, this phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, the modified cationic carbon has a high chemical potential for oxidation of the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

PAC ET AL. EXHIBIT 1019
Page 1833

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection

PAC ET AL. EXHIBIT 1019
Page 1834

system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.
- The inventive process uses existing hardware and operation procedures.
- The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjection with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated: the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or

PAC ET AL. EXHIBIT 1019
Page 1835

optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a *carbocation* that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine- containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1 -Preparation and Testing of Halogenated Carbon (& Comparative Example)

Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, TX (USA), although others are suitable, as will be recognized by those skilled in the

PAC ET AL. EXHIBIT 1019
Page 1836

art), was placed in a rotating plastic barrel with side blades (a 5 ft^3 (0.14 m^3) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°–50°C. The vapor pressure of the bromine was such that a dark red gas is generated a passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight to that the excess of nitrogen is released after the bromine is transfer to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2–5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5–17 wt%), but does not require further drying for use. The moisture is driven out at higher temperatures (>150°C), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G.E.; Miller, S.J. Chang, R.; Bergman, P. *Environmental Progress* **1998**, *17*, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (-400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125°C) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O_2 (6%), CO_2 (12%), SO_2 (600 ppm), NO (120 ppm) NO_2 (6 ppm), HCl (1 ppm), Hg^0 (11 $\mu g/m^3$), H_2O (15%), and N_2 (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations

PAC ET AL. EXHIBIT 1019
Page 1837

in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach FL USA), and a $SnCl_2$ cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to Figure 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%–1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30–60 minutes (breakthrough point), depending on the sorbent. Figure 4 illustrates the breakthrough curves for 5 wt/wt% brominated NORIT Darco FGD sorbent (37 mg + 113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a per cent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

Figure 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%–50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2 - Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3 - Liquid Phase (water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110°C for

PAC ET AL. EXHIBIT 1019
Page 1838

several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4 - Addition of the Optional Second Halide Component.

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5 - Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110°C in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6 - Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 μm) sorbent was developed, prepared, and tested.

Treatment - Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°–50°C, and the outlet from this gaseous bromine generator was connected via a 1/4 inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had

PAC ET AL. EXHIBIT 1019
Page 1839

combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the "Particulate Test Combustor" (hereinafter "PTC"), is a 550,000-Btu/hr (about 161 kW) pulverized coal ("PC")-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a "fabric filter") or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O_2, CO, CO_2, SO_2, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO_2 was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

PAC ET AL. EXHIBIT 1019
Page 1840

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m^3/min) of flue gas at 300°F (about 150°C), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300°F (150°C). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCMM (normal m^3/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in Figure 6. As can be observed in Figure 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter ("FF"). Note that in Figure 6 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or "MACM").

Referring now to Figure 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because >60 μm sorbent particles have been successfully demonstrated, superior mercury control can be obtained with >40 μm particles, which may be preferred in some applications, depending

PAC ET AL. EXHIBIT 1019
Page 1841

on the sorbent particle/ash separation system used. Note that in Figure 7 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet.

Example 7 - Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110°C for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8 - Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100°C in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu g/m^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, FL, USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus

PAC ET AL. EXHIBIT 1019
Page 1842

enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9 - Fluidized/Ebullated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10 - Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu g/m^3$. The ash and injected carbon were collected in the baghouse at 350°F to 375°F (about 175-190°C). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 $\mu g/m^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A - Addition of Optional Alkaline Component – Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with

PAC ET AL. EXHIBIT 1019
Page 1843

inert sand is shown in Figure 8, and the breakthrough curve for the mixture with CaO is shown in Figure 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B - Addition of Optional Alkaline Component – Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as "AC") and an alkali material upstream of a fabric filter. Typical results are illustrated in Figure 10. As shown in Figure 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12- Brominated Carbon Sorbent for Gasification Fuel Gas

Preparation of 5%Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol% solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt% brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by

PAC ET AL. EXHIBIT 1019
Page 1844

vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110°C until a stable weight was obtained The moisture was reduced to 15%.

Preparation of 5%Br2D-AC

A brominated sorbent was prepared from Br_2 addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5%PBr3-AC

A phosphohalogenated sorbent was prepared from PBr_3 using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere - Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/m^3 of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/m^3). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400°C). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no $SnCl_2$ trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5%Br2W-AC and 5%BrD-AC), and the phosphobrominated sorbent

PAC ET AL. EXHIBIT 1019
Page 1845

(5%PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100°C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400°C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400°C.

Table 1

Times for 50% Breakthrough
Maximum Observed Hg Concentrations for Sorbents
(10% Hydrogen Streams)

Sorbent	Temp (°C)	50% breakthrough (min)	Maximum [Hg] ($\mu g/m^3$)	Time (min)
F-400	250	6	20.3	6.5
5%Br2W-AC	250	>150	1.4	150
5%Br2W -AC	300	>180	4.3	180
5%Br2W-AC	350	160	15.1	180
5%Br2W-AC	400	60	13.9	65
5%PBr3-AC	250	>140	0.4	140
5%PBr3-AC	300	>150	0.5	150
5%PBr3-AC	350	>150	1.4	150
5%Br2D-AC	350	>180	2.1	180
5%Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications

PAC ET AL. EXHIBIT 1019
Page 1846

thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

PAC ET AL. EXHIBIT 1019
Page 1847

WE CLAIM:

1. A promoted carbon sorbent comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

2. The promoted carbon sorbent of claim 1 wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than 40 micrometers, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V halides, Group VI halides, hydrohalides, and combinations thereof.

3. The promoted carbon sorbent of claim 2 wherein the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon.

4. The promoted carbon sorbent of claim 3 further comprising an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

5. The promoted carbon sorbent of claim 4 further comprising an optional alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

6. The promoted carbon sorbent of claim 4 wherein the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

7. The promoted carbon sorbent of claim 6 wherein the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof.

8. The promoted carbon sorbent of claim 7 wherein the optional secondary component is selected from the group consisting of I_2, HI, and combinations thereof.

9. The promoted carbon sorbent of claim 8 wherein the promoter is substantially in vapor form when combined with the base activated carbon.

10. The promoted carbon sorbent of claim 8 wherein the promoter is combined with an

PAC ET AL. EXHIBIT 1019
Page 1848

organic solvent prior to reaction with the base activated carbon.

11. The promoted carbon sorbent of claim 8 wherein the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously.

12. The promoted carbon sorbent of claim 8 further comprising a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

13. The promoted carbon sorbent of claim 12 wherein the promoter is selected from the group consisting of Br_2, HBr, and combinations thereof.

14. The promoted carbon sorbent of claim 3 further comprising a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

15. The promoted carbon sorbent of claim 14 further comprising an optional alkaline component comprising an alkaline or alkaline earth element wherein the promoter is selected from the group consisting of Br_2, HBr, and combinations thereof.

16. A method comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream.

17. The method of claim 16 wherein the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon.

18. The method of claim 16 wherein the reaction product has an average particle size distribution greater than about 40 micrometers.

19. The method of claim 16 wherein the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof.

20. The method of claim 19 wherein the promoter is in the gas phase when contacting the activated carbon.

21. The method of claim 19 wherein the promoter is in an organic solvent when contacting the activated carbon.

PAC ET AL. EXHIBIT 1019
Page 1849

22. The method of claim 20 wherein the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

23. The method of claim 18 further comprising providing an optional alkaline component to improve the effectiveness of mercury removal.

24. The method of claim 20 further comprising reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

25. The method of claim 24 further comprising providing an optional alkaline component to improve the effectiveness of mercury removal.

26. The method of claim 24 wherein the promoter and optional secondary component are contacted simultaneously with the activated carbon.

27. The method of claim 24 wherein the optional secondary component comprises I_2 or HI.

28. The method of claim 20 further comprising adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

29. The method of claim 24 further comprising adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

30. A method for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas.

31. The method of claim 30 further comprising co-injecting an optional alkaline component into the mercury containing flue gas stream.

32. The method of claim 30 further comprising monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent.

33. The method of claim 30 wherein the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

PAC ET AL. EXHIBIT 1019
Page 1850

34. The method of claim 33 wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof.

35. The method of claim 34 wherein the promoter is selected from the group consisting of Br_2, HBr, Group V bromides, Group VI bromides, and combinations thereof.

36. The method of claim 35 wherein the promoter is reacted in the gas phase or as a vapor.

37. The method of claim 36 wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

38. The method of claim 37 wherein the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

39. The method of claim 38 wherein the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof.

40. The method of claim 39 further comprising co-injecting an optional alkaline component into the mercury containing flue gas stream.

41. The method of claim 39 wherein the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content.

42. The method of claim 41 wherein the optional secondary component is selected from the group consisting of I_2, HI, and combinations thereof.

43. The method of claim 42 wherein the optional secondary component is added in the gas phase or as a vapor.

44. The method of claim 41 further comprising adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

45. The method of claim 32 further comprising using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent.

46. The method of claim 40 further comprising monitoring the mercury content of the clean

PAC ET AL. EXHIBIT 1019
Page 1851

flue gas and using the monitored mercury content to control the composition of the sorbent and the alkaline-to-sorbent injection ratio.

47. The method of claim 45 wherein the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

48. A method for reducing the mercury content of a gas stream comprising the steps of injecting a powdered activated carbon sorbent having a mass-mean particle size >40μm into a gas stream containing mercury and ash particles, capturing mercury from the gas stream on the sorbent particles, mechanically separating the sorbent particles from the ash particles, and re-injecting the separated sorbent particles into the gas stream.

49. The method of claim 48 further comprising regenerating the sorbent particles to substantially remove contaminants therefrom to recover capacity for capturing mercury.

50. The method of claim 48 further comprising co-injecting into the gas stream an alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

51. The method of claim 48 wherein the powdered activated carbon sorbent further comprises a promoter selected from the group consisting of halides, halogens, and combinations thereof.

52. The method of claim 51 further comprising co-injecting into the gas stream an alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

53. The method of claim 48 wherein the particulate activated carbon sorbent has a mass-mean particle size >60μm.

54. The method of claim 52 wherein the particulate activated carbon sorbent has a mass-mean particle size >60μm.

PAC ET AL. EXHIBIT 1019
Page 1852

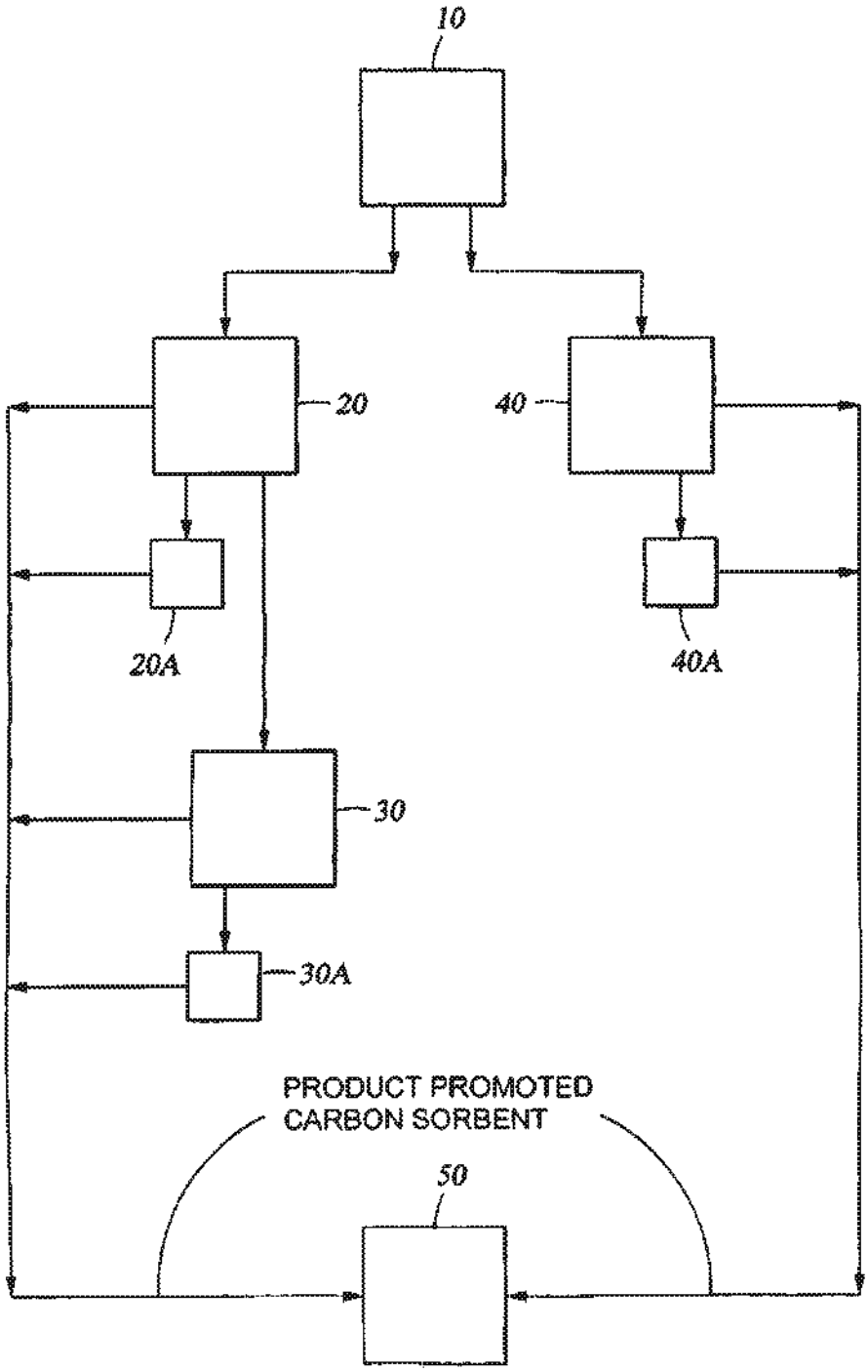


Fig. 1

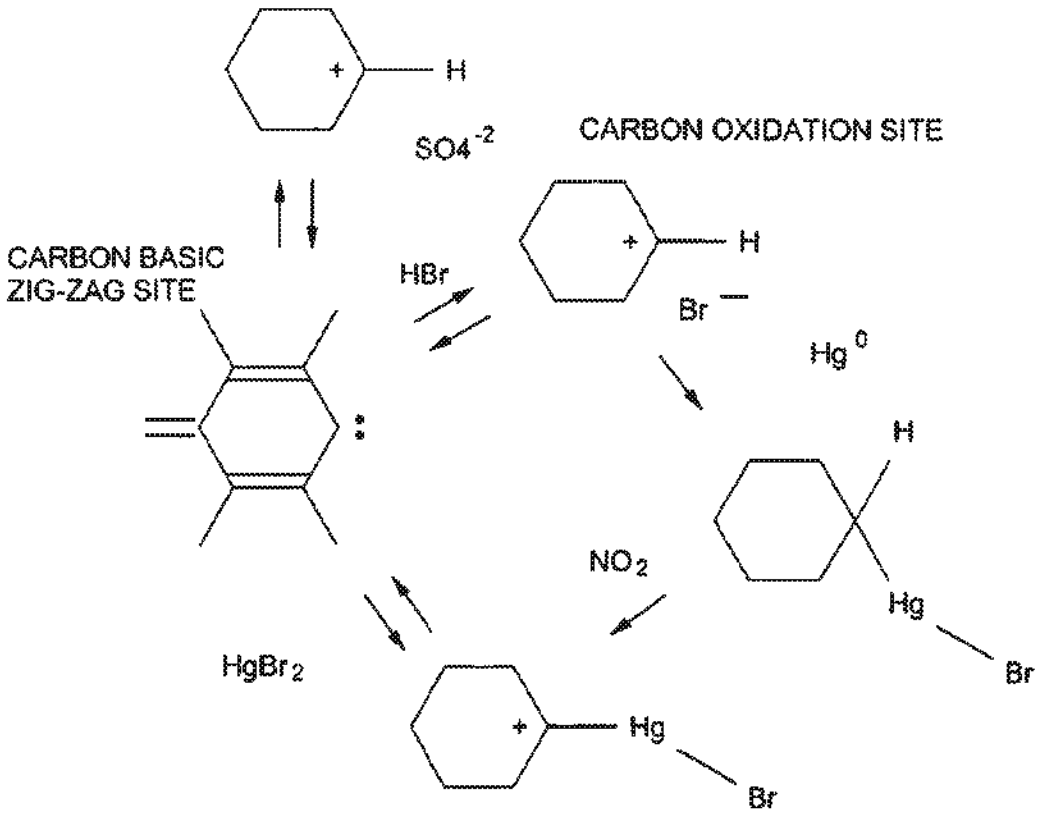


Fig. 2

PAC ET AL. EXHIBIT 1019
Page 1854

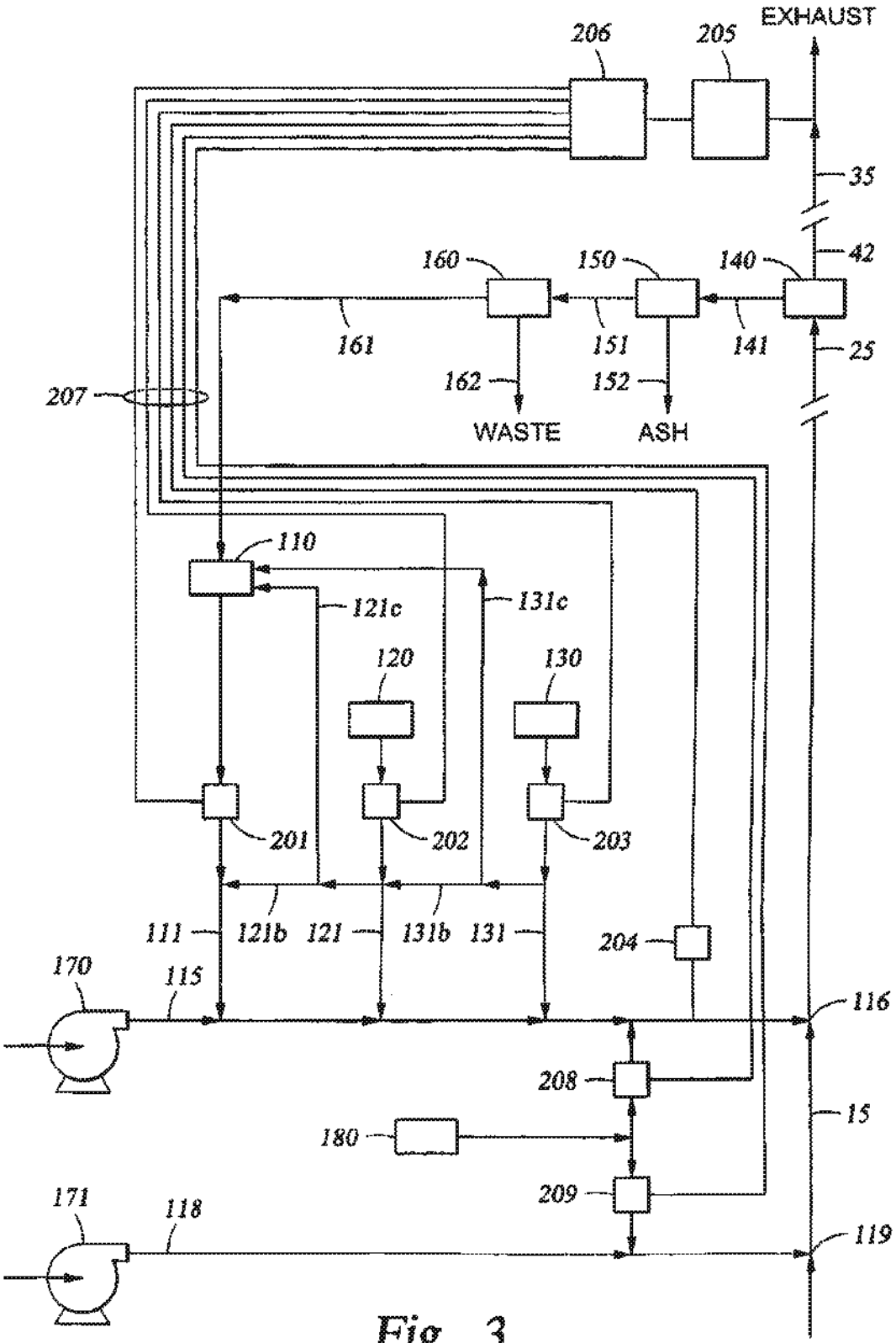

EXHAUST
206
205
35
42
160
150
140
161
151
141
25
162
152
207
WASTE
ASH
110
121c
131c
120
130
201
202
203
111
121b
121
131b
131
204
170
115
116
208
180
15
209
171
118
119

Fig. 3

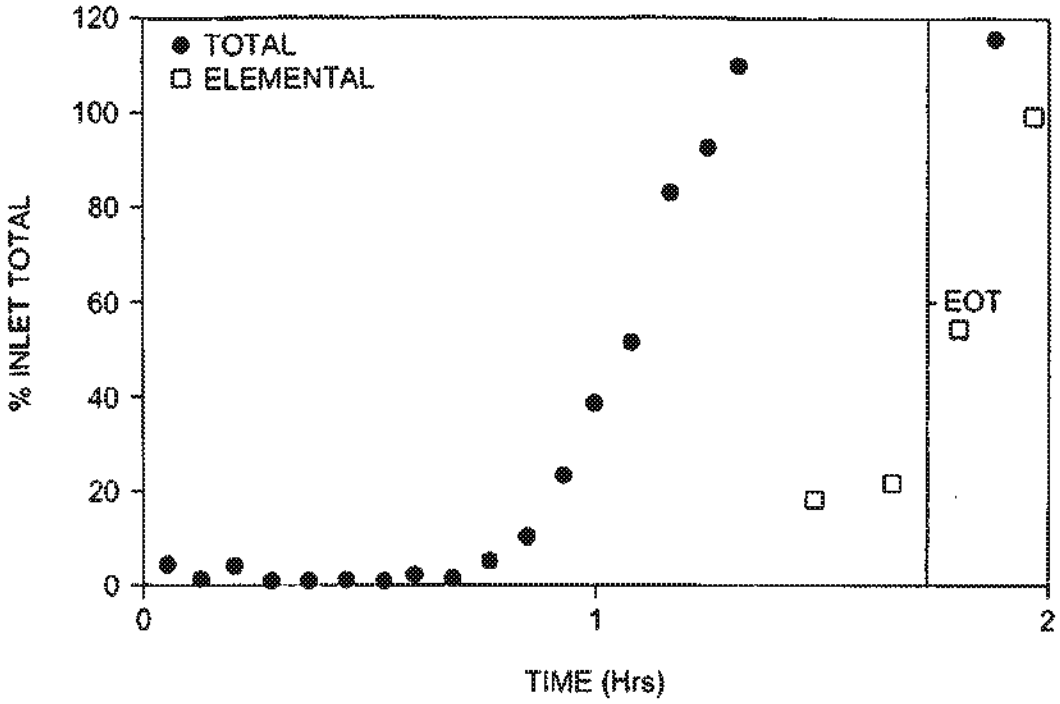

TOTAL
ELEMENTAL
EOT
% INLET TOTAL
TIME (Hrs)
0
20
40
60
80
100
120
0
1
2

Fig. 4

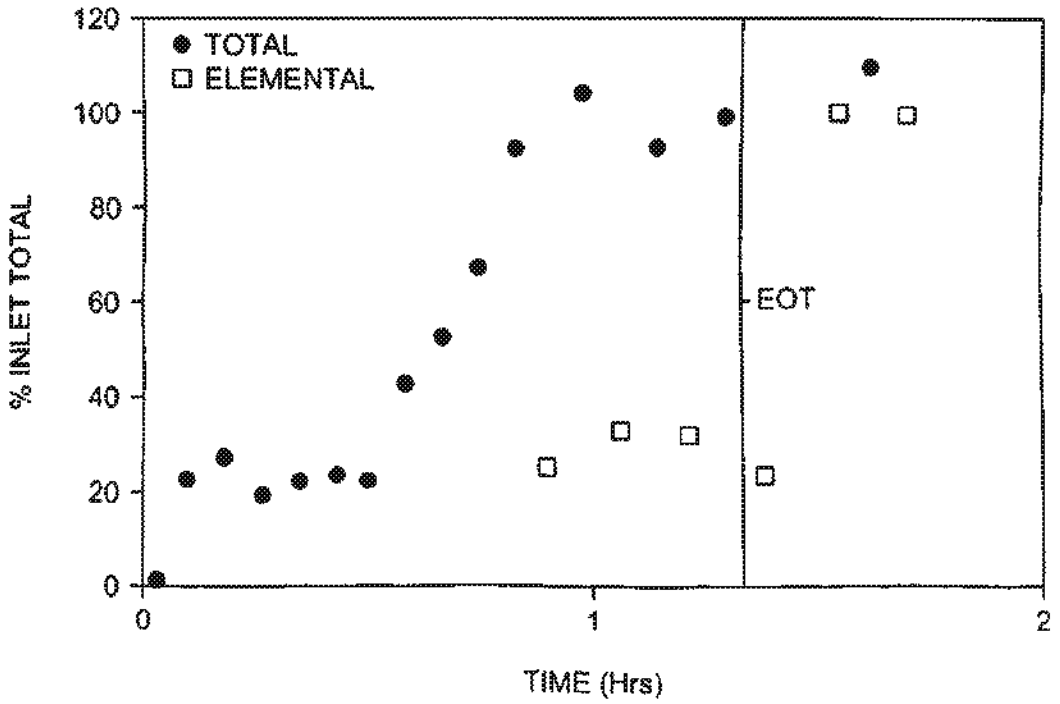

TOTAL
ELEMENTAL
EOT
% INLET TOTAL
TIME (Hrs)
0
20
40
60
80
100
120
0
1
2

Fig. 5

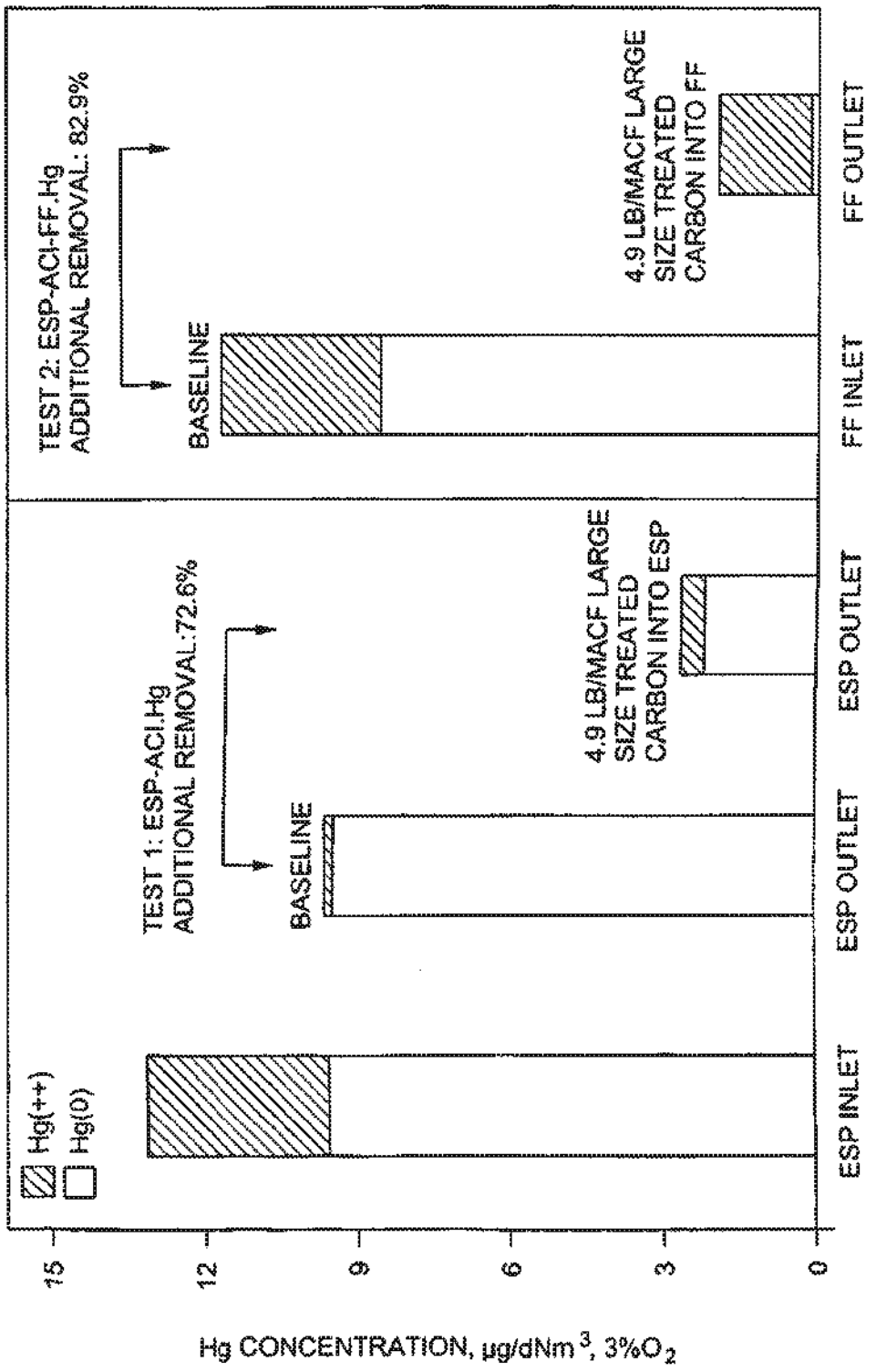


Fig. 6

PAC ET AL. EXHIBIT 1019
Page 1857

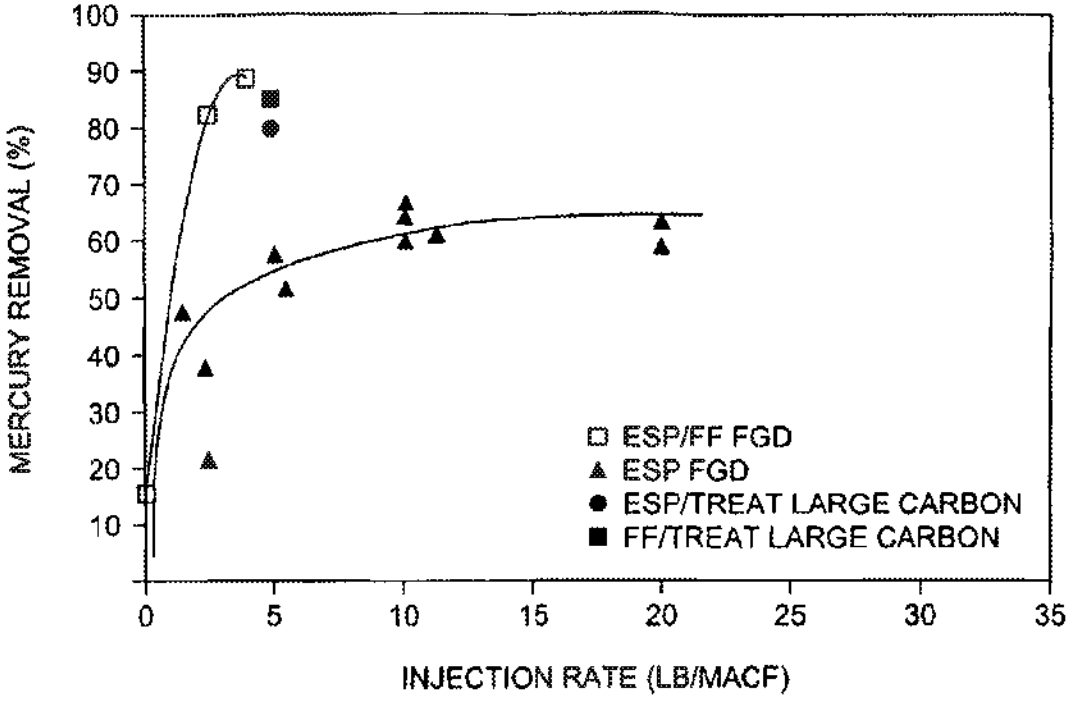


Fig. 7

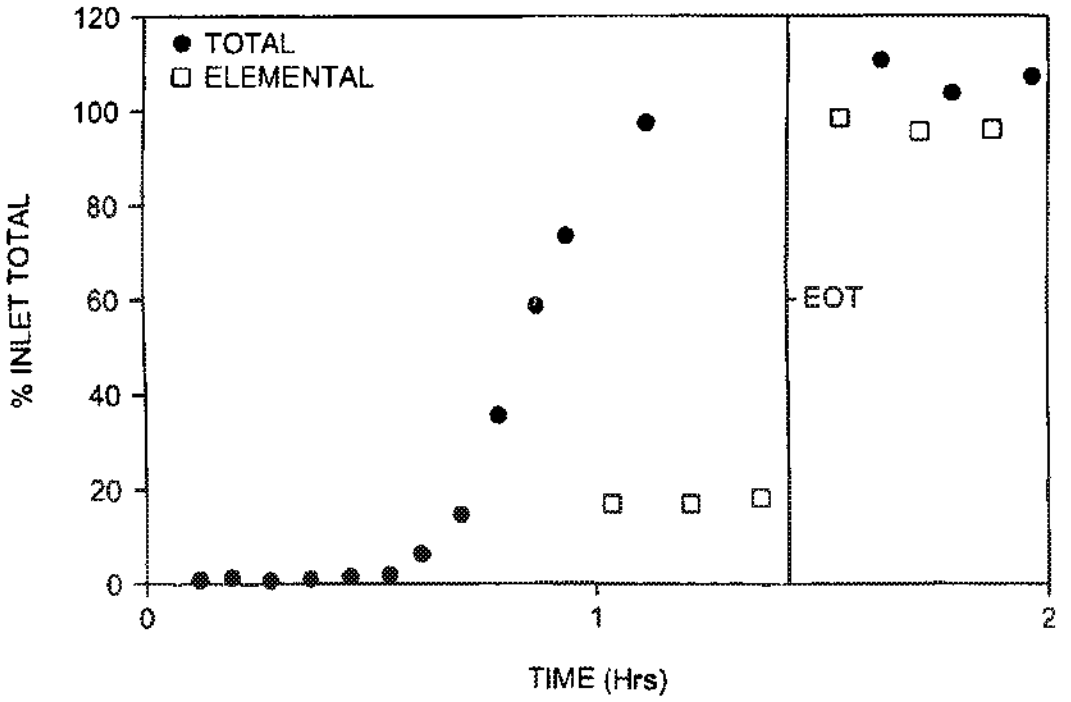


Fig. 8

PAC ET AL. EXHIBIT 1019
Page 1858

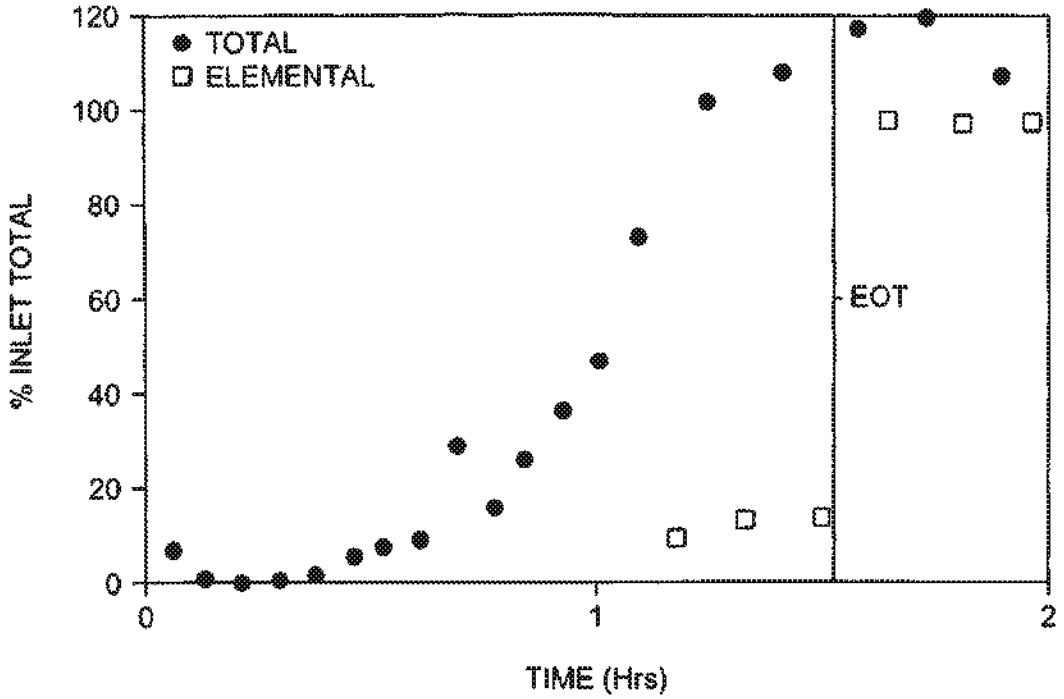


Fig. 9

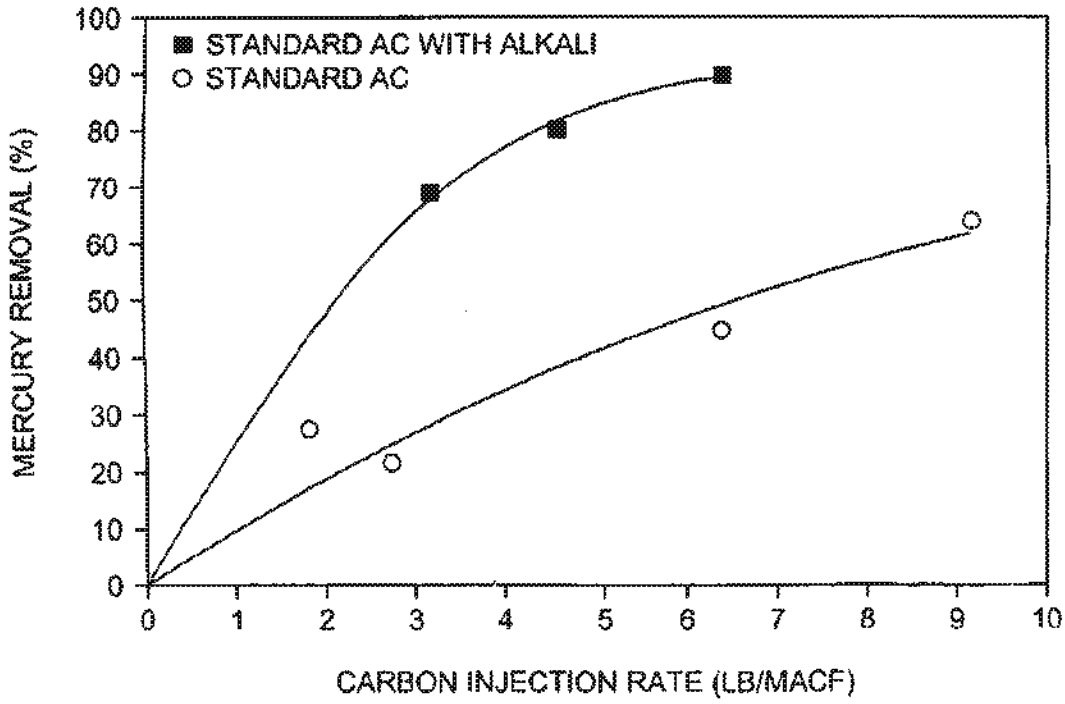


Fig. 10

PAC ET AL. EXHIBIT 1019
Page 1859

Espacenet

Bibliographic data: CN104619410 (B) — 2016-05-04

Carbon nanocomposite sorbent and methods of using the same for separation of one or more materials from a gas stream

Inventor(s):	OLSON EDWIN S. ; PAVLISH JOHN HENRY
Applicant(s):	ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION, INC
Classification:	**- international:** ***B01D53/02; B01D53/64; B01J20/12; B01J20/20; B01J20/30; B01J20/32***
	- cooperative: **B01D53/02**; **B01D53/508**; **B01D53/80**; **B01J20/12**; **B01J20/20**; **B01J20/205**; **B01J20/3078**; **B01J20/3204**; **B01J20/324**; B01D2251/108; B01D2253/102; B01D2253/108; B01D2253/11; B01D2253/25; B01D2253/304; B01D2258/0283
Application number:	CN2013833231 20130417
Priority number(s):	WO2013US36964 20130417 ; US201213453274 20120423
Also published as:	CN104619410 (A) US2013280156 (A1) US9011805 (B2) US2015098878 (A1) WO2013162968 (A2) more

Abstract of CN104619410 (A)

The present invention relates to carbon nanocomposite sorbents. The present invention provides carbon nanocomposite sorbents, methods for making the same, and methods for separation of a pollutant from a gas that includes that pollutant. Various embodiments provide a method for reducing the mercury content of a mercury-containing gas.

PAC ET AL. EXHIBIT 1019

(19)中华人民共和国国家知识产权局

(12)发明专利

(10)授权公告号 CN 104619410 B
(45)授权公告日 2016.05.04

(21)申请号 201380033231.6
(22)申请日 2013.04.17
(30)优先权数据
13/453274 2012.04.23 US
(85)PCT国际申请进入国家阶段日
2014.12.23
(86)PCT国际申请的申请数据
PCT/US2013/036964 2013.04.17
(87)PCT国际申请的公布数据
WO2013/162968 EN 2013.10.31
(73)专利权人 能源及环境研究中心基金会
地址 美国北达科他州
(72)发明人 E.S.奥尔森 J.H.帕夫利什
(74)专利代理机构 中国专利代理(香港)有限公司 72001
代理人 邹雪梅 徐厚才
(51)Int.Cl.
B01J 20/12(2006.01)
B01D 53/02(2006.01)
B01J 20/30(2006.01)
B01J 20/32(2006.01)
B01D 53/64(2006.01)
B01J 20/20(2006.01)
(56)对比文件
US 20110168018 A1,2011.07.14,
US 20090136401 A1,2009.05.28,
CN 101816922 A,2010.09.01,
US 20040076570 A1,2004.04.22,
审查员 孙思

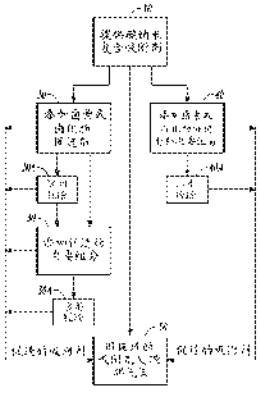
权利要求书2页 说明书24页 附图6页

(54)发明名称

碳纳米复合吸附剂及其用于从气流中分离一种或多种材料的方法

(57)摘要

本发明涉及碳纳米复合吸附剂。本发明提供碳纳米复合吸附剂、其制造方法和从包括污染物的气体中分离该污染物的方法。各种实施方案提供了降低含汞气体的汞含量的方法。



CN 104619410 B

1.一种用于降低含污染物气体的污染物含量的方法，所述方法包括：

提供或获得碳纳米复合吸附剂材料，其包括

提供或获得包含碳水化合物的碳前体，

提供或获得基底材料，

使所述碳前体与所述基底材料接触以提供纳米复合原材料，和

加热该纳米复合原材料，以提供所述碳纳米复合吸附剂；

提供或获得卤素或卤化物促进剂；

通过至少一部分吸附剂材料与卤素或卤化物促进剂化学反应促进该部分吸附剂材料以形成促进的吸附剂；

使至少部分促进的吸附剂与所述污染物接触以形成污染物-吸附剂组合物；和

从含污染物气体分离至少一部分所述污染物-吸收剂组合物以提供清洁气体。

2.权利要求1的方法，其中所述污染物是汞。

3.权利要求2的方法，其中所述促进的吸附剂与所述含汞气体中存在的至少70重量%的汞结合。

4.权利要求1的方法，其中促进包括向气流中以一定注射速率注入碳纳米复合吸附剂材料和以一定注射速率单独注入至少一种促进剂，由此飞行中的反应产生促进的吸附剂，其中所述促进剂选自分子卤素、卤化物及其组合，其中所述促进剂在气相中或作为蒸气反应，其中每100克碳纳米复合吸附剂材料加入1至30克促进剂。

5.权利要求1的方法，其中所述碳前体包含红糖、麦芽糖、焦糖、蔗糖、玉米糖浆、糖蜜、淀粉、或糖废品。

6.权利要求1的方法，其中所述基底材料包含硅藻土、粘土、沸石或矿物。

7.权利要求1的方法，其中从含污染物的气体中分离至少一部分所述污染物-吸附剂组合物包括从所述含污染物气体分离颗粒物，该颗粒物包含至少一部分所述污染物-吸附剂组合物。

8.权利要求1的方法，还包括降低含污染物的气体中的SO_2或SO_3的浓度。

9.权利要求1的方法，其中所述卤素或卤化物促进剂是包含蒸气形式、固体形式、在溶剂中或其组合的形式。

10.权利要求1的方法，其中所述卤素或卤化物促进剂包含第V族卤化物、第VI族卤化物或其混合物中的至少一种。

11.权利要求1的方法，其中促进剂前体转化成与所述吸附剂反应的卤素或卤化物促进剂。

12.权利要求1的方法，其中所述卤素或卤化物促进剂是NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$或HCl。

13.权利要求1的方法，其中所述接触在气相、液相或其组合中发生。

14.降低含汞气体的汞含量的方法，所述方法包括：

提供或获得碳纳米复合吸附剂，其包括：

提供或获得包含碳水化合物的碳前体；

提供或获得基底材料；

使碳前体和基底材料接触以提供纳米复合原材料；和

PAC ET AL. EXHIBIT 1019
Page 1862

加热所述纳米复合原材料以提供碳纳米复合吸附剂；

提供或获得卤素或卤化物促进剂；

通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进该部分吸附剂材料，从而形成促进的吸附剂；

使至少一部分促进的吸附剂与汞接触以形成汞-吸附剂组合物；和

从含污染物气体中分离至少一部分所述汞-吸附剂组合物。

PAC ET AL. EXHIBIT 1019
Page 1863

碳纳米复合吸附剂及其用于从气流中分离一种或多种材料的方法

[0001] 优先权声明

[0002] 本专利申请要求2012年4月23日提交的美国专利申请序号13/453,274的优先权，其全文并入本文作为参考。

[0003] 政府资助声明

[0004] 本发明在U.S. Department of Energy (DOE)依据名为"EERC-DOE Joint Program on Research and Development for Fossil Energy-Related Resources"的DOE Cooperative Agreement Number DE-FC26-08NT43291；名为"Fate and Control of Mercury and Trace Elements"的Subtask 4.8；EERC Fund Number 14990给予的政府资助下完成。美国政府在本发明中拥有某些权利。

[0005] 发明背景

[0006] 汞(Hg)排放由于它们的毒性和生物积累能力而成为健康和环境问题。美国环境保护署(EPA)已经颁发了用于控制来自垃圾能源化(waste-to-energy)、水泥生产和燃煤发电厂的Hg排放的规章。可以通过注入吸附剂，如活性炭捕获来自工业来源(例如发电厂)的烟气中的汞，然后可通过微粒收集装置除去。市场所需的标准吸附剂(例如活性炭)的量很大。标准吸附剂并非总是有效并随着注射速率提高而变得更昂贵。

[0007] 纳米复合材料是一种多相固体材料，其中一个相具有至少一个小于大约1000纳米的尺寸或其中小于大约1000纳米的重复距离将构成该材料的相隔开。纳米复合材料——其中一个或多个相是本体基质且一种或多种其它材料是纳米尺寸的相——具有独特的性质，该纳米复合材料的机械、电、热、光学、化学或催化性质明显不同于各组成材料。

[0008] 碳纳米复合材料的最初实例是通过将单体插入粘土中的层间间隙、使单体聚合并将该聚合物碳化制成。碳层的最小厚度为1.1纳米(Kyotani-1988)。在接下来的二十年，各种单体与几种粘土和其它多孔载体材料一起使用。在一些情况下，除去该复合材料的无机部分以研究类石墨的碳结构。在2004年，Bakandritsas等人使用蔗糖作为碳源生产碳-粘土纳米复合材料(Bakandritsas-2004)。对于粘土和石墨烯层，各层的厚度分别为大约1纳米和0.4纳米。稍后，这一团队描述了这些用于吸附水溶液中的气体(CO_2、CH_4、N_2)和有机溶质的用途(Bakandritsas-2005)。由于它们容易成型、具有高表面积并导电，使用源自蔗糖的碳-粘土纳米复合材料制造电极和传感器(Darder-2005, Gomez-Aviles-2007, Fernandez-Saavedra-2008, Gomez-Aviles-2010)。源自蔗糖的多孔碳-粘土纳米复合材料也已用于催化剂载体(Nguyen-Thanh-2006a, Nguyen-Thanh-2006b, Tkeue-2008)。

[0009] 在文献中已经描述了复合材料用于吸附金属离子，如Hg^{2+}的几个用途。这些包括下列材料：壳聚糖涂覆的陶瓷(Boddu-2002)、在粘土上的聚吡咯膜(Eisazadeh-2007)、在硅藻土的巯基官能化聚硅氧烷膜(Wang-2007)、在灰分上的聚苯胺膜(Ghorbani-2011)和聚苯胺与磷钨酸的复合材料(Zhang)。这些无一是碳纳米复合材料；相反，它们通常是沉积在载体上的聚合物膜并受限于稳定性以及再循环和加工困难。

[0010] 已用由非碳材料制成的几种类型的纳米复合材料从气流中分离元素或氧化汞。

PAC ET AL. EXHIBIT 1019
Page 1864

SiO_2-TiO_2纳米复合材料在紫外辐射下用于Hg捕获(Li-2008)。这种技术受困于必须有效照射含有细粒的燃烧流出物的困难。描述了磁铁矿-和Ag-浸渍的沸石纳米复合材料(Dong-2009)。Ag纳米复合材料被质疑本身代表重大的环境风险以及是高成分吸附剂。报道了用CeO_2-WO_3/TiO_2纳米复合材料捕获烟气中的Hg(Wan-2011)。这些非碳吸附剂具有不合期望的更高成本和更慢动力学。

[0011] 发明概述

[0012] 在各种实施方案中,本发明提供从包括一种材料的气体中分离所述材料的方法。在一些实施方案中,该材料可以是污染物或所述气体的不想要的成分。该方法包括提供或获得碳纳米复合吸附剂。该方法还包括使至少一部分所述材料与所述吸附剂接触以形成材料-吸附剂组合物(composition)。该方法还包括从含所述材料的气体中分离至少一部分所述材料-吸附剂组合物。该分离产生分离的或部分分离的气体。

[0013] 在各种实施方案中,本发明提供降低含污染物的气体的污染物含量的方法。该方法包括提供或获得碳纳米复合吸附剂。该方法包括提供或获得卤素或卤化物促进剂(promoter)。该方法包括促进至少一部分吸附剂材料。吸附剂材料的促进包括使吸附剂材料的所述部分与所述卤素或卤化物促进剂化学反应。吸附剂材料的促进产生促进的吸附剂。该方法包括使至少一部分促进的吸附剂与污染物接触。在一些实施方案中,该方法还可包括使所述污染物与未促进的吸附剂接触。促进的吸附剂与污染物的接触形成污染物-吸附剂组合物。该方法还包括分离至少一部分所述污染物-吸附剂组合物。该分离产生具有比原材料(例如未净化的)含污染物的气体低的污染物含量的净化气体。在各种实施方案中,该污染物可以是汞。

[0014] 在各种实施方案中,本发明提供形成碳纳米复合材料的方法。该方法包括获得或提供碳前体材料。该方法包括提供或获得基底材料。该方法包括使碳前体和基底材料接触以提供纳米复合原材料。该方法还包括加热所述纳米复合原材料以提供碳纳米复合吸附剂。在各种实施方案中,本发明提供由该方法生成的碳纳米复合材料。在一些实例中,本发明提供与所述纳米复合材料在所述方法的运行过程中遇到的各种材料结合的纳米复合材料,如与汞、与氧化汞或与含汞气体结合的纳米复合材料。在一些实施方案中,该方法可包括添加卤素或卤化物促进剂并使所述促进剂与所述吸附剂反应以形成促进的碳纳米复合吸附剂。

[0015] 令人惊讶地,尽管活性炭常规用于捕获烟气流中的污染物,但碳纳米复合材料以前尚未用于气相汞捕获。传统意见在于,碳纳米复合材料中的过量无机载体,如粘土阻碍污染物吸附在碳上。但是,令人惊讶地,根据本发明的一些实施方案,该非碳部分可增强污染物吸附在邻近的碳石墨烯层上。该纳米复合材料的碳部分的基面在碳纳米复合结构内确实严重受阻。但是,在该结构中非常充分暴露出碳边缘结构,而这些是有效用于污染物捕获(例如汞、硒、砷等)的碳部分。如本文所述,可通过与卤素、卤化氢或卤化铵的反应促进石墨烯边缘结构以产生对污染物,如汞的氧化和捕获具有高度反应性的碳正离子边缘结构。

[0016] 由于载体材料,如粘土本身是惰性的,某些载体材料促进污染物被碳层氧化也是出乎意料的。但是,根据本发明的一些实施方案,聚阴离子铝硅酸盐层(例如来自粘土)可以稳定邻近的石墨烯碳结构上的阳离子位点(这对污染物,如汞的氧化是必不可少的)的并发。对于由石墨烯层和极性无机结构构成的碳-硅藻(硅酸盐)纳米复合材料或其它纳米复

PAC ET AL. EXHIBIT 1019
Page 1865

合材料可发生相同的稳定效应。

[0017] 在包括通过由相应卤化铵的降解或反应获得的卤化氢化合物促进纳米复合材料的实施方案中，无机部分的另一有利作用是为铵盐的分解或反应释放的氨提供结合位点。结合的氨形成具有碱性特征的络合物，其与烟气中的SO_2反应并防止它们干扰污染物，如汞捕获在边缘结构上。

[0018] 在包括粘土作为载体的实施方案中无机载体的另一优点在于，该粘土稳定地分散在水性介质中。粘土通常难从水性介质中过滤或分离，但在与碳的纳米复合材料的形式下，该材料容易通过过滤从水性介质中分离。因此，该纳米复合材料可方便地用于捕获水环境中的汞。

[0019] 本发明可以有利地比其它方法更有效地从包括一种材料的气体中分离所述材料(例如污染物)。本发明与用于从含汞气体中除汞的其它方法和材料相比提供某些优点。本发明的各种实施方案的方法和材料可以比其它除汞方法更有效地从气体中捕获和脱除汞。本发明的各种实施方案的方法和材料可以比其它除汞方法更有效地运行。例如，各种实施方案的方法和材料与其它方法相比可以以更小的财政支出量除去给定量的汞。例如，各种实施方案的方法和材料与其它除汞方法相比，包括与包含碳吸附剂的其它除汞方法相比可以在给定的碳质量下除去更大量的汞。因此，各种实施方案的方法和材料与其它除汞方法相比能够使用更少的吸附剂材料(例如总体上更少的碳)以及处置更少的用过的吸附剂材料。

[0020] 在各种实施方案中，本发明提供降低含汞气体的汞含量的方法。该方法包括提供或获得碳纳米复合吸附剂。通过包括提供或获得碳前体和提供或获得基底材料的步骤制造所述碳纳米复合吸附剂。步骤还包括使碳前体和基底材料接触。该接触提供纳米复合原材料。步骤还包括加热所述纳米复合原材料。该加热提供所述碳纳米复合吸附剂。用于降低含汞气体的汞含量的方法还包括提供或获得卤素或卤化物促进剂。该方法包括促进至少一部分吸附剂材料。吸附剂材料的促进包括使吸附剂材料的所述部分与所述卤素或卤化物促进剂化学反应。吸附剂材料的促进产生促进的吸附剂。该方法包括使至少一部分促进的吸附剂与汞接触。促进的吸附剂与汞的接触形成汞-吸附剂组合物。该方法还包括从所述气体中分离至少一部分所述汞-吸附剂组合物。该分离产生具有比未净化气体低的汞含量的净化气体。

[0021] 在各种实施方案中，本发明提供制造碳纳米复合吸附剂的方法。该方法包括提供或获得碳前体。该方法包括提供或获得基底材料。该方法包括使碳前体和基底材料接触。碳前体和基底材料的接触提供了纳米复合原材料。该方法还包括加热所述纳米复合原材料。所述纳米复合原材料的加热提供了所述碳纳米复合吸附剂。

[0022] 附图简述

[0023] 在不一定按比例绘制的附图中，几个视图中的类似数字描述基本类似的部件。具有不同字母后缀的类似数字代表基本类似的部件的不同情况。附图通常示例，例如但不作为限制，本文中论述的各种实施方案。

[0024] 图1示意性示例根据各种实施方案制备促进的碳吸附剂的方法。

[0025] 图2示例根据各种实施方案导致汞氧化和捕获的化学反应的提出的机械模型。

[0026] 图3A和3B示意性示例根据各种实施方案制备促进的碳吸附剂和烟气(例如来自燃

PAC ET AL. EXHIBIT 1019
Page 1866

烧)和/或来自气化系统的产物气体中的烟气除汞方法。

[0027] 图4示例根据各种实施方案的NanoG-CM测试的微粒试验燃烧器(particulate test combustor)(PTC)结果。

[0028] 图5示例根据各种实施方案的NanoG-CM测试的PTC结果。

[0029] 图6示例根据各种实施方案,在高硫烟气中用复合吸附剂捕获飞行中的汞的模型结果。

[0030] 发明详述

[0031] 现在详细提到所公开的主题的某些权利要求,在附图中示例其实例。尽管将联系枚举的权利要求描述所公开的主题,但要理解的是,它们无意将所公开的主题限于这些权利要求。相反,所公开的主题意在涵盖可包括在如权利要求规定的本公开的主题的范围内的所有替代物、修改和等同物。

[0032] 在本说明书中提到"一个实施方案"、"一种实施方案""一个实施例实施方案"等是指所述实施方案可包括特定要素、结构或特征,但不一定每一实施方案都包括该特定要素、结构或特征。此外,此类术语不一定是指同一实施方案。此外,当联系一个实施方案描述特定要素、结构或特征时,其意味着联系其它实施方案应用此类要素、结构或特征在本领域技术人员的知识范围内,无论是否明确描述。

[0033] 以范围格式表示的值应以灵活方式解释以不仅包括作为该范围的界限明确列举的数值,还包括该范围内包含的所有单个数值或子范围,就像明确列举各数值和子范围那样。例如,"大约0.1%至大约5%"的浓度范围应被解释为不仅包括大约0.1重量%至大约5重量%的明确列举的浓度,还包括所述范围内的各浓度(例如1%、2%、3%和4%)和子范围(例如0.1%至0.5%,1.1%至2.2%,3.3%至4.4%)。

[0034] 在本文中,除非上下文清楚地另有规定,术语"一种"、"一个"或"该"用于包括一种(个)或多于一种(个)。除非另有说明,术语"或"用于表示非排他的"或"。此外,要理解的是,本文所用的并且没有另行定义的用词或术语仅用于说明而非限制。章节标题的任何使用意在有助于阅读本文而非解释为限制;与章节标题相关的信息可能出现在该特定章节内或外。此外,本文中提到的所有出版物、专利和专利文献全文并入本文作为参考,就像逐一并入作为参考一样。在本文和并入本文作为参考的那些文献之间的用法不一致的情况下,并入的参考文献中的用法应被视为补充本文的用法;对于不可调和的矛盾,以本文中的用法为准。

[0035] 在本文所述的制造方法中,步骤可以以任何次序进行而不背离本发明的原理,除非明确地列举时间或操作上的次序。

[0036] 此外,指定的步骤可以同时进行,除非明确的权利要求用语提到它们单独进行。例如,要求保护的实施X的步骤和要求保护的实施Y的步骤可以在单个操作内同时进行,所产生的方法落在要求保护的方法的字面范围内。

[0037] 定义

[0038] 术语"大约"允许数值或范围的一定程度的可变性,例如在指定的数值或指定的范围界限的10%内,5%内或1%内。当给出一个范围或一连串数值的名单时,除非另有规定,也公开了该范围内的任何数值或给定的一连串数值之间的任何数值。

[0039] 本文所用的术语"烃"是指包括碳和氢原子的官能团或分子。该术语还是指通常包

PAC ET AL. EXHIBIT 1019
Page 1867

括碳和氢原子但其中所有氢原子被其它官能团取代的官能团或分子。

[0040] 本文所用的术语"孔隙"是指固体物中的任何尺寸或形状的凹陷、狭缝或空穴。孔隙可以贯穿物体或部分穿过物体。一个孔隙可与其它孔隙相交。

[0041] 本文所用的术语"溶剂"是指可以溶解固体、液体或气体的液体。溶剂的非限制性实例是硅酮、有机化合物、水、醇、离子液体和超临界流体。

[0042] 本文所用的术语"空气"是指具有与通常在地平面取自大气的气体的天然组成大致相同的组成的气体混合物。在一些实例中，空气取自周围环境。空气的组成包括大约78%氮气、21%氧气、1%氩气和0.04%二氧化碳，以及少量的其它气体。

[0043] 本文所用的术语"室温"是指环境温度，其可以为例如大约15℃至大约28℃。

[0044] 本文所用的"基本"是指大多数或大部分，例如至少大约50%、60%、70%、80%、90%、95%、96%、97%、98%、99%、99.5%、99.9%、99.99%或至少大约99.999%或更大。

[0045] 本文所用的"纳米复合材料"是指一种多相固体材料，其中一个相具有至少一个小于大约1000纳米的尺寸或其中小于大约1000纳米的重复距离将构成该材料的至少一些相隔开。在一些实施方案中，一个相具有至少一个大约1纳米-1000纳米的尺寸或大约1-1000纳米的的重复距离将构成该材料的至少一些相隔开；在另一些实施方案中，该范围的下限可以小于大约1纳米。

[0046] 本文所用的"相"是指一个空间区域，其中材料的所有物理性质基本均匀，如物理状态、结构和化学。例如，液态和气态可以是两个不同的相。例如，分布在基底上的碳材料可以是两个不同的相。例如，分布在多孔基底上的碳材料可以是两个不同的相。

[0047] 本文所用的"矿物"是指通过生物地球化学过程形成的天然存在的固体化学物质，其具有例如特有的化学组成、高度有序的原子结构和特定的物理性质。

[0048] 描述

[0049] 本发明的各种实施方案提供用于从气体中分离材料的方法和材料。在一些实施方案中，该材料可以是污染物或不想要的成分。在另一些实施方案中，该材料可以是任何合适的材料。该气体包括该材料；例如，该材料可以溶解或悬浮在该气体中。该材料包括碳纳米复合吸附剂。该方法包括提供或获得碳纳米复合吸附剂。该方法包括使气体中的至少一部分所述材料与所述吸附剂接触以形成材料-吸附剂组合物。该方法还包括从该气体中分离颗粒物。颗粒物包括至少一部分所述材料-吸附剂组合物。该分离产生分离的气体——其中所述材料的量低于原材料气体。在本文中给出实施方案的许多具体实例，其中被分离的材料是汞，其中用卤化物或卤素处理(例如促进)碳纳米复合吸附剂，或其中用其它材料处理碳纳米复合吸附剂。但是，本领域普通技术人员会由这些实例类推并且会认识到实施方案包括使用任何合适的碳纳米复合材料从气体中分离任何合适的材料(例如任何合适的污染物，例如砷、硒等)。

[0050] 在各种实施方案中，从气体中分离的材料是污染物(例如不想要或不合意的成分)并且希望从气体中除去该材料以净化气体。污染物可包括汞。污染物可包括元素汞。污染物可包括氧化汞。在各种实施方案中，该方法可包括提供促进剂。可以使该促进剂与至少一部分吸附剂材料化学反应，以形成促进的吸附剂。与污染物接触的吸附剂可包括促进的吸附剂。在各种实施方案中，该促进剂可以是卤素或卤化物促进剂。

[0051] 降低含汞气体的汞含量

PAC ET AL. EXHIBIT 1019
Page 1868

[0052] 在各种实施方案中，本发明提供用于降低含汞气体的汞含量的方法和材料。该方法包括提供或获得碳纳米复合吸附剂。该方法可包括提供或获得卤素或卤化物促进剂。该方法可包括通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。该方法包括使至少一部分促进的吸附剂与汞接触以形成汞-吸附剂组合物。在各种实施方案中，与汞接触的吸附剂也可包括未促进的吸附剂。该方法还包括从含汞气体中分离至少一部分汞-吸附剂组合物。该分离产生具有比原材料气体低的汞含量的净化气体。该含汞气体中的汞可以是汞的任何合适的形式，例如元素汞。汞可以悬浮或溶解在该气体中。在一些实施方案中，促进剂可以是HBr或NH_4Br，在一些实例中，可通过溴化铵NH_4Br的降解或反应提供HBr。在一些实施方案中，促进剂(例如HBr)或促进剂前体(例如NH_4Br)可以与碳纳米复合吸附剂分开或与碳纳米复合吸附剂一起以一定注射速率注入烟气中(例如可以在注射前施加到吸附剂中)。

[0053] 碳纳米复合吸附剂

[0054] 本发明实施方案提供的方法使用碳纳米复合吸附剂从气体中除去材料，例如从含汞气体中除汞。纳米复合材料由两个或更多个相构成，以使这些相在纳米级尺寸(例如1000纳米或更小)下互相密切连接。当这些纳米复合材料高度多孔，尤其是微米多孔或纳米多孔时，两种纳米复合材料的密切连接可产生该高表面积以及相应高的催化活性。当催化活性的材料，如某些形式的碳分散在具有高表面积的本体(bulk)基底上时，情况尤其如此。碳纳米复合材料可包括涂布在无机载体上或插入无机载体中的石墨烯片的薄层。

[0055] 在一些实施方案中，该碳纳米复合吸附剂可以含有大约50%或更少的碳，或大约3重量%至大约50重量%碳，或大约5重量%至大约10重量%碳。在一些实施方案中，该碳纳米复合吸附剂可以含有大约1重量%至大约99.5重量%的本体基底，或大约50重量%至大约97重量%的本体基底，或大约90重量%至大约95重量%的本体基底(例如硅藻土、蒙脱石粘土等)。

[0056] 本发明的纳米复合材料可以是任何合适的碳纳米复合材料。在一些实例中，该纳米复合材料可以是分布在适当多孔或适当高表面积的基底上的适当形式的碳。该纳米复合材料可以制造或可以由商业途径获得。在一些实施方案中，由商业途径获得该纳米复合材料，并可能需要进一步加工步骤以适当活化碳以使用于分离材料，如分离汞。适当活化该纳米复合材料的进一步加工步骤可包括用热处理(例如煅烧)、用碱处理、用卤化物或卤素处理(例如促进)或它们的组合。例如，在一些实施方案中，用卤化物或卤素处理纳米复合材料可促进纳米复合材料以在纳米复合材料中形成可将汞从元素汞转化成氧化汞(例如汞氧化物)的活性位点。在一些实施方案中，不促进该纳米复合材料。例如，在一些实施方案中，用酸或碱处理纳米复合材料可以使纳米复合材料准备好用卤化物或卤素促进，或可以使纳米复合材料获得合适的反应性。在另一些实施方案中，在使用卤化物或卤素促进之前或在使用吸附剂从气体中除去汞或其它材料之前不用酸或碱处理。

[0057] 该方法可包括使至少一部分纳米复合吸附剂与气体中的材料，如汞接触以形成组合物，如汞-吸附剂组合物。本发明不依赖于任何特定的作用机制；只要使用碳纳米复合吸附剂从气体中除去该材料，作为本发明的一个实施方案包含该方法。在一些实施方案中，汞以其元素形式被该吸附剂吸收；汞-吸附剂组合物可包括吸附剂和汞的元素形式。在一些实施方案中，汞被该吸附剂通过化学反应(如氧化)转化，以使来自该气体的汞转化成汞的氧化物(例如HgO)；汞-吸附剂组合物可包括吸附剂和汞的转化形式，如氧化汞。在一些实施方

PAC ET AL. EXHIBIT 1019
Page 1869

案中，汞-吸附剂组合物可包括元素汞和转化汞，如氧化汞的组合。在一些实例中，元素汞的吸收或汞的转化可改变该吸附剂，以使吸附剂在形成该组合物后至少略微不同；例如在特定形式的汞原子转化成氧化汞后，造成转化的吸附剂的活性位置可能变得无反应性或反应性较低。

[0058] 在一些实例中，元素汞或转化的汞可保持吸收在吸附剂上直至在稍后的分离步骤中除去该汞-吸附剂组合物。例如，元素汞或转化的汞可以被吸收到，或反应并吸收到吸附剂组合物中或上，以使含汞气流中至少大约1重量%、3重量%、5重量%、10重量%、20重量%、30重量%、40重量%、50重量%、60重量%、70重量%、80重量%、90重量%、95重量%、96重量%、97重量%、98重量%、99重量%、99.9重量%、99.99重量%或大约99.999重量%或更多的汞被吸收到，或反应并吸收到吸附剂组合物中或上。在一些实施方案中，在从气体中分离汞-吸附剂组合物之前，可以从该汞-吸附剂组合物中释放元素汞或转化的汞；例如，可以从该汞-吸附剂组合物中释放少于大约1重量%、3重量%、5重量%、10重量%、20重量%、30重量%、40重量%、50重量%、60重量%、70重量%、80重量%、90重量%、95重量%或少于大约99重量%的汞。在一些实例中，大部分被吸收的元素汞或转化的汞可保持为汞-吸附剂组合物的一部分直至在稍后的分离步骤中除去该汞-吸附剂组合物。在一些实例中，从汞-吸附剂组合物中释放的转化汞可稍后通过分离步骤从该气体中除去。在一些实例中，已从汞-吸附剂组合物中释放的元素汞或转化的汞可以接触碳纳米复合吸附剂以形成稍后通过分离步骤除去的汞-吸附剂组合物。

[0059] 在各种实施方案中，该碳纳米复合吸附剂包括与含汞气体中的汞结合的结合位点。在一些实例中，该吸附剂材料包括与卤素或卤化物反应或用卤素或卤化物浸渍的碳以形成促进的吸附剂中的汞结合位点。在一些实例中，该吸附剂材料可包括至少部分通过用碱处理活化的碳，其中该碱活化碳可以与卤素、卤化氢和第V或VI族卤化物反应或被卤素、卤化氢和第V或VI族卤化物浸渍以形成促进的吸附剂中的汞结合位点。在一些实例中，该碳中的结合位点与含汞气体中的汞反应以形成汞-吸附剂组合物。在一些实例中，该碳的至少一部分结合位点与含汞气体中的氧化汞反应以形成汞-吸附剂组合物。

[0060] 在一些实施方案中，该碳纳米复合材料中的至少一部分碳是石墨烯形式的碳。石墨烯形式的碳在一些实施方案中可包括较高浓度的适合作为纳米复合材料的活性位点的位置。在一些实例中，石墨烯碳的某些部分可具有适合作为纳米复合材料的活性位点的位置的最高浓度：在一些实施方案中在边缘，在一些实施方案中在非边缘位置。适合作为活性位点的此类位置可通过如本文所述用卤化物或卤素处理活化。在各种实施方案中，该碳纳米复合材料中的碳可具有至少大约1重量%、2重量%、3重量%、4重量%、5重量%、10重量%、20重量%、30重量%、40重量%、50重量%、60重量%、70重量%、80重量%、90重量%、95重量%、96重量%、97重量%、98重量%、99重量%、99.9重量%、99.99重量%或大于大约99.999重量%的石墨烯形式的碳。

[0061] 在一些实施方案中，该碳纳米复合吸附剂具有大于40微米或大于60微米的平均粒径或大于要处理的烟气流中的飞灰或夹带灰分的粒度分布，以使碳纳米复合吸附剂和灰分可以在分离步骤中通过物理手段分离。

[0062] 在一个实例中，该纳米复合材料可以是当该多孔结构中所含的卤化物盐在注入加热管道的过程中分解时被促进的(针对气相Hg氧化)碳纳米复合材料。在一些实例中，该卤

PAC ET AL. EXHIBIT 1019
Page 1870

化物盐可以是溴化铵。在一些实例中，该碳纳米复合材料可包括石墨烯。在一些实例中，该纳米复合材料的非碳部分包括高表面积的多孔无机基质。

[0063] 形成碳纳米复合吸附剂的方法

[0064] 该碳纳米复合吸附剂可以获得、可以合成或它们的任何组合。例如，获得的碳纳米复合材料在适用于本发明的方法的实施方案之前可能需要进一步处理。各种实施方案提供形成碳纳米复合吸附剂的方法、由此形成的碳纳米复合吸附剂或碳纳米复合吸附剂与含汞气体的组合。例如，制造碳纳米复合吸附剂的方法可包括提供或获得碳前体，其中该碳前体提供碳纳米复合吸附剂中的碳。该方法可包括提供或获得基底材料，其中该基底材料提供碳纳米复合吸附剂中的本体基底。该方法可包括使碳前体和基底材料接触以提供纳米复合原材料。该方法可包括加热该纳米复合原材料。纳米复合原材料的加热提供了纳米复合吸附剂。在使用前，可任选对该纳米复合吸附剂施以加工步骤，如用碱处理，如用卤素或卤化物处理，这能在碳纳米复合材料上形成可与元素汞反应以将汞例如转化成氧化汞（例如汞氧化物）的活性位点。

[0065] 在一些实例中，使用基底，如粘土（例如提供开放和多孔的下部结构的基底），可以使碳水化合物（例如碳前体）与该基底接触。可以加热所得混合物，这产生具有低碳密度的碳层，其覆盖该基底材料的开放多孔结构。在一些实施方案中，在加热该混合物时，基底可以溶胀。可以通过由加热步骤造成的碳前体的化学反应，包括分解反应，包括例如热解、脱水或脱羧反应制造碳层。在一些实施方案中，制成的碳层包括石墨烯形式的碳，例如作为石墨烯带。石墨烯形式的碳，尤其在其边缘，在一些实施方案中可包括较高浓度的适合作为纳米复合材料的活性位点的位置。该碳涂布在高度多孔基质中无规堆叠的粘土粒子的表面。在实例中，可以将卤化物或卤素引入吸附剂，促进碳并增强吸附剂对汞的反应性。卤化物或卤素可以以各种形式引入。

[0066] 在一些实施方案中，可以“在飞行中”产生促进的吸附剂。这可以通过例如使卤素的任何组合的蒸气在飞行中与碳纳米复合吸附剂接触实现。可以通过在输运空气流或含汞的污染气流（要从中除汞）中使卤素的任何组合的蒸气与碳纳米复合吸附剂接触实现碳纳米复合吸附剂在飞行中的促进。可以将粒子分散在输运空气（或其它气体）流中，其将该卤素-/卤化物促进的碳吸附剂粒子送往烟道或其它污染气流，然后从中除汞。在一些实施方案中，可以将粒子直接分散在烟气流中。

[0067] 在飞行中促进的简单性和所带来的成本节省是有利的。可以消除处理设施的资本设备成本、运行成本和运输成本。在飞行中的制备可以利用现有硬件和运行程序并有助于确保促进的吸附剂始终新鲜并因此更有反应性。在飞行中的制备能够快速现场调节吸附剂的促进程度以确保反应性足以匹配烟气变化的要求（如改变燃料或降低负荷时可能需要的那样），因此进一步优化汞捕获的经济性和效率。

[0068] 碳前体

[0069] 制造碳纳米复合吸附剂的方法可包括提供或获得碳前体，其中该碳前体提供碳纳米复合吸附剂中的碳。可以通过由加热步骤造成的碳前体的化学反应，包括分解反应，包括例如热解、脱水或脱羧反应制造该纳米复合材料中的碳层。

[0070] 碳前体可包括任何合适的碳前体，以使加热步骤将碳前体和基底转化成合适的碳纳米复合吸附剂。例如，碳前体可以是任何糖源，如碳水化合物（糖类），包括例如红糖、麦芽

PAC ET AL. EXHIBIT 1019
Page 1871

糖、焦糖、蔗糖、玉米糖浆、糖蜜、糖或糖加工废品，如甜菜糖废品、蔗糖废品等。碳前体可以是任何合适的淀粉或淀粉源。

[0071] 在一些实例中，碳前体可以以碳纳米复合吸附剂的原材料的大约1重量%至大约99重量%，大约20重量%至大约80重量%，或大约40重量%至大约60重量%存在。在一些实例中，碳前体可以以碳纳米复合吸附剂的原材料的大约50%或更少碳、或大约3重量%至大约50重量%碳、或大约5重量%至大约10重量%碳存在。这一段中的重量%是指基于碳前体和基底材料的总重量的重量百分比。

[0072] 基底材料

[0073] 制造碳纳米复合吸附剂的方法可包括提供或获得基底材料，其中该基底材料提供碳纳米复合吸附剂中的本体基底。

[0074] 该基底材料可包括任何合适的基底材料，以使加热步骤将碳前体和基底材料转化成合适的碳纳米复合吸附剂。该基底可包括任何合适的多孔材料。例如，该基底材料可以是硅藻土、沸石、多孔矿物(例如粘土)，包括例如蒙脱石(例如蒙脱土、膨润土、绿脱石、皂石)、高岭土、伊利石、绿泥石、海泡石或绿坡缕石。在一些实例中，该基底可包括聚合物、非金属、金属、类金属、陶瓷或混合物和共混物，以及它们的复合材料和合金。该材料可以是合成的或天然存在的或天然衍生的材料。合成聚合物的实例包括任何常见的热塑性材料和热固性材料。金属的实例包括铝、钛、铜、钢和不锈钢。陶瓷的实例包括任何形式的氧化铝、氧化锆、二氧化钛和二氧化硅。天然存在或天然衍生的材料的实例包括木材、木复合材料、纸、乙酸纤维素和地质地层，如花岗岩或石灰石。非金属的实例包括各种形式的碳，如石墨或碳。类金属的实例包括硅或锗。多孔材料可以是建筑材料，如混凝土或沥青。

[0075] 在一些实例中，基底材料可以以碳纳米复合吸附剂的原材料的大约1重量%至大约99重量%，大约20重量%至大约80重量%，或大约40重量%至大约60重量%存在。这一段中的重量%是指基于碳前体和基底材料的总重量的重量百分比。

[0076] 接触和加热

[0077] 制造碳纳米复合吸附剂的方法可包括使碳前体和基底材料接触以提供纳米复合原材料。该方法可包括加热(例如提供能量给)纳米复合原材料。加热(或以其它手段提供能量给)纳米复合原材料提供了纳米复合吸附剂。

[0078] 该接触可以以任何合适的方式进行。该接触将碳前体和基底材料混合，以便在加热该凝聚体(conglomeration)时(或施以任何其它合适的能量源)时，形成碳纳米复合吸附剂。可以进行该接触以使碳水化合物大致均匀分布在基底上。在一些实例中，可以添加水或另一溶剂以助于碳前体分布在基底上。在碳前体和基底的混合物中包括水的实例中，该凝聚体可以在加热之前干燥。干燥可以以任何传统方式进行(例如对流、传导、微波等)，包括在溶剂的沸点附近或以上(在水的情况下为例如50℃ 120℃或更高)、在大气压下、在压力下或在真空下加热。

[0079] 然后可以加热碳前体和基底的接触组合物以形成碳纳米复合吸附剂。该加热足以造成将碳前体转化成碳纳米复合材料中存在的碳形式的化学反应(例如分解反应)，包括例如热解、脱水或脱羧反应。该加热可以在任何合适的温度下进行以充分形成碳纳米复合材料，例如大约50℃、100℃、200℃、300℃、400℃、500℃、600℃、700℃、800℃、900℃、1000℃、1100℃或大约1200℃。该加热可以进行任何合适的时间以充分形成碳纳米复合材料，例如

PAC ET AL. EXHIBIT 1019
Page 1872

超过大约1分钟、2分钟、5分钟、10分钟、30分钟、1小时、1.5小时、2小时、3小时、4小时、5小时、10小时或超过大约24小时。该加热可以在任何合适的装置中进行，例如能使加热的空气在被加热的混合物周围流动的装置或炉。可以根据装置和纳米复合材料加速或延长该加热。

[0080] 卤素或卤化物促进剂

[0081] "卤素"被定义为周期表第VIIA族中包括的元素成员(第VIIA族[CAS]相当于第VIIB族[IUPAC])。卤素的分子元素形式，包括F_2、Cl_2、Br_2和I_2相对不与热烟气中的元素汞反应。任何卤素离子、气体或化合物可以是促进剂。

[0082] 降低含汞气体的汞含量的方法的实施方案包括提供或获得卤素或卤化物促进剂。该方法包括促进至少一部分吸附剂材料。吸附剂材料的促进包括使一部分吸附剂材料与卤素或卤化物促进剂化学反应或用卤素或卤化物促进剂浸渍一部分吸附剂材料。该卤素或卤化物促进剂可衍生自另一化合物(例如促进剂前体)的反应或降解。吸附剂材料的促进产生促进的吸附剂。吸附剂材料的促进可以在注入气流中之前、在注入气流中的过程中、在注入气流中后进行，或它们的组合，其中该气流可以是含汞气流、输运气流或其组合。在一些实例中，可以在促进剂和吸附剂反应之前将促进剂添加到吸附剂中，以使该促进剂添加至的气流的热造成吸附剂的促进。例如，该促进剂可以作为气体、作为溶解在液体中的气体或作为固体，如盐，或溶解在液体(例如水)中的其它物质(例如酸)添加。在促进剂在液体，如水中加入的实例中，可以使水干燥，这可以使促进剂附着到纳米复合吸附剂上、浸渍纳米复合吸附剂或与纳米复合吸附剂反应，或它们的组合。在一些实例中，预添加的促进剂可以是铵盐，如氯化铵、溴化铵或碘化铵，包括例如单-、二-、三-或四烷基卤化铵，或NH_4^+卤化物盐。在一些实例中，可以在接近促进时或在促进时将促进剂添加到吸附剂中；例如，促进剂可以与吸附剂一起添加到气流中或其在加热的气流，如含汞气流或进料气流内接触吸附剂。在一些实例中，该促进剂可以是NH_4Br。

[0083] 在一些实施方案中，该促进剂可以是HBr，在一些实例中，可通过促进剂前体，如溴化铵、溴化钠或溴化钙的降解或反应提供HBr。该促进剂可以是HCl，在一些实例中，可通过促进剂前体，如氯化铵、氯化钠或氯化钙的降解或反应提供HCl。该促进剂可以是HF，在一些实例中，可通过促进剂前体，如氟化铵、氟化钠或氟化钙的降解或反应提供HF。在一些实例中，促进剂(例如HBr或HCl)或促进剂前体(例如NH_4Br、NaBr、$CaBr_2$、NH_4Cl、NaCl、$CaCl_2$)可以与碳纳米复合吸附剂分开或与碳纳米复合吸附剂一起注射到烟气中(例如可以在注射前施加到吸附剂中，在相同位置同时注射，或在不同位置同时注射)。

[0084] 无意将实施方案局限于任何特定的作用机制，在各种实施方案中，将卤素或来自卤化氢酸的质子添加到碳边缘结构上的碱性卡宾位点上形成了碳正离子，其从中性汞原子接收电子，以形成结合到吸附剂表面上的氧化汞物类。该反应性位点也可以在碳上的活性位点生成反应性卤素基团或碳基团。由此该碳纳米复合吸附剂提供可氧化汞并促进其捕获在碳纳米复合吸附剂上的高反应性含卤素试剂。在一些实施方案中，含有溴或由溴或溴试剂促进的吸附剂预计比由氯或氯试剂促进的相应吸附剂更具反应性并且比由碘或碘试剂促进的吸附剂便宜。

[0085] 卤素和酸性物类与促进的碳纳米复合吸附剂上的结合位点的反应可产生用于氧化汞的活性位点。其它金属离子，如碱、锡、砷、镓、Sb、Pb、Bi、Cd、Ag、Cu、Zn、Se或其它污染物

PAC ET AL. EXHIBIT 1019
Page 1873

也可以与该碳上的氧化位点反应。

[0086] 在一些实施方案中，添加到碳纳米复合吸附剂中并与其反应的卤素或卤化物促进剂可包括，例如但不限于，蒸气或气态形式的分子卤素、在有机溶剂中的分子卤素、蒸气、液体或溶液形式(例如在水或非水溶剂，如醇或其它有机溶剂中)的第V族或第VI族卤化物，分别例如PBr_3或SCl_2。

[0087] 还提供有机溶剂包括氯化烃，如二氯甲烷，烃溶剂，包括例如，石油醚、轻石油(ligroin)、戊烷、己烷、甲苯和苯，二硫化碳、废溶剂、醚、再循环溶剂、超临界溶剂，如超临界CO_2，水(尽管在第V族或第VI族卤化物的情况中不行)和如本领域技术人员显而易见的其它溶剂的实施方案。

[0088] 在一些实施方案中，该方法可包括将附加的卤素或卤化物促进剂添加到所述促进的吸附剂中。该附加的卤素或卤化物可以是本文中被描述为适合作为第一卤素或卤化物的任何卤素或卤化物。例如，该附加的卤素或卤化物促进剂可包括HI、HBr、HCl、与卤素结合的第V族元素或与卤素结合的第VI族元素。

[0089] 在各种实施方案中，促进至少一部分吸附剂材料的步骤可以至少部分在含汞气体与该吸附剂接触之前进行。在一些实例中，促进至少一部分吸附剂的步骤可以至少部分在含汞气体与该吸附剂接触的过程中进行。在一些实例中，可以将碳纳米复合吸附剂以一定注射速率注射到气流中，其中将至少一种促进剂以一定注射速率单独注射到气流中，由此飞行中的反应产生促进的吸附剂。在一些实例中，该促进剂可以在气相中或作为蒸气反应。在一些实例中，每100克碳纳米复合吸附剂材料加入大约0.01克至大约200克，或大约0.1克至大约100克，或大约1克至大约30克促进剂。在一些实例中，吸附剂和促进剂注入的气流之一或两者可以是输运气体、烟气流(例如含汞气体)或其组合。在一些实例中，注入气体中的促进剂注射速率和吸附剂注射速率至少部分由净化气体的监测汞含量确定。

[0090] 吸附剂和含汞气体中的汞接触

[0091] 在降低含汞气体的汞含量的方法的实施方案中，该方法可包括使至少一部分促进的吸附剂与含汞气体中的汞接触。促进的吸附剂与含汞气体中的汞的接触包括使促进的吸附剂与含汞气体接触。促进的吸附剂与汞的接触形成汞-吸附剂组合物。该接触可以在任何合适的位置进行。例如，该接触可以在气体中进行。在另一实施方案中，该接触可以在水性液中进行。在另一实例中，该接触可以在气体中进行，随后也可以在水相，如洗涤器中进行接触。

[0092] 在各种实施方案中，可以使用汞排放的测量结果作为反馈以助于控制吸附剂注射速率。由此可以实现对吸附剂和任选组分水平的更严密控制，这有助于确保以最低限度的促进剂和吸附剂要求满足除汞要求，由此使相关的成本最小化。在一个实施方案中，在注射位置下游，例如在烟肉的废气中连续测量汞排放。在各种实施方案中，至少一部分促进的吸附剂与含汞气体中的汞的接触可以在颗粒物控制装置之间进行。

[0093] 从含汞气体中分离至少一部分汞-吸附剂组合物

[0094] 在降低含汞气体的汞含量的方法的实施方案中，该方法包括从气体中分离至少一部分汞-吸附剂组合物。该分离产生具有比原材料含汞气体低的汞含量的净化气体。在一些实施方案中，从含汞气体中分离至少一部分汞-吸附剂组合物包括从该气体中分离颗粒物，其中所述颗粒物包含至少一部分汞-吸附剂组合物。

PAC ET AL. EXHIBIT 1019
Page 1874

[0095] 在一些实例中，从含汞气体中分离颗粒物的步骤包括在颗粒物分离器中从该气体中分离颗粒物，该颗粒物分离器可以是任何合适的分离器。该颗粒物分离器可包括一个或多个旋风分离器、静电除尘器、织物分离器、洗涤器或如本领域中已知的其它颗粒物脱除装置。在一些实施方案中，可以使用静电除尘器，接着洗涤器。在另一些实施方案中，可以使用静电除尘器，无洗涤器，或可以使用另一颗粒物分离器。可充当颗粒物分离器的一些装置还可具有其它功能，例如洗涤器还可如下文进一步描述从气流中除去SO_2或SO_3。在包括汞与吸附剂在水相中，例如在洗涤器中接触的实施方案中，通过汞与吸附剂在水相中的反应或相互作用而在水相内发生的该气体的除汞可被视为从该气体中分离汞-吸附剂组合物。

[0096] 在一些实例中，通过从含汞气体中分离颗粒物，可以从含汞气流中除去至少大约20重量%、30重量%、40重量%、50重量%、60重量%、70重量%、80重量%、90重量%、95重量%、96重量%、97重量%、98重量%、99重量%、99.9重量%、99.99重量%或大约99.999重量%或更多的汞。如本文中论述，汞可以以元素汞形式、转化的汞，如氧化汞（例如汞氧化物）形式除去。

[0097] 洗涤器

[0098] 在降低含污染物的气体的污染物含量的方法的各种实施方案中，可以使用水洗涤器。水洗涤器能使水性液体或水性浆料接触气流。洗涤器可以将水性材料喷洒、喷雾或以其它方式分布在气流流过其中的空间内，以提高在洗涤器中接触该气体的液体的表面积。该水溶液可落到洗涤器底部，在此其可再循环回顶部，或取出以再生、净化或更换。该水洗涤器可以是任何合适的水洗涤器。在一些实例中，该水洗涤器可以从气流中除去一种或多种污染物。

[0099] 洗涤器可以从气流中除去颗粒物。例如，当包含颗粒物的气流经过洗涤器时，接触到微滴或其它形式的水溶液的颗粒物会粘在或浸渍在该水溶液中。随着水溶液落到洗涤器的底部，粒子随其落下。该水溶液可以带着其中的至少一些粒子再循环回洗涤器顶部。该水溶液可具有任何合适的稠度，如自由流动的透明液体、具有悬浮固体的液体或任何合适粘度的浆料。连续或分批地，可以净化或更换洗涤器中的水溶液，以除去例如粒子、污染物或污染物副产物。在一个实例中，可以如US 2007/0167309中所述分离和再生水溶液中的吸附剂。

[0100] 在各种实施方案中，该方法可包括从含污染物的气体中除去至少一些SO_2或SO_3（例如降低SO_2或SO_3的浓度）。可以以任何合适的方式进行脱除。在一些实例中，水洗涤器可以例如通过洗涤器中的水中存在的化学化合物与SO_2或SO_3的反应从气流中除去SO_2或SO_3。洗涤器中的水中包括的可与SO_2或SO_3反应的化学化合物的一些实例包括在水中形成碱性溶液的盐，例如具有任何合适的抗衡离子，例如铵（NH_4^+）、钠（Na^+）、钾（K^+）、镁（Mg^{+2}）或钙（Ca^{+2}）的碳酸盐（CO_3^{-2}）、碳酸氢盐（HCO_3^-）或氨基甲酸盐（$OCONH_2^-$）。例如，该碱性盐可以是碳酸铵（$(NH_4)_2CO_3$）、碳酸氢铵（$(NH_4)HCO_3$）或氨基甲酸铵（$(NH_4)OCONH_2$）。

[0101] 在各种实施方案中，促进剂或促进剂前体可以在洗涤器的水溶液中。在一些实施方案中，可以将促进剂（例如HBr）直接添加到水洗涤器中的水中。在一些实例中，可以将促进剂前体（例如NH_4Br）直接添加到水洗涤器中的水中，其可以在此分解形成促进剂（例如HBr）。可以将促进剂前体注射到热气体（例如热载气或烟气流）中，其可以在此转化成促进剂，随后该气流可进入洗涤器，在此该前体吸收或溶解在洗涤器中的水中。该促进剂或促进剂前体可以以任何合适的方式进入洗涤器的任何合适的部分，例如其可以在进入洗涤器之

PAC ET AL. EXHIBIT 1019
Page 1875

前进入烟气流，其可以单独注射到洗涤器的气相中，或其可以注射到洗涤器的水相中。

[0102] 在一些实施方案中，洗涤器中的水溶液可包括活性炭纳米复合吸附剂。在这样的实施方案中，该洗涤器可通过使该活化的吸附剂在水相中与来自气流的一种或多种污染物反应或吸收来自气流的一种或多种污染物而从气流中除去一种或多种污染物，如汞。该纳米复合材料可以以任何合适的方式在任何合适的位置进入洗涤器，例如其可以在进入洗涤器之前进入烟气流，其可以单独注射到洗涤器的气相中，或其可以注射到洗涤器的水相中。任选地，包括活性炭纳米复合吸附剂的水溶液可包括可与该气流中的污染物反应的其它化学品，以使该洗涤器可除去多于一种类型的污染物。例如，除活性炭纳米复合吸附剂外，水洗涤器溶液还可包括可与SO_2反应的碱性盐。

[0103] 在一些实例中，碳纳米复合材料可以在该洗涤器中活化，如在洗涤器的水中包括促进剂的实施方案中。可以将碳纳米复合材料直接添加到洗涤器中(例如添加到气相或液相中)，或在洗涤器之前添加到流入洗涤器的气流中。可以在颗粒物控制装置(例如ESP)和洗涤器之间的任何合适的点加入碳纳米复合材料。在一些实例中，可以将碳纳米复合材料和促进剂或促进剂前体都注射到热气流(例如热载气或烟气流)中，在此在进入洗涤器之前可以形成促进的碳纳米复合吸附剂。在一些实施方案中，可以用促进剂或促进剂前体涂布碳纳米复合材料并将涂布的碳纳米复合材料注射到热气体(例如热载气或烟气流)中，其可在此转化成促进剂，随后吸收在洗涤器中的水中。

[0104] 在包括ESP和洗涤器的实施方案中，碳纳米复合材料可任选在ESP之前以及在湿洗涤器中用于污染物脱除。在这种实施方案中，ESP可除去纳米复合材料-污染物。或者，该碳纳米复合材料可用在洗涤器中并且不在ESP之前使用。或者，该碳纳米复合材料可以仅在ESP之前使用并且不用在洗涤器中或不主要用在ESP中。

[0105] 碱性组分

[0106] 在一些实例中，从含汞气流中除汞的方法可包括将碱性(alkaline)(例如碱性(basic))组分注射到含汞气体中。在一些实例中，该碱性组分包括碱金属或碱土金属元素的氧化物、氢氧化物、碳酸盐或磷酸盐。

[0107] 在各种实例中，与碳纳米复合吸附剂分开或一起添加碱性组分可改进汞捕获，在一些实例中超过促进的和未促进的碳纳米复合吸附剂。各种因素会影响碱性组分的添加效力，例如烟气污染物、烟气成分(例如SO_2、NO_x、HCl等)、运行温度、汞形式和汞浓度。在一些实例中，可以调节碱性组分/活性炭比率以针对给定的现场条件组进行优化。

[0108] 稳定剂

[0109] 在一些实例中，可以将稳定剂添加到促进的吸附剂中。该稳定剂可以是汞稳定剂。在一些实施方案中，提供了将汞稳定剂添加到促进的碳吸附剂中以制造双功能吸附剂的方法。此类稳定剂可以在卤素/卤化物的添加和反应之前或之后依序加入。在一些实施方案中，卤素/卤化物包括Br或HBr，且汞-稳定剂可包括S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5及其组合。

[0110] 吸附剂的再生

[0111] 在用于从含汞气流中分离汞的方法或材料的任何实施方案中，可以再生该碳吸附剂；可以除去来自烟气的使吸附剂中毒的污染物；并可以将吸附剂再促进以恢复汞吸附活性。再生的吸附剂然后再用于该方法。在共同待审的共有PCT专利申请No. PCT/US04/12828

PAC ET AL. EXHIBIT 1019
Page 1876

(名为"PROCESS FOR REGENERATING A SPENT SORBENT",其全文并入本文作为参考)中描述了吸附剂再生技术的详细实例。

[0112] 示例性方法

[0113] 在各种实施方案中,除来自燃烧系统的烟气外,本文中论述的碳纳米复合吸附剂、除汞方法和任选添加剂还可用于来自气化系统、合成气发生器的产物或排出气体和其它含汞气流的汞控制。因此,应该理解的是,本说明书通篇所用的术语燃烧系统和烟气如本领域技术人员理解的那样同样适用于气化系统和合成气或燃料气。

[0114] 现在参照图1,显示了示例根据各种实施方案制备促进的碳吸附剂的方法的方框流程图。方框10示例提供碳纳米复合吸附剂,在方框20处示例添加卤素或卤化物促进剂,其与碳反应以产生促进的碳纳米复合吸附剂。在卤素或卤化物在例如溶剂中加入的实施方案中,可以如方框20A所示除去溶剂。方框30指示添加在方框30中示例的任选次要组分,其与方框20或20A的产物反应以产生促进的碳纳米复合吸附剂。在卤素或卤化物促进剂和/或次要组分在例如溶剂中加入的实施方案中,可以如方框30A所示除去溶剂。

[0115] 在图1中,步骤50之前的步骤在用促进的吸附剂处理烟气流之前产生促进的吸附剂。一种或多种促进剂的添加和与促进剂的反应或相互作用(这导致该吸附剂的促进)可以在任何合适的位置进行。在一些实例中,可以在热气流中,如在烟气流中,或如在热载气流中促进该吸附剂。在一些实施方案中,可以在将吸附剂注射到热气流中之前将促进剂添加到吸附剂中。在一些实施方案中,可以将促进剂与吸附剂一起添加到热气流中,在本文中称作吸附剂的"飞行中"促进。因此,在一些实施方案中,在步骤50之前,促进剂和吸附剂可以一起或分开注射到烟气流或另一热气流中。

[0116] 再参照图1,路径10-40包括如方框10所示提供碳纳米复合吸附剂和如方框40所示将卤素或卤化物促进剂和次要组分一起添加到吸附剂中,它们与吸附剂反应以产生促进的碳纳米复合吸附剂。在一种或多种组分在溶剂中加入的实施方案中,可以如方框40A所示提供溶剂脱除步骤。

[0117] 再参照图1,也示例了如方框50所示用如本文所述制备的促进的碳纳米复合吸附剂处理烟气流的实施方案。

[0118] 现在参照图2,示例了由科学证据展开的解释促进化合物的性质的理论,其无意将本发明的实施方案限于任何具体操作理论。本发明的方法包括使用碳纳米复合材料以任何合适的方式从气体中除汞。

[0119] 例如,如图2中所示,溴化氢可以与碳纳米复合吸附剂的不饱和结构反应。可以由例如溴化铵提供溴化氢。仅举例而言,碳纳米复合吸附剂上的碳的反应性部分可以是该碳的石墨烯片结构的边缘上的卡宾物类。分子溴或其它溴化合物可反应形成类似结构——其具有可有效用于氧化汞(其随后被该吸附剂捕获)的正碳。

[0120] 含碳的溴化物化合物的形成提高了碳纳米复合材料对汞和其它污染物的反应性。另外,所得溴化物化合物独特地适合促进汞的氧化。该氧化的效率可来自该卤化物对氧化过程中汞上的正电荷开发的促进效应,这在化学领域中已知为特定的催化效应。因此,随着汞电子被吸引到正碳上,卤素阴离子电子可以从另一侧推入,以稳定汞上的正电荷开发和降低该氧化过程的能量要求。由于该离子的外4p轨道中的高度可极化电子,溴化物尤其具有反应性。因此,将HBr或Br_2添加到碳纳米复合材料中可形成类似的溴化碳,其中正碳可借

PAC ET AL. EXHIBIT 1019
Page 1877

助溴离子氧化汞。

[0121] 图3A显示汞控制系统100的示意性流程图，其包括根据本发明的实施方案制备促进的碳吸附剂和烟气除汞。提供了碳纳米复合吸附剂储器110、任选的卤素/卤化物促进剂储器120、任选的次要组分储器130和任选的碱组分储器180，它们各自分别具有相应的流量控制装置201、202、203和207/208/209。具有相应的流量控制器201、202和203的储器110、120和130可以与传输线路113和115一起独立地使用，一起使用或完全不使用。例如，具有控制器201的储器110可以与传输线路113一起使用以独立地和单独地在注射点114注入材料，同时，具有相应的流量控制器202和/或203的任选储器120和/或130可以与传输线路115一起使用以独立地和单独地在注射点116注入材料。与任选的碱组分储器180一起，任选的流量控制装置207、208和209可以独立使用，一起使用或完全不使用。

[0122] 储器110、120、130和180通过它们各自的流量控制装置并经由相应的管路连向传输线路113和115。任选的碱组分储器180也可以通过各自的流量控制装置并经由相应的管路连向传输线路118。由气体源169向传输线路113提供空气、氮气或其它输运气体源以携带从储器110、120、130和180排出的材料并将此类材料经注射点114注射到污染的烟气流15中。由气体源170向传输线路115提供空气、氮气或其它输运气体源以携带从储器110、120、130和180排出的材料并将此类材料经注射点116注射到污染的烟气流15中。由气体源171向传输线路118提供空气、氮气或其它输运气体源以携带从储器180排出的材料并将此类材料经注射点119注射到烟气流15中。气体源169、170和171可以视需要相同或不同。或者，可以通过气体源170向传输线路113、115和118提供输运气体(没有显示，从源170连向传输线路113和/或118)。尽管气体源169、170和171在图3A中显示为压缩机或鼓风机，如本领域普通技术人员会认识到的本领域中已知的任何传输能量源是可接受的。例如，在120作为液体添加的情况下，169可以是泵。

[0123] 为清楚起见，在图3A中显示了单注射点114、116和119，尽管本领域普通技术人员会理解，多注射点也在本发明的范围内。将光学密度测量装置204连向传输线路113或115(或118，未显示)以提供随时间变化的代表传输线路113、115或118内的光学密度的信号。

[0124] 在注射点116和119下游提供颗粒物分离器140。例如但非限制地，颗粒物分离器140可包括一个或多个织物过滤器、一个或多个静电除尘器(下文称作“ESP”)或如本领域中已知的其它颗粒物脱除装置。应该进一步指出，可相继或并列存在多于一个颗粒物分离器140，当并列存在、相继存在或存在它们的组合时，注射点116和119可以在140上游和/或下游的位置。颗粒物分离器140可至少产生主要气态(“净化”)流42和包括分离的固体材料的流141。吸附剂/灰分分离器150可以将流141分离成主要灰分流152和主要吸附剂流151。或者，未显示地，流141可作为废物流弃置或直接送往任选的吸附剂再生器160。然后可将流151送往任选的吸附剂再生器160，这产生再生吸附剂流161和废物流162。

[0125] 在任选的ESP 140后提供任选的水洗涤器190。水洗涤器190可以与ESP 140一起或不与ESP 140一起提供。洗涤器190可以从气流中除去颗粒物，可以通过与碱性水性液体的化学反应从气流中除去污染物，如SO_2，可以通过与洗涤器中的活性炭纳米复合吸附剂反应或被其吸收从气流中除去污染物，如汞，或它们的任何合适的组合。除了或代替在单元140之前注入和促进碳纳米复合吸附剂，可以向水洗涤器190提供促进剂120或促进剂前体。可以将该促进剂或促进剂前体注射到气流42中，或可以直接提供到洗涤器中(没有显示120/

PAC ET AL. EXHIBIT 1019
Page 1878

130和190之间的传输线路)。促进剂或促进剂前体可以作为用促进剂或促进剂前体涂布或与促进剂或促进剂前体结合的碳纳米复合吸附剂在洗涤器190之前提供或提供到洗涤器190中。涂布或结合的吸附剂/前体的促进可以在洗涤器190中,在该洗涤器前的气流42中或在向42或190输送活化的纳米复合材料的加热载气线路(未显示)中进行。除了或代替在单元140之前注入和促进碳纳米复合吸附剂,可以向水洗涤器190提供碳纳米复合材料。可以将该碳纳米复合材料注射到气流42中,或可以直接提供到洗涤器中(没有显示110和190之间的传输线路)。洗涤器中的水溶液可以在分批或连续法中再生或更换,以除去吸收的颗粒物、吸收的污染物或吸收的污染物副产物。

[0126] 在废气流35中提供对汞的任选连续排放监测器(下文称作"CEM")205以提供随时间变化的代表废气流35中的汞浓度的电信号。任选的汞CEM 205和流量控制器201、202、203、207、208和209经由任选线路227(或无线)电连接到任选的数字计算机(或控制器)206上,其接收和加工信号并可以控制促进的碳吸附剂的制备和注射到污染的烟气流15中。

[0127] 在示例性运行中,可以将碳纳米复合吸附剂和/或任选的促进剂和/或任选的碱组分注射到污染的烟气流15中。在注入的材料与污染的烟气流15接触后,注入的材料降低汞浓度,以将污染的烟气转化成汞减少的烟气流25。分别地,可以通过分离器140从汞减少的烟气流25中除去注入的材料,弃置或通过任选分离器150进一步分离,和弃置或通过任选再生器160再生。或者或另外,洗涤器190可以借助促进的碳纳米复合材料除去SO_2、污染物,如汞,除去颗粒物,或它们的任何组合。然后通过任选的CEM 205监测汞减少的"净化"烟气流42和/或35的汞含量,这向任选的计算机/控制器206提供相应的信号。来自206的逻辑和优化信号随后可根据本领域中公知的控制算法调节流量控制器201、202、203、207、208、209以使废气流35中的汞浓度保持在所需界限内。也可以手工或通过另一些自动化手段根据本领域中公知的控制算法调节流量控制器201、202、203、207、208、209以使废气流35中的汞浓度保持在所需界限内。

[0128] 再参照图3A,示例了用于制备和注射碳纳米复合吸附剂、促进的碳吸附剂、卤素和卤化物促进剂和/或碱组分的几个实施方案。流111用于从储器110引入碳纳米复合吸附剂,其手动或在计算机206的指导下通过流量控制器201计量加入。卤素/卤化物可以根据几个提供的方法的任一种与碳纳米复合吸附剂结合和反应。卤素/卤化物(120和/或130)可经由传输线路121(和/或131)直接并入传输线路115(或113)中,在其内在注射点116(或114)之前与碳纳米复合吸附剂(例如在储器110)接触和反应。这一选项是在本文中被称作根据本发明的促进的碳吸附剂的"飞行中"制备的一种形式。此外,卤素/卤化物(120和/或130)可通过传输线路121(和/或131)经由烟气流15并入传输线路115和注射点116,其在传输线路113中传输并在注射点114注入碳纳米复合材料后与烟气流15中的碳纳米复合材料(例如来自储器110)接触和反应。这一选项是在本文中被称作根据本发明的促进的碳纳米复合吸附剂的"飞行中"制备的另一形式。此外,卤素/卤化物可经由传输线路121b与进入传输线路113和/或115之前的碳纳米复合吸附剂合并。再进一步,卤素/卤化物可以通过经传输线路121c引入储器110而与碳纳米复合吸附剂接触和反应。当例如储器110包括碳纳米复合吸附剂的沸腾床或流化床时,可以使用这一选项,卤素/卤化物以气体形式或作为蒸气流经该床。在另一些实施方案中,卤素/卤化物可以如上文论述以液体形式或在溶剂中与碳纳米复合吸附剂接触,然后如果必要,如参照图1论述的实施方案中提到的那样,提供溶剂脱除(未

PAC ET AL. EXHIBIT 1019
Page 1879

显示在图3A中)。

[0129] 类似地,任选的次要组分可以经由传输线路131直接在传输线路115(和/或113)中,或任选如上文参照卤素/卤化物所述经由传输线路131b和131c接触和反应。

[0130] 类似地,来自储器180的任选的碱组分可以直接在传输线路113和/或115中添加,或可以由传输线路118单独注入,以保持独立和/或在烟气流15的下游结合以与碳纳米复合吸附剂、促进的碳或任选的次要组分协同作用。可以针对现场特有的运行条件和烟气条件优化任选碱组分的量的现场变化(相对于碳纳米复合吸附剂、促进的碳或任选的次要组分)。

[0131] 图3B显示汞控制系统300的示意性流程图,其包括根据本发明的实施方案制备促进的碳吸附剂和烟气除汞。碳吸附剂310可以经线路395注射到位置396或经线路390注射到位置391。促进的碳吸附剂320可以经线路395注射到位置396或经线路390注射到位置391。碳吸附剂310可以在飞行中促进,如通过将线路390和/或395将碳吸附剂310注射到位置391和/或396并经线路380将卤素/卤化物促进剂340注射到位置385,或通过经线路390和/或395将碳吸附剂310注射到位置391和/或396并经线路350将卤素/卤化物促进剂340注射到位置355和/或经线路360将卤素/卤化物促进剂340注射到位置365和/或经线路370将卤素/卤化物促进剂340注射到位置375。

[0132] 除了或代替在任选的ESP单元之前使用促进的碳纳米复合材料,可以使用任选的洗涤器单元通过在该洗涤器中使用促进的碳而除去污染物,如汞,通过在该洗涤器中使用碱性水溶液而除去污染物,如SO_2,在该洗涤器中除去颗粒物,或它们的任何组合。材料,如促进剂或碳纳米复合吸附剂可以在洗涤器中或在ESP和洗涤器之间注射到洗涤器中。促进的吸附剂320可以经线路397注射到洗涤器中。碳吸附剂310可以在飞行中促进,例如通过碳吸附剂310经由加热载体线路(未显示)与促进剂340一起注射到洗涤器中。卤素/卤化物促进剂340可以经线路381添加到洗涤器中,同时经线路397加入碳吸附剂310,并可以在洗涤器内促进该吸附剂。

[0133] 在组分之间的接触和反应在液相或溶剂相中进行的一些实施方案中,可以提供此类液体和/或浆料混合物的搅拌。在一些实施方案中,卤素/卤化物促进剂和任选的次要组分以溶液形式注射到碳纳米复合吸附剂中或上。在一些这样的实施方案中,可随后提供如本领域中已知的干燥、过滤、离心、沉降、滗析或其它溶剂脱除法。

[0134] 在该卤素/卤化物促进剂是气体或蒸气形式的实施方案中,其可以酌情在空气、氮气或其它气体中稀释。可以使卤化物/卤素气体,例如气态HBr或Br_2经过颗粒或纤维状的碳纳米复合吸附剂的沸腾床或流化床,可以通过气体夹带从该床的顶部取出如此制成的促进的碳吸附剂以供注射。

[0135] 在一些实施方案中,次要组分可包括碘或其它卤素、氢卤化物,包括但不限于HI、HBr、HCl、与分子卤素结合的第V族或第VI族元素,如SCl_2等。在一些实施方案中,该促进的碳吸附剂可包括大约1克至大约30克卤素/卤化物/100克碳纳米复合吸附剂材料。在一些实施方案中,该促进的碳吸附剂可包括占卤素/卤化物组分的浓度大约1重量%至大约15重量%的浓度的次要组分。

[0136] 在另一些实施方案中,可以将该促进的碳纳米复合吸附剂施加到基底上。在另一些实施方案中,可以使如此制成的基底与污染的烟气或气化系统产物气流接触以减少汞。

PAC ET AL. EXHIBIT 1019
Page 1880

这样的基底可以是整块的，旋转、移动或以本领域技术人员已知的各种方式暴露在气流中。基底可包括例如蜂窝结构、织物、过滤器、板等。

实施例

[0137] 参照作为示例提供的下列实施例更好地理解本发明。本发明不限于本文中给出的实施例。

[0138] 实施例1. 来自商业蔗糖蜜的介孔活性炭(AC)纳米复合材料

[0139] 实施例1.1. NanoG-CM

[0140] 将获自Aldrich的高表面积蒙脱土(粘土)(200克)快速添加到用更少量的水(200克/140毫升)稀释的Brer Rabbit糖蜜(未硫化)中并搅拌以制造稠糊。

[0141] 一旦所有粘土被糖蜜润湿，将该糊在110℃下干燥整夜以除去过量水。或者，将较少部分的糊在微波中加热1分钟。较小批量在炉中在110℃下更快(1小时)干燥。

[0142] 将干燥的固体分两批加载到圆柱形钢管中并在管式炉中在氮气流过该床的同时加热至700℃。将排出的气体鼓过脱水器(water trap)。继续加热1小时。该管在氮气下缓慢冷却至环境温度并排空。将所得黑色复合碳块称重并在研钵和研杵中研磨。将产物纳米复合材料分成两个筛分粒度——大于325目和大约325目。大约325目材料用于Hg捕获试验。

[0143] 纳米复合材料的产量为217克。

[0144] 实施例1.2. NanoG-CB.

[0145] 制备类似于NanoG-CM，只是用高钠膨润土代替蒙脱土。由10.0克膨润土获得的产量为10.1克。

[0146] 实施例1.3. 促进剂的浸渍

[0147] 实施例1.3.1. 溴化铵

[0148] 将溴化铵的水溶液(7.3克/35毫升)添加到54克325目纳米复合材料中并搅拌形成糊。该糊在110℃下干燥并再研磨。

[0149] 实施例1.3.2. 溴化氢

[0150] 将HBr水溶液(0.1 N)添加到NanoG-CM(10克)中并将该混合物搅拌1小时。过滤该浆料并在110℃下干燥。

[0151] 实施例1.3.3. 溴.

[0152] 将溴蒸气(0.5克)转移到含有粉状复合材料(10克)的管瓶中，其吸附到其中。

[0153] 实施例1.3.4. 硫

[0154] 将元素硫(1克)溶解在二硫化碳(20毫升)中并加入10克NanoG-CM。在搅拌整夜后，除去二硫化碳。

[0155] 实施例2. 来自American Crystal Sugar (ACS) Raffinate的介孔活性碳纳米复合材料

[0156] 前一版本的NanoG-CM碳复合材料使用蔗糖蜜制成。使用当地ACS糖蜜会提供更方便的来源；例如可大量(大约170吨)供应由糖和甜菜碱提取剩余的低价值残液。但是，溶解的无机盐的量比商业蔗糖蜜高得多(>10%)，糖含量较低。

[0157] 使用ASC残液和两种类型的粘土制备纳米复合材料：来自Aldrich的高溶胀高钠膨润土和低溶胀蒙脱土。两者都细研磨。

PAC ET AL. EXHIBIT 1019
Page 1881

[0158] 实施例2.1. NanoG-ACSB.

[0159] 通过将10克干燥膨润土添加到80克水中并用研钵和研杵研磨，使膨润土溶胀。将ACS残液(10克)添加到胶凝的混合物中并通过研磨混合。在静置整夜以使残液中的糖进一步分散到粘土中后，将该混合物在微波中以满功率加热1分钟以形成该凝胶中的大孔隙度。将该凝胶在干燥炉中在110℃下干燥整夜。

[0160] 将干燥的固体分两批加载到圆柱形钢管中并在管式炉中在氮气流过该床的同时加热至700℃。将排出的气体鼓过脱水器。继续加热1小时。该管在氮气下缓慢冷却至环境温度并排空。将所得黑色复合碳块称重并在研钵和研杵中研磨。

[0161] 纳米复合材料的产量为10.2克。

[0162] 实施例2.2. NanoG-2ACSB

[0163] 制备类似于NanoG-ACSB，只是添加的残液的重量翻倍。产量为10.5克。

[0164] 实施例2.3. NanoG-2ACSM.

[0165] 制备类似于NanoG-CM，使用10克Aldrich蒙脱土和20克ACS残液，且量翻倍。产量为10.5克。

[0166] 实施例2.4. NanoG-2ACSB-Washed.

[0167] NanoG-2ACSB的样品用水搅拌整夜，过滤，然后用0.1 N HBr搅拌2小时。过滤该浆料并将该复合材料在110℃下干燥。

[0168] 实施例2.5. 促进剂的浸渍

[0169] 实施例2.5.1. 溴化铵.

[0170] 溴化铵水溶液(1.1克/5毫升)添加到10克纳米复合材料并搅拌形成糊。该糊在110℃下干燥并再研磨。

[0171] 实施例2.5.2. 溴.

[0172] 将溴蒸气(0.5克)转移到含有粉状复合材料的管瓶中，其部分吸附(化学吸附)到其中。

[0173] 实施例3. NanoG吸附剂的实验室规模Hg吸附试验

[0174] 进行实验室规模Hg吸附试验以评估该吸附剂在床构造下吸附烟气中的元素Hg蒸气的性能。这些结果概括在表1中。尽管在极短接触时间下对注射模式中的性能的评估不太准确，但初始反应性(作为%Hg捕获)和初始斜率给出短时标内的反应性的初步测定。当初始斜率平坦时，存在许多活性位点，并发现较高的反应性。陡峭的初始斜率涉及快速突破和相应的较低反应性。

[0175] 由蔗糖蜜制成的NanoG复合吸附剂(NanoG-CM)在实验开始时提供优异的反应性(98%-99%捕获)并维持高捕获效率15分钟(平坦斜率)。另一方面，ACS残液与由蔗糖蜜制成的复合材料相比提供较低反应性和较低容量(较短的50%突破时间)。由于较低的糖含量、较高的盐含量和可能不同的燃尽速率，ACS复合材料中所含的碳量明显较低。用双倍量的糖蜜制成的复合材料的反应性低于较低剂量。可以通过由ACS残液制成的复合材料的孔隙中的盐堵塞解释这些结果。将水添加到该吸附剂中时大量H_2S的析出与在孔隙中形成KxS(源自硫酸盐的还原以及高钾含量)相一致。当洗涤ACS残液吸附剂以溶解掉盐时，反应性和容量明显改进。

[0176] 表1. NanoG吸附剂的固定床筛选的概要结果

PAC ET AL. EXHIBIT 1019
Page 1882

[0177]

吸附剂	促进剂	初始反应性，%Hg捕获	初始斜率	50%突破时间，hr
NanoG-CM	Br_2	98	平坦	0.45
NanoG-CM	NH_4Br	99	平坦	0.38
NanoG-CM	HBr	97	中等	0.29
NanoG-CM	S	92	陡峭	0.06
NanoG-2ACSM	Br_2	67	陡峭	0.02
NanoG-2ACSB	Br_2	95	陡峭	0.16
NanoG-2ACSB	NH_4Br	90	陡峭	0.29
NanoG-ACSB	NH_4Br	97	中等	0.32
NanoG-2ACSB-浅渗过的	Br_2	97	中等	0.53

[0178] 尽管AC的硫化产生对Hg具有良好反应性的碳，但将硫添加到NanoG吸附剂中没有带来良好的容量。硫有可能堵塞这些吸附剂中可提供的有限量孔隙率的孔。

[0179] HBr与Br_2的比较表明Br_2产生更高的反应性和容量。其原因可能是在通过气相沉积制成的吸附剂中，这些复合吸附剂中的碳正离子-溴离子对的水合程度更低并更具反应性。

[0180] 溴化铵-促进的吸附剂提供极好的反应性和容量——与在加热时孔隙中的溴化铵分解形成氨和气态HBr相一致。HBr与沉积在邻近的纳米碳表面上的碳结合，以装饰粘土层(片)。氨也截留在该复合材料的酸性粘土层内，在此其可用于在烟气中的SO_3在碳表面上氧化之前拦截该SO_3。

[0181] 实施例4．中试评估

[0182] 在Center for Air Toxic Metals® (CATM®)-赞助的颗粒物试验燃烧器(PTC)运行过程中以中试规模评估NanoG-CM。用于该评估的煤是亚烟煤Montana Powder River Basin (PRB) (Absaloka)并与市售未处理的碳进行比较。

[0183] 对于市售标准AC和两种形式的NanoG-CM，来自PTC试验的结果概括在图4中。图4显示在总注射吸附剂基础上的NanoG-CM测试的PTC结果。用中等能量离解技术(moderate energy dissociation technology)(MEDT)吸附剂强化添加剂(SEA)选项测试标准AC和未处理过的NanoG-CM。如附图中所示，标准AC的结果较好；但是，该NanoG-CM确实表现出飞行中捕获潜力。用NanoG-CM的处理过的样品获得更有前途的结果。通过为扩展MEDT SEA进行的一组试验确定，用于NanoG-CM的预处理在预空气加热器温度下最有效。因此，在该处理过的NanoG-CM的评估过程中，将其注射到管道系统中烟气温度为大约715°F的点。

[0184] 图4表明该NanoG-CM材料表现出作为飞行中的汞吸附剂的潜力，但总注射吸附剂速率高于标准AC。但是，另一比较是以碳组分为基础评估试验结果，因为对复合吸附剂的基本的经济假设在于，AC组分可能比无机基底贵一个量级。来自图4的结果重新定标在图5中以描绘这二个选项的相当的仅以碳计的注射速率。图5显示以碳组分为基础的NanoG-CM试

PAC ET AL. EXHIBIT 1019
Page 1883

验的PTC结果。标准AC结果保持不变，因为它们被视为100% AC(没有扣除碳的矿物组分)，但NanoG-CM数据表现出低得多的仅以碳计的注射速率，因为NanoG-CM的平均碳含量仅为8%。

[0185] 图5的仅以碳计的结果证实该纳米复合吸附剂的至少一个有益方面：提高的碳利用率。图5中的标准AC和NanoG-CM结果的比较表明标准AC的大部分碳含量(例如内部)未被利用并且没有成为总体汞捕获中的一个因素。这强化了一种机械的理解，即主要是表面和近表面位点对汞在飞行中的捕获是重要的。改进的碳利用率对易消耗的吸附剂成本具有有益影响，例如如果增加的或更复杂的生产步骤没有压倒基础材料的成本优势。此外，改进的碳利用率使得更容易满足飞灰中，例如要用于混凝土的飞灰中的碳含量限制。

[0186] 碳层和内部基底之间的协同效应是该碳纳米复合吸附剂的一个优点。在一个实例中，协同效应来自于包括两种吸附剂的单一粒子：传统AC和对烟气中的酸性气组分具有反应性的无机基底。为了证实纳米复合吸附剂的潜在益处，对具有不同活性炭表面覆盖率的复合吸附剂使用飞行中的捕获的应用模型，结果呈现在图6中。图6显示在高硫烟气(3000 ppm SO_2，15 ppm SO_3)中用复合吸附剂在飞行中捕获汞的模型结果。该烟气模型代表含有显著量的SO_3的高硫煤，其如100%AC参考曲线所示限制了汞捕获。通过50%和10% AC曲线显示该复合吸附剂的协同益处的评估。考虑到所用的保守估计，益处可能超过该模型所表现出的那些。

[0187] 已经使用的术语和措辞用作描述性而非限制性术语，并且在此类术语和措辞的使用中无意排除所展示和描述的特征或其部分的任何等同物，而是要认识，可以在要求保护的本发明的范围内作出各种修改。因此，应该理解的是，尽管已通过优选实施方案和任选特征具体公开了本发明，但本领域技术人员可以采用本文中公开的概念的修改和变动，且这样的修改和变动被认为在如所附权利要求规定的本发明的范围内。

[0188] 附加实施方案

[0189] 本发明提供下列示例性实施方案，其编号不应被解释为指示重要性的级别：

[0190] 实施方案1提供了从包含一种材料的气体中分离所述材料的方法，其包括提供或获得碳纳米复合吸附剂；使至少一部分所述材料与所述吸附剂接触以形成材料-吸附剂组合物；和从含所述材料的气体中分离至少一部分所述材料-吸附剂组合物以产生分离的气体。

[0191] 实施方案2提供了实施方案1的方法，其中所述材料是污染物。

[0192] 实施方案3提供了实施方案2的方法，其中所述污染物是汞。

[0193] 实施方案4提供了实施方案2-3任一项的方法，进一步包括提供促进剂；和通过使至少一部分吸附剂材料与所述促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；其中与至少一部分污染物接触的吸附剂包含促进的吸附剂。

[0194] 实施方案5提供了实施方案4的方法，其中所述促进剂是卤素或卤化物促进剂。

[0195] 实施方案6提供了降低含污染物的气体的污染物含量的方法，其包括提供或获得碳纳米复合吸附剂材料；提供或获得卤素或卤化物促进剂；通过使至少一部分吸附剂材料与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；使至少一部分促进的吸附剂与含污染物的气体中的污染物接触以形成污染物-吸附剂组合物；和从所述含污染物的气体中分离颗粒物，所述颗粒物包含至少一部分所述污染物吸附剂组合物，以产生净化气体。

PAC ET AL. EXHIBIT 1019
Page 1884

[0196] 实施方案7提供了实施方案6的方法，其中所述污染物是汞。

[0197] 实施方案8提供了实施方案6-7任一项的方法，其中获得或提供碳纳米复合吸附剂包括提供或获得碳前体；提供或获得基底材料；使碳前体和基底材料接触以提供纳米复合原材料；加热所述纳米复合原材料以提供碳纳米复合吸附剂。

[0198] 实施方案9提供了实施方案8的方法，进一步包括使加热的纳米复合原材料与酸或碱反应以提供碳纳米复合吸附剂。

[0199] 实施方案10提供了实施方案8-9任一项的方法，其中所述碳前体包含碳水化合物。

[0200] 实施方案11提供了实施方案8-10任一项的方法，其中所述碳前体包含红糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜或糖废品(sugar waste product)。

[0201] 实施方案12提供了实施方案8-11任一项的方法，其中所述基底材料包含硅藻土、粘土、沸石或矿物。

[0202] 实施方案13提供了实施方案8-12任一项的方法，其中所述加热包括加热至超过大约100℃。

[0203] 实施方案14提供了实施方案6-13任一项的方法，其中所述吸附剂材料包含与含污染物的气体中的污染物结合的结合位点。

[0204] 实施方案15提供了实施方案6-14任一项的方法，其中所述吸附剂材料包含已与卤素、卤化氢和第V族和第VI族卤化物反应或被卤素、卤化氢和第V族和第VI族卤化物浸渍的碳以形成所述促进的吸附剂中的污染物结合位点。

[0205] 实施方案16提供实施方案15的方法，其中促进的AC中的结合位点与含污染物的气体中的污染物结合以形成污染物-吸附剂组合物。

[0206] 实施方案17提供了实施方案15-16任一项的方法，其中促进的AC中的结合位点与含污染物的气体中的污染物反应以形成污染物-吸附剂组合物。

[0207] 实施方案18提供了实施方案15-17任一项的方法，其中AC的至少一部分结合位点与含污染物的气体中的氧化污染物反应以形成另一污染物-吸附剂化学组合物。

[0208] 实施方案19提供了实施方案6-18任一项的方法，其中从含污染物的气体中分离颗粒物的步骤包括在包含一个或多个ESP的颗粒物分离器中分离。

[0209] 实施方案20提供了实施方案7-19任一项的方法，其中所述含汞气体中的汞包含元素汞。

[0210] 实施方案21提供了实施方案7-20任一项的方法，其中所述汞-吸附剂组合物中的汞是氧化汞。

[0211] 实施方案22提供了实施方案7-21任一项的方法，其中所述促进的吸附剂与所述含汞气体中存在的至少大约70重量%的汞结合。

[0212] 实施方案23提供了实施方案6-22任一项的方法，其中所述卤素或卤化物促进剂是包含蒸气形式、固体形式、在溶剂中或其组合的形式。

[0213] 实施方案24提供了实施方案6-23任一项的方法，其中所述卤素或卤化物促进剂包含第V族卤化物和第VI族卤化物中的至少一种。

[0214] 实施方案25提供了实施方案6-24任一项的方法，其中所述吸附剂上的或随所述吸附剂注入的促进剂前体转化成与所述吸附剂反应的卤素或卤化物促进剂。

[0215] 实施方案26提供了实施方案6-25任一项的方法，其中所述卤素或卤化物促进剂是

PAC ET AL. EXHIBIT 1019
Page 1885

NH_4Br、NaBr、HBr、NaCl、$CaCl_2$或HCl。

[0216] 实施方案27提供了实施方案6-26任一项的方法，进一步包括将碱性组分注入含污染物的气体中。

[0217] 实施方案28提供了实施方案27的方法，其中所述碱性组分包含碱金属或碱土金属元素的氧化物、氢氧化物、碳酸盐或磷酸盐。

[0218] 实施方案29提供了实施方案6-28任一项的方法，进一步包括将附加的卤素或卤化物促进剂添加到所述促进的吸附剂中。

[0219] 实施方案30提供了实施方案29的方法，其中所述附加的卤素或卤化物促进剂包含HI、HBr、HCl、与卤素结合的第V族元素(a Group V element with halogen)或与卤素结合的第VI族元素。

[0220] 实施方案31提供了实施方案6-30任一项的方法，进一步包括将稳定剂添加到所述促进的吸附剂中。

[0221] 实施方案32提供了实施方案31的方法，其中所述稳定剂包含S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2和P_2S_5中的至少一种。

[0222] 实施方案33提供了实施方案6-32任一项的方法，其中促进至少一部分吸附剂材料的步骤至少部分在含污染物的气体与促进的吸附剂接触之前进行。

[0223] 实施方案34提供了实施方案6-33任一项的方法，进一步包括向气流中以一定注射速率注入碳纳米复合吸附剂和以一定注射速率单独注入至少一种促进剂，由此飞行中的反应产生促进的吸附剂，其中所述促进剂选自分子卤素、卤化物及其组合，其中所述促进剂在气相中或作为蒸气反应，其中每大约100克碳纳米复合吸附剂材料加入大约1至大约30克促进剂。

[0224] 实施方案35提供了实施方案34的方法，其中所述气流是含污染物的气体。

[0225] 实施方案36提供了根据实施方案35的方法，其中所述气流是输运气体。

[0226] 实施方案37提供了实施方案34-36任一项的方法，其中注入气体中的促进剂注射速率和吸附剂注射速率至少部分由所述净化气体的监测污染物含量确定。

[0227] 实施方案38提供了实施方案6-37任一项的方法，进一步包括由所述污染物-吸附剂化学组合物再生所述促进的吸附剂的步骤。

[0228] 实施方案39提供了实施方案38的方法，进一步包括使用再生的促进的吸附剂从含污染物的气体中除去该污染物。

[0229] 实施方案40提供了实施方案6-39任一项的方法，其中所述促进、所述接触和所述分离中的至少一项在水洗涤器中进行。

[0230] 实施方案41提供了实施方案40的方法，其中所述促进在洗涤器中进行，其中所述洗涤器包括包含所述促进剂的水性浆料。

[0231] 实施方案42提供了实施方案40-41任一项的方法，其中所述接触在洗涤器中进行，其中所述洗涤器包括包含活性炭纳米复合吸附剂的水性浆料。

[0232] 实施方案43提供了降低含汞气体的汞含量的方法，其包括提供或获得碳纳米复合吸附剂，通过下列步骤制造所述碳纳米复合吸附剂：提供或获得碳前体、提供或获得基底材料、使碳前体和基底材料接触以提供纳米复合原材料、和加热所述纳米复合原材料以提供所述碳纳米复合吸附剂；提供或获得卤素或卤化物促进剂；通过使至少一部分吸附剂材料

PAC ET AL. EXHIBIT 1019
Page 1886

与所述卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂；使至少一部分促进的吸附剂与汞接触以形成汞-吸附剂组合物；和从含汞气体中分离至少一部分所述汞-吸附剂组合物。

[0233] 实施方案44提供了制造碳纳米复合吸附剂的方法，其包括提供或获得碳前体；提供或获得基底材料；使碳前体和基底材料接触以提供纳米复合原材料；加热所述纳米复合原材料以提供碳纳米复合吸附剂。

[0234] 实施方案45提供了通过实施方案44的方法制成的碳纳米复合吸附剂。

[0235] 实施方案46提供了通过一种方法制成的促进的碳纳米复合吸附剂，所述方法包括通过使至少一部分实施方案45的吸附剂材料与卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。

[0236] 实施方案47提供了通过使实施方案45-46任一项的碳纳米复合吸附剂与含汞气体接触制成的汞-吸附剂组合物。

[0237] 实施方案48提供了与汞或氧化汞接触的实施方案45-47任一项的碳纳米复合吸附剂。

[0238] 实施方案49提供了通过一种方法制成的促进的碳纳米复合吸附剂，所述方法包括通过使至少一部分碳纳米复合吸附剂材料与卤素或卤化物促进剂化学反应来促进吸附剂材料的所述部分，从而形成促进的吸附剂。

[0239] 实施方案50提供了实施方案1-49任一项或任何组合的装置或方法，其任选构造成使得所叙述的所有要素或选项都可供使用或选择。

PAC ET AL. EXHIBIT 1019
Page 1887

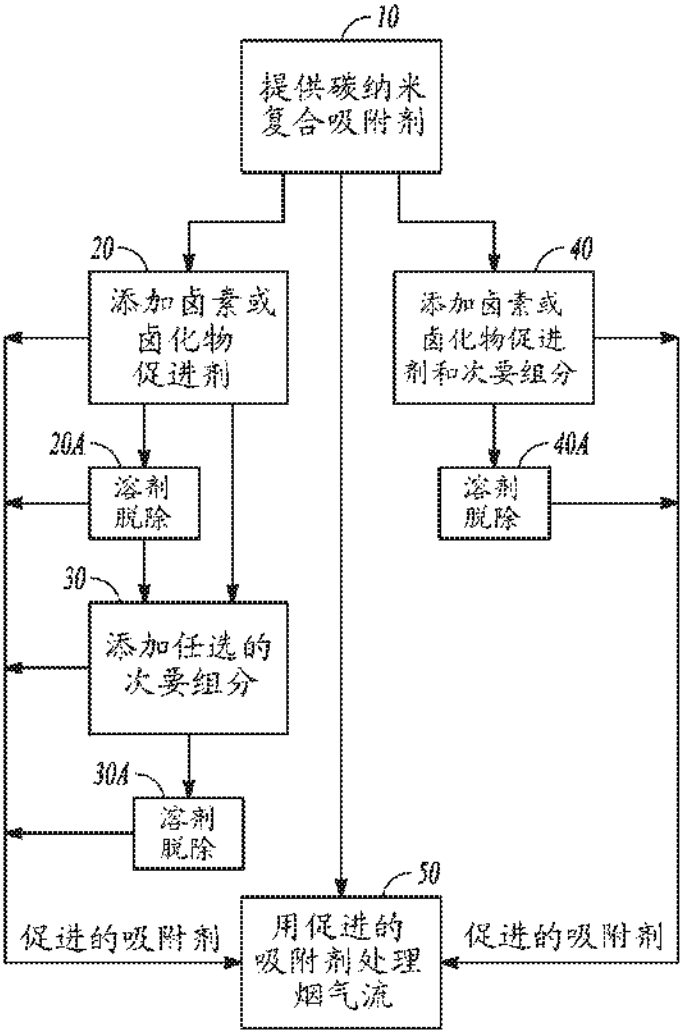


图 1

PAC ET AL. EXHIBIT 1019
Page 1888

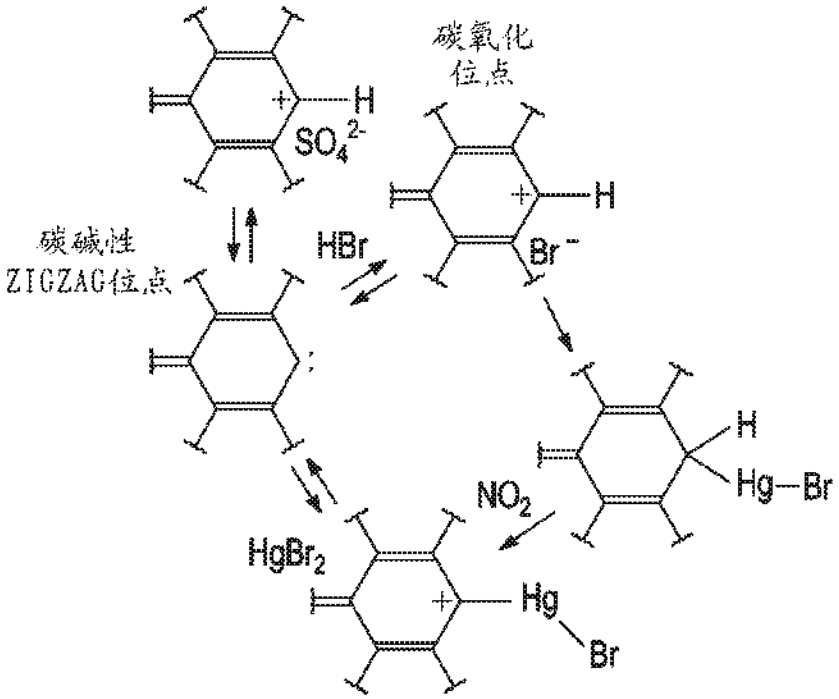


图 2

PAC ET AL. EXHIBIT 1019
Page 1889

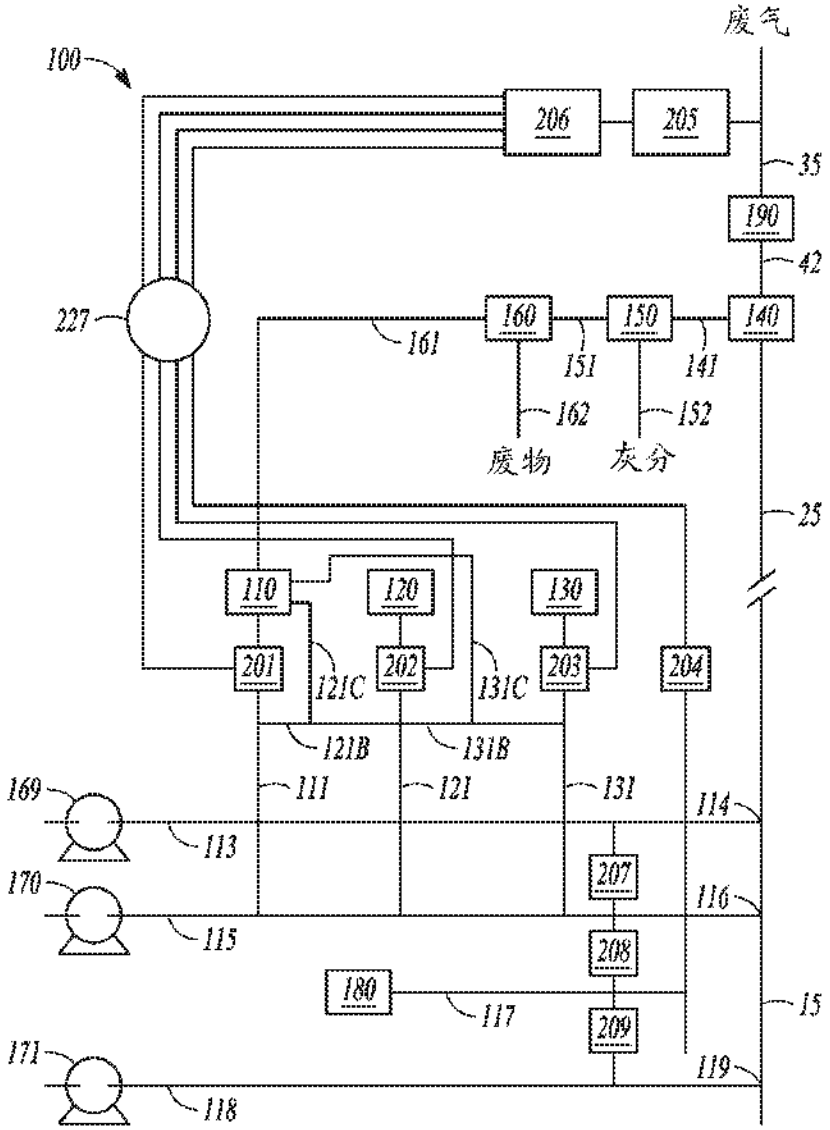


图 3A

PAC ET AL. EXHIBIT 1019
Page 1890

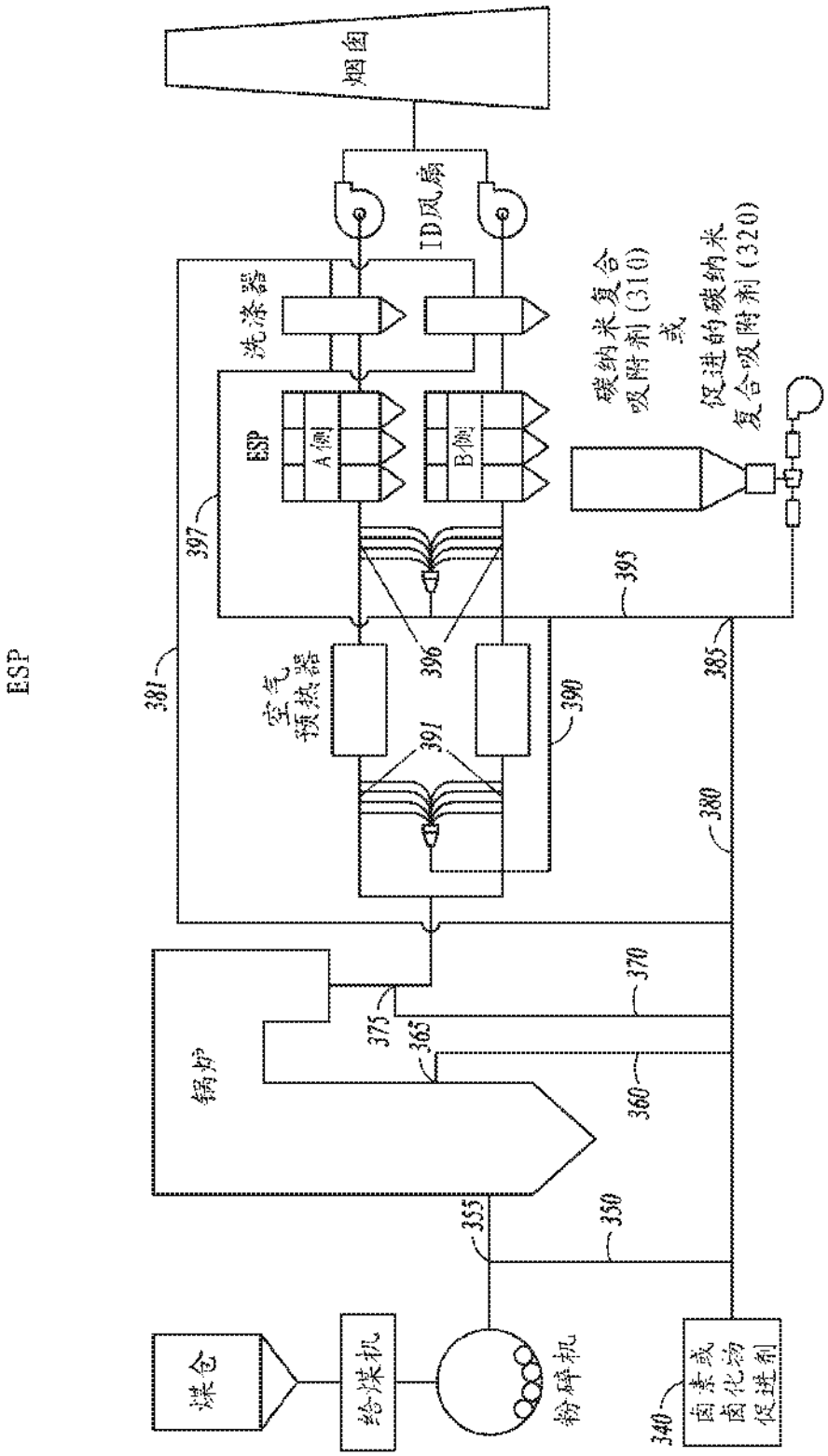


图 3B

PAC ET AL. EXHIBIT 1019
Page 1891

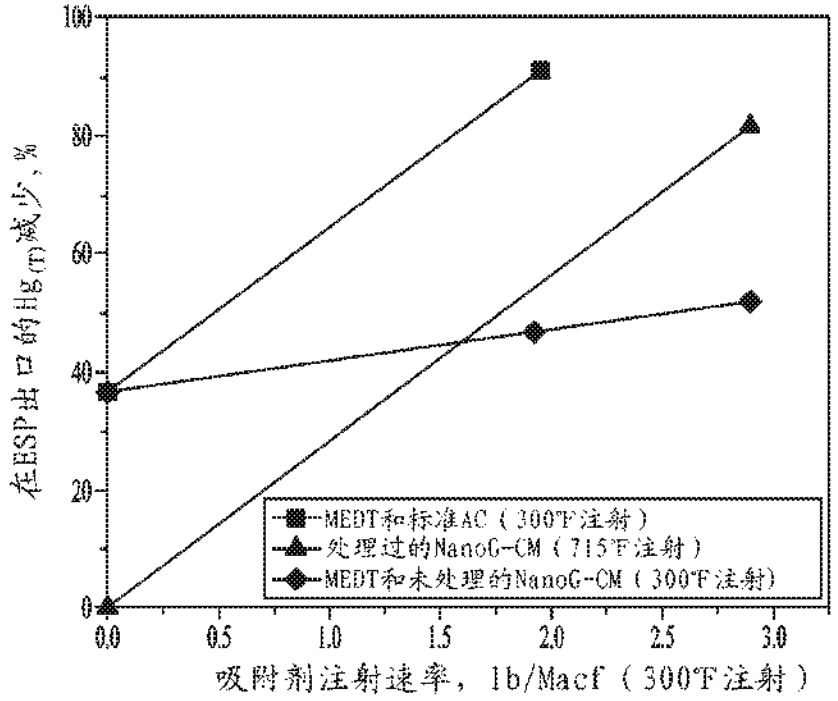


图 4

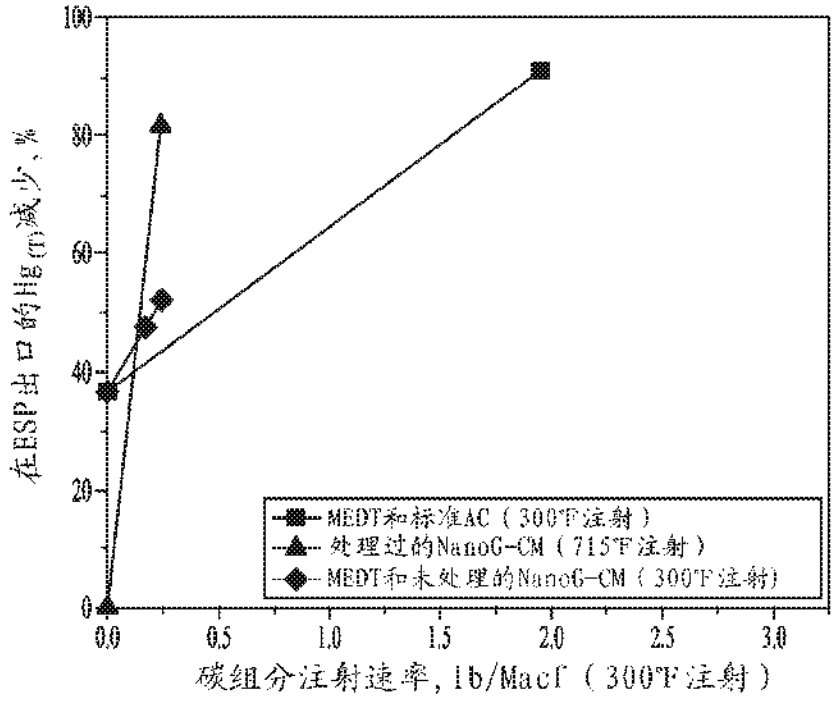


图 5

PAC ET AL. EXHIBIT 1019
Page 1892

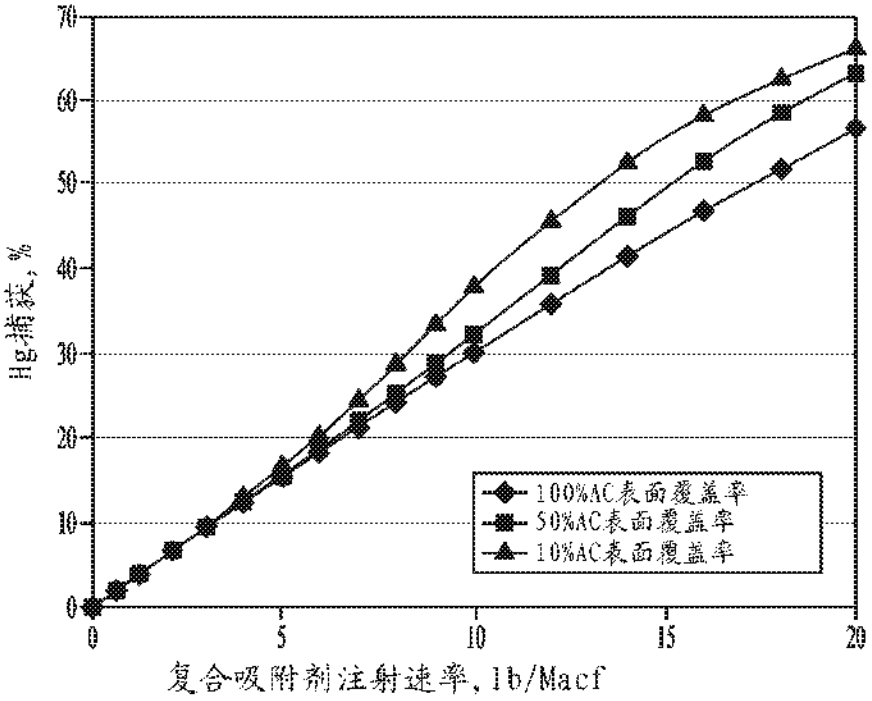


图 6

PAC ET AL. EXHIBIT 1019
Page 1893

Espacenet

Bibliographic data: CN105188910 (A) — 2015-12-23

ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME

Inventor(s):

Applicant(s):

Classification: - international: ***B01D53/02; B01D53/10; B01J20/20; B01J20/32; C01B31/08***
- cooperative: **B01D53/02**; **B01D53/64**; **B01J20/20**; **B01J20/28004**; **B01J20/3204**; **B01J20/3208**; **B01J20/3236**; **B01J20/324**; **B01J20/3293**; **C01B31/083**; **C01B31/10**; B01D2253/102; B01D2253/25; B01D2253/304; B01D2257/602; B01D2258/0283; B01D53/025; B01D53/04; B01D53/10; B01D53/8665

Application number: CN2014825701 20140303

Priority number(s): WO2014US19916 20140303 ; US201361773549P 20130306

Also published as: US2014255279 (A1) WO2014137907 (A2) WO2014137907 (A3) CA2904039 (A1)

Abstract not available for CN105188910 (A)
Abstract of corresponding document: US2014255279 (A1)

The present invention relates to activated carbon sorbents including nitrogen. In various embodiments, the present invention provides an activated carbon sorbent including a halogen- or halide-promoted activated carbon, the activated carbon sorbent particles including nitrogen in a surface layer of the sorbent particles. In various embodiments, the present invention provides a method of reducing the pollutant content in a pollutant-containing gas using the activated carbon sorbent. In various embodiments, the activated carbon sorbent can remove mercury from a mercury-containing gas that includes sulfur(VI) such as SO3 more efficiently than other sorbents.

(19)中华人民共和国国家知识产权局

(12)发明专利申请

(10)申请公布号 CN 105188910 A
(43)申请公布日 2015.12.23

(21)申请号 201480025701.9

(22)申请日 2014.03.03

(30)优先权数据
61/773549 2013.03.06 US

(85)PCT国际申请进入国家阶段日
2015.11.06

(86)PCT国际申请的申请数据
PCT/US2014/019916 2014.03.03

(87)PCT国际申请的公布数据
WO2014/137907 EN 2014.09.12

(71)申请人 能源及环境研究中心基金会
地址 美国北达科他州

(72)发明人 E.S.奥尔森 J.H.帕夫利什

(74)专利代理机构 中国专利代理(香港)有限公司 72001
代理人 周蓉 石克虎

(51)Int.Cl.
B01J 20/20(2006.01)
B01D 53/02(2006.01)
B01D 53/10(2006.01)
B01J 20/32(2006.01)
C01B 31/08(2006.01)

权利要求书5页 说明书25页

(54)发明名称

含氮活性炭吸附剂和使用其的方法

(57)摘要

本发明涉及含氮的活性炭吸附剂。在各种实施方式中，本发明提供了包含卤素或卤化物促进的活性炭的活性炭吸附剂，活性炭吸附剂颗粒在吸附剂颗粒的表层包含氮。在各种实施方式中，本发明提供了使用活性炭吸附剂来降低包含污染物的气体中污染物含量的方法。在各种实施方式中，所述活性炭吸附剂可比其它吸附剂更有效地从包含硫(VI)例如SO_3的含汞气体中除去汞。

CN 105188910 A

1. 降低包含污染物的气体中的污染物含量的方法，所述方法包括：

获得或提供包含活性炭吸附剂颗粒的活性炭吸附剂，在所述吸附剂颗粒表层含有氮；

使包含污染物的气体与所述活性炭吸附剂接触，以形成污染物－吸附剂组合物；和

从所述包含污染物的气体中分离至少一些所述污染物－吸附剂组合物，以产生分离的气体。

2. 权利要求 1 所述的方法，其中所述污染物包含汞，且所述包含污染物的气体是含汞气体。

3. 权利要求 1-2 中任一项所述的方法，其中在所述吸附剂颗粒的表层中的氮的浓度高于在所述吸附剂颗粒的核中的氮的浓度。

4. 权利要求 2-3 中任一项所述的方法，其中所述活性炭吸附剂与至少约 70 wt% 的存在于所述含汞气体中的汞结合。

5. 权利要求 2-4 中任一项所述的方法，其中所述含汞气体进一步包括一定浓度的硫 (VI)，且在所述含汞气体中硫 (VI) 的摩尔浓度为大于约 3 ppm，且相对于相应活性炭吸附剂，所述活性炭吸附剂以更高的吸收速率形成汞－吸附剂组合物，所述相应活性炭吸附剂包含以下至少一种 a) 在相应颗粒表层中更少的氮或基本无氮，b) 更少或基本无卤化物或卤素促进，其中包含所述活性炭吸附剂颗粒的所述活性炭吸附剂是卤化物或卤素促进的，和 c) 更少或基本无无机基体载体，其中包含所述活性炭吸附剂颗粒的所述活性炭吸附剂是无机基体负载的。

6. 权利要求 1-5 中任一项所述的方法，其中所述包含污染物的气体进一步包含一定浓度的硫 (VI)，且在所述包含污染物的气体中硫 (VI) 的浓度为约 3 ppm － 2000 ppm。

7. 权利要求 1-6 中任一项所述的方法，其中氮基本均匀分布在所述活性炭吸附剂颗粒的核中。

8. 权利要求 1-7 中任一项所述的方法，其中与在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在所述表层中的氮减少通过 SO_3^{2-} 和 HSO_3^- 中的至少一种进行活性炭中的碳正离子的中和。

9. 权利要求 1-8 中任一项所述的方法，其中与在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在所述表层中的氮至少部分阻止在所述活性炭中的碳正离子受到 SO_3^{2-} 和 HSO_3^- 中的至少一种的影响。

10. 权利要求 1-9 中任一项所述的方法，进一步包括：获得或提供未促进的碳吸附剂；获得或提供促进剂；并通过使所述未促进的吸附剂的一部分与所述促进剂接触来促进至少一部分所述未促进的吸附剂，以形成所述活性炭吸附剂。

11. 权利要求 10 所述的方法，其中所述促进剂包括卤素或卤化物促进剂。

12. 权利要求 10-11 中任一项所述的方法，其中所述促进剂包括以下物质中的至少一种：卤素、第 V 主族卤化物、第 VI 主族卤化物、卤化氢、卤化铵、碱土金属卤化物和碱土金属卤化物。

13. 权利要求 10-12 中任一项所述的方法，其中所述促进剂包括以下物质中的至少一种：HI、IBr、ICl、NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$ 和 HCl。

14. 权利要求 10-13 中任一项所述的方法，其中所述促进剂是包括以下中的至少一种的形式：蒸汽形式、在溶剂中、作为液体、作为固体、和它们的组合。

PAC ET AL. EXHIBIT 1019
Page 1896

15. 权利要求 10-14 中任一项所述的方法，其中所述促进发生于含水洗涤器中，其中所述洗涤器包含含所述促进剂的水性浆料。

16. 权利要求 1-15 中任一项所述的方法，其中使所述包含污染物的气体与所述活性炭吸附剂接触包括向所述包含污染物的气体中添加所述活性炭吸附剂。

17. 权利要求 1-16 中任一项所述的方法，其中所述活性炭吸附剂为以下中的至少一种：在固定床中、在活动床中、在洗涤器中、在过滤器中或悬浮在包含污染物的气体中。

18. 权利要求 1-17 中任一项所述的方法，其中所述活性炭吸附剂颗粒的核包含约 0 wt% - 约 99 wt% 的氮。

19. 权利要求 1-18 中任一项所述的方法，其中所述活性炭吸附剂颗粒的核包含约 1 wt% - 约 6 wt% 的氮。

20. 权利要求 1-19 中任一项所述的方法，其中所述活性炭吸附剂颗粒的表层包含约 0.001 wt% - 约 99 wt% 的氮。

21. 权利要求 1-20 中任一项所述的方法，其中所述活性炭吸附剂颗粒的表层包含约 5 wt% - 约 80 wt% 的氮。

22. 权利要求 1-21 中任一项所述的方法，其中所述活性炭吸附剂的表层包含在所述颗粒表面的层，所述层具有所述颗粒半径的约 0.001% 至约 99% 的厚度。

23. 权利要求 1-22 中任一项所述的方法，其中所述活性炭吸附剂颗粒的表层包含在所述颗粒表面的层，所述层具有所述颗粒半径的约 0.001% 至约 50% 的厚度。

24. 权利要求 1-23 中任一项所述的方法，其中所述活性炭吸附剂颗粒具有约 0.1 μm 至约 1000 μm 的平均直径。

25. 权利要求 1-24 中任一项所述的方法，其中所述吸附剂颗粒的表层是连续的表层。

26. 权利要求 1-25 中任一项所述的方法，其中获得或提供所述活性炭吸附剂包括：

获得或提供含氮碳前体；和

使用加热、微波和辐照中的至少一种处理所述碳前体，以提供所述活性炭吸附剂。

27. 权利要求 26 所述的方法，其中所述碳前体包括含碳的含碳物质和含氮的含氮物质。

28. 权利要求 27 所述的方法，其中所述含碳物质包括以下物质中的至少一种：黄糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜、葡聚糖、半乳聚糖、木聚糖和糖废品。

29. 权利要求 27-28 中任一项所述的方法，其中所述含氮物质包括含氮有机化合物或含氮无机化合物。

30. 权利要求 27-29 中任一项所述的方法，其中所述含氮物质包括氮杂环、含氮聚合物或共聚物、腈、氨基甲酸酯、氨基酸、硝基苯、羟胺、尿素、肼、氨基磺酸或它们的组合。

31. 权利要求 26-30 中任一项所述的方法，进一步包括：

获得或提供基质材料；

使所述碳前体和所述基质材料接触，以提供吸附剂原材料；和

使用加热、微波和辐照中的至少一种处理所述吸附剂原材料，以提供所述活性炭吸附剂。

32. 权利要求 31 所述的方法，其中加热所述吸附剂原材料提供第二吸附剂原材料，进一步包括使所述第二吸附剂原材料与酸性物质或碱性物质反应，以提供所述活性炭吸附

PAC ET AL. EXHIBIT 1019
Page 1897

剂。

33. 权利要求 31-32 中任一项所述的方法，其中所述基质包括硅藻土、粘土、沸石或矿物中的至少一种。

34. 权利要求 31-33 中任一项所述的方法，其中加热所述吸附剂原材料包括加热至约 100℃ - 约 1200 ℃。

35. 权利要求 31-34 中任一项所述的方法，其中所述活性炭吸附剂包括碳纳米复合材料吸附剂。

36. 权利要求 1-35 中任一项所述的方法，其中所述活性炭吸附剂包含一个或更多个结合位点。

37. 权利要求 36 所述的方法，其中至少一部分在所述活性炭吸附剂中的结合位点与所述污染物和所述污染物的氧化种类中的至少一种反应，以形成所述污染物 - 吸附剂组合物。

38. 权利要求 1-37 中任一项所述的方法，其中从所述含污染物的气体中分离至少一些所述污染物 - 吸附剂组合物包括在微粒分离器中分离。

39. 权利要求 38 所述的方法，其中所述微粒分离器包括静电除尘器 (ESP)、袋滤室、湿式洗涤器、过滤器、旋风分离器、织物分离器、或它们的任意组合。

40. 权利要求 10-39 中任一项所述的方法，其中促进剂前体转化成为所述卤素或卤化物促进剂，其随后与所述活性炭吸附剂反应以产生所述活性炭材料。

41. 权利要求 40 所述的方法，其中所述促进剂前体为在所述未促进的吸附剂上和与所述未促进的吸附剂一起添加中的至少一种。

42. 权利要求 1-41 中任一项所述的方法，进一步包括在所述接触期间或在所述接触之前的至少一种情况下，将碱性组分添加进入所述包含污染物的气体中。

43. 权利要求 42 所述的方法，其中所述碱性组分包括以下物质中的至少一种：碱元素、碱土元素或碱土元素的氧化物、氢氧化物、碳酸盐或磷酸盐、和包括它们的化合物或材料。

44. 权利要求 1-43 中任一项所述的方法，其中所述活性炭吸附剂包含稳定剂，所述稳定剂包含 S、Se 中的至少一种、或它们的混合物。

45. 权利要求 1-44 中任一项所述的方法，其中所述活性炭吸附剂包含稳定剂，所述稳定剂包括 H_2S、SO_3、H_2Se、SeO_2、CS_2、P_2S_5 中的至少一种、或它们的混合物。

46. 权利要求 1-45 中任一项所述的方法，进一步包括使所述污染物 - 吸附剂组合物再生，以产生再生的活性炭吸附剂。

47. 权利要求 1-46 中任一项所述的方法，其中所述活性炭吸附剂是再生的活性炭吸附剂。

48. 权利要求 1-47 中任一项所述的方法，其中所述接触和所述分离中的至少一者发生于含水洗涤器中。

49. 权利要求 48 所述的方法，其中所述洗涤器包含含所述活性炭吸附剂的水性浆料。

50. 降低含汞气体的汞含量的方法，所述方法包括：

获得或提供含氮碳前体；

获得或提供基质材料；

使所述碳前体和所述基质材料接触，以提供无机基体负载的吸附剂原材料；

PAC ET AL. EXHIBIT 1019
Page 1898

加热所述无机基体负载的吸附剂原材料，以提供未促进的吸附剂；

通过使所述未促进的吸附剂的一部分与促进剂进行化学反应来促进至少一部分所述未促进的吸附剂，以形成包含活性炭吸附剂颗粒的促进的无机基体负载的活性炭吸附剂，在所述吸附剂颗粒的表层中包含氮；

使含汞气体与所述活性炭吸附剂接触，以形成汞-吸附剂组合物；并从所述含汞气体中分离出至少一些所述汞-吸附剂组合物，以产生分离的气体；

其中所述含汞气体具有约3-2000 ppm摩尔浓度的硫(VI)，且第一量的所述活性炭吸附剂以第一汞吸附速率形成汞-吸附剂组合物，其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体。

51.制备活性炭吸附剂的方法，包括：

获得或提供未促进的含氮碳吸附剂；

通过使所述未促进的吸附剂的一部分与促进剂接触来促进至少一部分所述未促进的吸附剂，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂，其中在吸附剂颗粒的表层的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

52.权利要求51所述的方法，进一步包括：

获得或提供含氮碳前体；

获得或提供基质材料；使所述碳前体和所述基质材料接触，以提供吸附剂原材料；和

处理所述吸附剂原材料，以提供所述未促进的含氮碳吸附剂。

53.权利要求52所述的方法，其中获得或提供所述含氮碳前体包括：

获得或提供含碳的含碳物质和含氮的含氮物质；和

使所述含碳物质和所述含氮物质接触并加热，以提供所述含氮碳前体。

54.制备活性炭吸附剂的方法，包括：

使含碳物质和含氮物质接触，以提供未促进的含氮碳吸附剂；和

通过使所述未促进的吸附剂的一部分与促进剂接触来促进至少一部分所述未促进的吸附剂，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂，

其中在所述吸附剂颗粒中的氮的浓度高于在所述含碳物质中的氮的浓度。

55.活性炭吸附剂，其通过权利要求51-54中任一项所述的方法制备。

56.活性炭吸附剂，包含：卤素或卤化物促进的活性炭，所述活性炭包含活性炭吸附剂颗粒，在所述吸附剂颗粒的表层包含氮。

57.权利要求56所述的活性炭吸附剂，其中在所述吸附剂颗粒的表层中的氮的浓度高于在所述吸附剂颗粒的核中的氮的浓度。

58.权利要求56-57中任一项所述的活性炭吸附剂，其中所述活性炭吸附剂颗粒具有约0.1 μm至约1000 μm的平均直径。

59.权利要求56-58中任一项所述的活性炭吸附剂，其中所述活性炭为以下情况中的至少一种：卤素促进、第V主族卤化物促进、第VI主族卤化物促进、卤化氢促进、卤化铵促进、碱土金属卤化物促进、和碱土金属卤化物促进。

60.权利要求56-59中任一项所述的活性炭吸附剂，其中所述活性炭吸附剂是无机基

PAC ET AL. EXHIBIT 1019
Page 1899

体负载的，所述无机基体载体包括硅藻土、粘土、沸石或矿物中的至少一种。

61. 权利要求 56-60 中任一项所述的活性炭吸附剂，其中氮基本上均匀分布在所述活性炭吸附剂颗粒的核中。

62. 权利要求 56-61 中任一项所述的活性炭吸附剂，其中与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在所述颗粒的表层中的氮至少部分减少活性炭吸附剂中的碳正离子通过 HSO_3^- 或 SO_3^{2-} 的中和。

63. 权利要求 56-62 中任一项所述的活性炭吸附剂，其中与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在所述颗粒的表层中的氮至少部分阻止活性炭中的碳正离子与 HSO_3^- 或 SO_3^{2-} 形成离子键。

64. 权利要求 56-63 中任一项所述的活性炭吸附剂，其中第一量的活性炭吸附剂以第一汞吸附速率在含汞气体组合物中形成汞 - 吸附剂组合物，其中在所述气体组合物中硫 (VI) 的摩尔浓度约为 3 - 2000 ppm，且其中所述第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含以下至少一种 a) 在相应颗粒表层中更少的氮或基本无氮，b) 更少或基本无卤化物或卤素促进，和 c) 更少或基本无无机基体载体，其中所述活性炭吸附剂是无机基体负载的。

65. 权利要求 56-64 中任一项所述的活性炭吸附剂，其中氮由含氮有机化合物或含氮无机化合物获得。

66. 权利要求 56-65 中任一项所述的活性炭吸附剂，其中氮由以下物质获得：吲哚、喹喔啉、咔唑、异喹啉、硝基苯、尿素、氨基磺酸、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮 - 醋酸乙烯酯共聚物、乙烯基吡咯烷酮 - 丙烯酸共聚物、乙烯基吡咯烷酮 - 马来酸共聚物、聚氨丙啶、丙氨酸、哌嗪、喹诺酮、喹喔啉、二氮杂二环辛烷、氨基酸、铵盐或它们的组合。

67. 用于从含汞气体中除去汞的活性炭吸附剂，所述吸附剂包含：

卤素或卤化物促进的含有活性炭颗粒的活性炭，所述颗粒在表层中含有氮，在所述表层中的氮浓度足够以达到以下目的中的至少之一：a) 与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，减少活性炭吸附剂中的碳正离子通过 HSO_3^- 或 SO_3^{2-} 的中和，和 b) 与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮相应活性炭吸附剂相比较，至少部分阻止活性炭中的碳正离子与 HSO_3^- 或 SO_3^{2-} 形成离子键。

PAC ET AL. EXHIBIT 1019
Page 1900

含氮活性炭吸附剂和使用其的方法

[0001] 相关申请的交叉引用

本申请要求2013年3月6号提交的美国临时专利申请系列号61/773,549的优选权的权益，其公开内容在此经引用以其全部内容并入本文。

[0002] 发明背景

因为汞的毒性和生物累积的能力，汞(Hg)排放已成为健康和环境问题。美国国家环境保护局(U.S. Environmental Protection Agency)(EPA)已颁布法规用于控制来自废物再生能源(waste-to-energy)、水泥生产和烧煤发电厂的汞排放。来自工业来源(如发电厂)的烟道气中的汞可被吸附剂例如活性炭捕获，所述吸附剂随后可由微粒分离设备除去。供应市场需要大量的标准吸附剂(如活性炭)。标准吸附剂不总是有效的，且随着使用的量增大变得更加昂贵。

[0003] 当硫(VI)(如SO_3,H_2SO_4)存在于气流中时，可发生通过活性炭吸附剂从气流中捕获汞的抑制作用，在更高的浓度下，抑制作用增强。硫(VI)摩尔浓度在3 ppm以上的汞捕获受到限制。许多公用工程希望在约5-6 ppm的最小值操作SO_3注射系统以改善灰分可回收性。但是，约6 ppm的硫(VI)浓度可使元素汞捕获减少约25%-50%或更多。介于这种减少，经济节约地获得所需的汞水平变得困难，如果不是不可能的话。当硫(VI)浓度增加如此小的量时，存在汞吸附的严重抑制的原因的科学理解是有限的。

发明内容

[0004]

在各种实施方式中，本发明提供了活性炭吸附剂。所述活性吸附剂包含卤素或卤化物促进的碳。所述活性炭包含含氮的活性炭吸附剂颗粒。在吸附剂颗粒表层中的氮的浓度至少是以下情况之一1)高于在吸附剂颗粒核中的氮的浓度和2)高于在从其中获得吸附剂颗粒的碳材料中的氮的浓度。

[0005] 在各种实施方式中，本发明提供了制备活性炭吸附剂的方法。所述方法包括使含碳物质与含氮物质接触，以提供含氮的未促进的碳吸附剂。所述方法还包括通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成包含含氮的活性炭吸附剂颗粒的活性炭吸附剂，其中在吸附剂颗粒中的氮的浓度高于在含碳物质中的氮的浓度。

[0006] 在各种实施方式中，本发明提供了用于从含汞气体中除去汞的活性炭吸附剂。所述活性炭吸附剂包括卤素或卤化物促进的无机活性炭颗粒，在吸附剂颗粒的表层包含氮。氮原子以足够的浓度在活性炭吸附剂颗粒的表层以达到以下目的中的至少之一a)与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，减少活性炭吸附剂中的碳正离子通过HSO_3^-或SO_3^{2-}的中和，和b)与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，至少部分阻止活性炭中的碳正离子与HSO_3^-或SO_3^{2-}形成离子键。

[0007] 在各种实施方式中，本发明提供了减少包含污染物的气体中的污染物含量的方

PAC ET AL. EXHIBIT 1019
Page 1901

法。所述方法包括获得或提供包括活性炭吸附剂颗粒的活性炭吸附剂，在吸附剂颗粒表层包含氮。所述方法包括使包含污染物的气体与活性炭吸附剂接触。所述接触形成污染物－吸附剂组合物。所述方法还包括从包含污染物的气体中分离出至少一些污染物－吸附剂组合物。所述分离产生分离的气体。

[0008] 在各种实施方式中，本发明提供了用于降低含汞气体的汞含量的方法。所述方法包括获得或提供碳前体。所述碳前体包含氮。所述方法包括获得或提供基质材料。所述方法包括使碳前体与基质材料接触。所述接触提供无机基体负载的吸附剂原材料。所述方法包括加热无机基体负载的吸附剂原材料。所述加热提供未促进的吸附剂。所述方法包括通过使未促进的吸附剂的一部分与促进剂接触（如化学反应）来促进至少一部分未促进的吸附剂，以形成促进的无机基体负载的活性炭吸附剂。所述活性炭吸附剂包括活性炭吸附剂颗粒，在吸附剂颗粒的表层包含氮。所述方法包括使含汞气体与活性炭吸附剂接触。所述接触形成汞－吸附剂组合物。所述方法还包括从含汞气体中分离至少一些汞－吸附剂组合物。所述分离产生分离的气体。硫(VI)在含汞气体中的摩尔浓度约为3-1000 ppm。第一量的活性炭吸附剂以第一汞吸附速率形成汞－吸附剂组合物。第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体。

[0009] 在各种实施方式中，本发明提供了制备活性炭吸附剂的方法。所述方法包括获得或提供未促进的含氮的碳吸附剂。所述方法包括通过使未促进的吸附剂的一部分与促进剂接触（如化学反应）来促进至少一部分未促进的吸附剂，以形成包含活性炭吸附剂颗粒的活性炭吸附剂，在吸附剂颗粒的表层包含氮。

[0010] 本发明的各种实施方式提供了某些超越其它活性炭吸附剂和使用其的方法的优势，其中至少一些是意想不到的。在一些实施方式中，活性炭吸附剂能比其它方法更有效地分离物质（如污染物），从包括那种物质的气体中。在各种实施方式中，活性炭的除汞效率超过或匹配常规方法的效率，而伴随附加的益处，例如成本降低。本发明的各种实施方式的方法和材料可比其它除汞方法更加有效地操作。在一些实施方式中，与其它方法相比较，各种实施方式的方法和材料可用更少量的财务支出除去给定量的汞。例如，与其它除汞方法相比较，包括与包含碳吸附剂的其它除汞方法相比较，对于给定质量的碳，各种实施方式的方法和材料可除去更大量的汞。

[0011] 例如，在一些实施方式中，给定质量的含氮活性炭吸附剂可以高于相同质量的相应活性炭吸附剂的速率从含汞气流中吸收汞，所述含汞气流包含硫(VI)（如SO_3、H_2SO_4等），例如大于约3 ppm硫(VI)，例如约3-200 ppm硫(VI)，3-1000 ppm硫(VI)，或约3-10 ppm硫(VI)，所述相应活性炭吸附剂包含更少的氮或不含氮，例如在相应颗粒表层中包含更低浓度的氮或无氮。在一些实施方式中，活性炭吸附剂中的碳正离子比其它活性炭吸附剂，例如在相应颗粒表层包含更少的氮或基本不含氮的其它活性炭吸附剂，更少地被来自SO_3的离子，例如SO_3^{2-}或HSO_3^{-}中和。在一些实施方式中，活性炭吸附剂中的碳正离子比在其它活性炭吸附剂中，例如在相应颗粒表层包含更少的氮或基本不含氮的其它活性炭吸附剂中，更多地至少部分阻止来自SO_3的离子，例如SO_3^{2-}或HSO_3^{-}。

[0012] 在一些实施方式中，吸附剂可再生和再利用，减少了废吸附剂的处理并降低除汞

PAC ET AL. EXHIBIT 1019
Page 1902

成本。在一些实施方式中，活性炭吸附剂的制备和促进可有利地现场发生。现场制备和促进可具有优势，包括例如：分离制备设施或位置的设备成本和操作成本的降低或消除、运输成本的降低或消除、更新鲜的和反应性更高的吸附剂、处理的减少、组合物的现场定制（例如当改变燃料或减少载量时）。

[0013] 在一些实施方式中，与无机组分可能阻碍污染物在活性炭上的吸附的传统教导相反，吸附剂中的无机基体载体可增强污染物在活性炭中的吸附，例如在最接近的和氧化反应性的碳石墨烯层上。在各种实施方式中，无机基体载体可稳定阳离子位点在最接近的石墨烯碳结构上的发展，所述碳结构可氧化污染物例如汞。在包括通过从相应卤化铵的降解或反应获得的卤化氢化合物促进的无机基体负载的纳米复合材料的实施方式中，无机部分的另一有利的作用可以是为由二者择一的铵盐的分解或反应所释放的氨提供结合位点。结合的氨可形成具有碱性特征的复合物，其可与包含污染物的气体中的 SO_2 或 SO_3 反应，并可阻止它们干扰污染物（例如汞）在活性炭上的活性位点中或接近活性炭上的活性位点的吸附。

[0014] 粘土常常难以从水性介质中过滤或分离。在一些包括粘土作为无机基体载体的实施方式中，粘土有利地被稳定以分散在水性介质中，并可容易地经过滤从水性介质中分离。

[0015] 发明详述

现在将详细参考本公开主题的某些实施方式。尽管本公开主题将结合枚举的权利要求来描述，但是将理解例示的主题不意欲将权利要求限制于本公开主题。

[0016] 以范围格式表述的值应当以灵活方式解释为不仅包括如范围限制明确所述的数值，而且包括在那个范围之内的所有个体数值或子范围，如同各数值和子范围被明确所述一样。例如，“约 0.1% 至约 5%”或“约 0.1% 至 5%”的范围应当解释为不仅包括约 0.1% 至约 5%，而且包括在所表明范围之内的个体值（如 1%、2%、3% 和 4%）和子范围（如 0.1% 至 0.5%、1.1% 至 2.2%、3.3% 至 4.4%）。“约 X 至 Y”的陈述与“约 X 至约 Y”具有相同的意义，除非另外表明。类似地，“约 X、Y 或约 Z”的陈述与“约 X、约 Y、或约 Z”具有相同的意义，除非另外表明。

[0017] 在本文件中，术语“一”或“所述”用于包括一或多于一，除非上下文另外清楚地规定。术语“或”用于指非排他性的“或”，除非另外表明。另外，要理解在此使用且未另外定义的措辞或术语仅用于描述目的，而非限制目的。段落标题的任何使用意欲帮助文件阅读而不解释为限制；与段落标题相关的信息可能出现在那个具体段落之内或以外。此外，在本文件中参考的所有出版物、专利和专利文献均在此经引用以它们的全部内容并入，如同单独经引用并入一样。在本文件和如此经引用并入的那些文件之间存在不一致的用法的情况中，在并入的参考中的用法应认为是对于本文件的补充；对于不可调和的不一致，以本文件中的用法为准。

[0018] 在在此描述的制备方法中，可以不偏离本发明原理的任何顺序进行步骤，除非在明确叙述暂时顺序或操作顺序时。此外，特定的步骤可同时进行，除非明确的权项语言叙述它们分开进行。例如，做 X 的要求保护的步骤和做 Y 的要求保护的步骤可在单一操作之内同时进行，且所得的过程将落在要求保护的过程的字面范围内。

[0019] 定义

在此使用的术语“约”可允许在值或范围中变化的程度，例如，在所述值或所述范围的

PAC ET AL. EXHIBIT 1019
Page 1903

限制的 10% 之内、5% 之内或 1% 之内。

[0020] 在此使用的术语“基本上”是指大多数、或多半，如在至少约 50%、60%、70%、80%、90%、95%、96%、97%、98%、99%、99.5%、99.9%、99.99%，或至少约 99.999% 或更多中。

[0021] 在此使用的术语“数均分子量”是指样品中个体分子的分子量的普通算术平均值。其定义为用样品中所有分子的总重量除以样品中分子的总数目。在实验上，数均分子量 (M_n) 通过以下分析测定：通过公式 $M_n = \Sigma M_i n_i / \Sigma n_i$，样品分成种类 i 的分子量部分，所述种类 i 具有 n_i 个分子量 M_i 的分子。数均分子量可通过各种各样熟知的方法包括凝胶渗透色谱法、光谱端基分析 (spectroscopic end group analysis) 和渗透压力测定法来测量。

[0022] 在此使用的术语“重均分子量”指 (M_w)，其等于 $\Sigma M_i^2 n_i / \Sigma M_i n_i$，其中 n_i 是分子量 M_i 的分子的数目。在各种实例中，重均分子量可使用光散射、小角中子散射、X- 射线散射和沉降速率测定。

[0023] 在此使用的术语“溶剂”是指可溶解固体、液体或气体的液体。溶剂的非限制性实例是硅氧烷、有机化合物、水、醇、离子液体和超临界流体。

[0024] 在此使用的术语“空气”是指气体混合物，其具有与取自大气，通常在地平面的气体的天然组成近似相同的组成。在一些实例中，空气取自周围环境。空气具有包括接近 78% 的氮、21% 的氧、1% 的氩和 0.04% 的二氧化碳，以及少量的其它气体的组成。

[0025] 在此使用的术语“室温”是指约 15℃至 28℃的温度。

[0026] 在此使用的“矿物”是指天然存在的固态化学物质，其通过生物地球化学过程形成，具有，例如，特有的化学组成、高度有序的原子结构和特殊的物理性质。

[0027] 描述

在各种实施方式中，本发明提供了用于降低汞含量的活性炭吸附剂和相关方法，用于在燃烧系统中使用，在所述燃烧系统的烟道气中固有地具有高水平的硫 (VI)（如 SO_3，或可从其获得的相关化合物，例如 H_2SO_4 或其它硫酸盐），和用于在使用 SO_3 注射用于灰分调节用于改善的灰分收集的工厂中使用。在一些实例中，通过克服能在高 SO_3 或高硫酸盐（如高硫 (VI)）系统中抑制汞捕获的动力学效应和平衡效应，所述方法可在高硫 (VI) 含量的烟道气中获得高的汞捕获率。所述活性炭吸附剂包含活性炭吸附剂颗粒。在吸附剂颗粒的表层的氮的浓度可高于在吸附剂颗粒的核中的氮的浓度。在一些实例中，所述活性炭吸附剂可为促进的。

[0028] 在各种实施方式中，活性炭吸附剂和相关方法可在中等温度下（如约 25-330℃，或约 50-500℃），有效除去空气或烟道气流中的元素汞蒸汽。在一些实例中，活性炭不掺杂硫或金属卤化物，其在更高温度下可以是不稳定的。

[0029] 在一些实施方式中，除去过程不包括像在低温下发生的那种元素汞的吸附，但是可包括汞与氧化剂的催化反应，以形成包括结合到活性炭表面的汞的有机汞化合物，其中汞可通过如与酸的反应被释放，以提供具有低蒸汽压的汞 (II) 种类，例如硫酸汞、溴化汞或氯化汞。离子汞 (II) 形式可为氧化物或用于所述过程中的任选的酸的盐（例如来自硫酸的硫酸盐），其可具有更低的挥发性。活性炭可展现归因于，例如，众多活性催化位点的高速率的氧化催化活性，且同时具有用于有机汞化合物产生的大的表面积并因此快速产生转化的汞 (II) 盐。

[0030] 含氮的活性炭吸附剂。

PAC ET AL. EXHIBIT 1019
Page 1904

[0031] 在各种实施方式中，本发明提供了活性炭吸附剂。所述活性炭吸附剂可包含卤素或卤化物促进的活性炭颗粒；在其它实施方式中，所述活性炭吸附剂是未促进的。在一些实例中，所述活性炭可具有无机基体载体。

[0032] 所述活性炭吸附剂可包含活性炭吸附剂颗粒。在吸附剂颗粒的表层的氮的浓度可至少是以下情况之一 1）高于在吸附剂颗粒的核中的氮的浓度和 2）高于在从其中获得活性炭吸附剂颗粒的活性炭材料中的氮的浓度。各颗粒的表层可独立地为连续的（如未破坏的，具有最小的间隙或没有间隙）或非连续的。所述表层可能在颗粒的外表面。各颗粒的表层可独立地具有任意合适的厚度。所述表层可具有可变的厚度，或可具有基本一致的厚度。在一些实施方式中，所述表层可具有颗粒半径的约 0.000,001% 至约 99.99% 的厚度，颗粒半径的 0.001% 至 99%、0.001% 至约 50%、1% 至约 50%、0.1% 至 25%、或约 25% 至 50% 的厚度。若颗粒是非球形的，则半径可估算为约颗粒的最大尺寸的一半。

[0033] 在一些实施方式中，各活性炭颗粒可在表层中独立地包含比在核中高约 1.001 倍的氮浓度，或更低，或在表层中包含比在核中高约 1.01、1.1、1.2、1.4、1.6、1.8、2、3、4、5、6、7、8、9、10、15、20、50、100 倍，或约 1000 倍的氮浓度。在一些实施方式中，在表层中的氮的浓度可为约 0.000,001 wt% 或更少的氮，或约 0.001 wt%、0.01 wt%、0.1 wt%、1 wt%、2 wt%、3 wt%、4 wt%、5 wt%、10 wt%、15 wt%、20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%，或约 90 wt% 或更多的氮。在一些实例中，在表层中的氮的浓度可为约 0.001 wt% - 99 wt% 氮，5 wt% - 80 wt%，或约 5-60 wt%。在各种实施方式中，在核中的氮的浓度可为约 0 wt%、0.000,001 wt%，或约 0.001 wt%、0.01 wt%、0.1 wt%、1 wt%、2 wt%、3 wt%、4 wt%、5 wt%、10 wt%、15 wt%、20 wt%、50 wt%、或 90 wt% 或更多。在一些实例中，在核中的氮的浓度可为约 0.001 wt% - 99 wt% 氮，0.1 wt% - 20 wt% 或约 1 wt% - 6 wt%。

[0034] 所述活性炭吸附剂可为任意合适的形式。例如，活性炭可为颗粒状或细颗粒。所述活性炭可具有任何合适的形状，例如球形或不规则的。所述活性炭可具有约 0.1 nm 或更小的平均直径，或约 1 nm、10 nm、100 nm、1 μm、10 μm、100 μm、1 mm、或约 10 mm 或更大的平均直径。在一些实例中，活性炭具有约 0.01 μm 或更小的直径，或约 0.1 μm、1 μm、2 μm、3 μm、4 μm、5 μm、10 μm、20 μm、30 μm、40 μm、50 μm、60 μm、70 μm、80 μm、90 μm、100 μm、1000 μm 或更大的直径。在一些实例中，颗粒的直径约为 0.1-1000 μm，或 1-100 μm，或约 1-30 μm。若颗粒是非球形的，直径可估算为颗粒的最长尺寸。含汞的活性炭吸附剂的吸收容量可为约 0.000,1 mg 汞每克吸附剂或更少，或约 0.001 mg/g、0.01、0.1、1、2、3、4、5、10、15、20、25、30、35、40、45、50、55、60、65、70、75、80、85、90、95、100、110、120、150、200、300、400、500、750、或约 1 g 汞每克吸附剂或更多。

[0035] 在一些实施方式中，活性炭中的至少一些碳是碳的石墨烯（graphene）形式。在一些实施方式中，石墨烯形式的碳可包括更高浓度的适合作为活性位点的位置。在一些实例中，石墨烯碳的某些部分可具有最高浓度的适合作为活性位点的位置；在一些实例中在边缘处，在一些实例中在非边缘位置。如在此所描述的，此类适合作为活性位点的位置可通过使用卤化物或卤素处理来活化。在各种实施方式中，活性炭吸附剂中的碳可为至少约 1 wt%、2 wt%、3 wt%、4 wt%、5 wt%、10 wt%、20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%、90 wt%、95 wt%、96 wt%、97 wt%、98 wt%、99 wt%、99.9 wt%、99.99 wt%、或大于约 99.999 wt% 的石墨烯形式的碳。

PAC ET AL. EXHIBIT 1019
Page 1905

[0036] 在一些实施方式中，氮基本上遍及活性炭颗粒均匀分布。在一些实施方式中，氮基本上均匀分布在活性炭吸附剂颗粒的核中；在其它实施方式中，氮在核中可具有任意合适的分布。在一些实施方式中，氮基本上均匀分布在活性炭吸附剂颗粒的表层。在一些实施方式中，氮在表层中不是均匀分布的；如，氮可具有梯度，最高浓度在表层外部和较低浓度在表层内部。

[0037] 氮在活性炭内可为任意合适的形式。在一些实例中，氮可为氮原子，其结合一个或更多个氢原子或一个或更多个其它原子，所述其它原子是，例如，为活性炭框架的部分的含碳基团（如活性炭骨架或其附件），或结合有机基团。在一些实例中，例如，氮可为中性的或可带有正电荷（如铵）或负电荷。氮可具有任意合适的氧化态，例如 0 或 1。氮可结合 4 个、3 个、2 个、1 个或 0 个氢原子。氮可在 0、1、2、3 或 4 个位置结合一个或更多个活性炭框架。在一些实施方式中，氮可包括与活性炭的碳框架或与其它官能团结合的一个或两个双键或一个三键，如此使得氮结合 1、2 或 3 个碳原子。

[0038] 活性炭中的氮可由任意含氮化合物，例如含氮的有机或无机化合物，例如通过热解或碳化获得。在一些实例中，氮由任意含氮杂环获得或是所述任意含氮杂环的部分，或由任意其它含氮化合物获得。例如，氮可由以下物质获得：吲哚、喹喔啉、咔唑、异喹啉、哌嗪、喹诺酮、喹喔啉、二氮杂二环辛烷、聚丙烯腈、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮 - 醋酸乙烯酯共聚物、乙烯基吡咯烷酮 - 丙烯酸共聚物、乙烯基吡咯烷酮 - 马来酸共聚物、聚氨丙啶、氨基酸（如丙氨酸、精氨酸、天冬酰胺、天冬氨酸、半胱氨酸、谷氨酰胺、谷氨酸、甘氨酸、组氨酸、异亮氨酸、亮氨酸、赖氨酸、蛋氨酸、苯丙氨酸、脯氨酸、丝氨酸、苏氨酸、色氨酸、酪氨酸、或缬氨酸）、苯胺（analine）、硝基苯、羟胺、尿素、肼、氨基磺酸、腈类、氨基甲酸酯类、异氰酸酯类、尿烷类、或它们的组合。在一些实例中，活性炭中的氮可由含氮无机化合物获得或是所述含氮无机化合物的部分，所述含氮无机化合物例如氨、溴化铵、氯化铵、硝酸、亚硝酸、二氧化氮、含 NO_3 的化合物、含 NO_2 的化合物等。

[0039] 在各种实施方式中，含氮活性炭吸附剂可在给定浓度的硫（VI）中以比其它吸附剂更高的速率吸收污染物，例如汞。在一些实例中，第一量的活性炭吸附剂以第一汞吸附速率在含汞气体组合物中形成汞 - 吸附剂组合物，其中硫（VI）在气体组合物中的摩尔浓度约为 3 - 2000 ppm，其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种 a）在相应颗粒表层中更少（如更低浓度）的氮或基本无氮，b）更少或基本无卤化物或卤素促进，和 c）更少或基本无无机基体载体。

[0040] 活性炭吸附剂的操作原理不意欲受限于在此提出的任何特定的操作理论。在一些实施方式中，与在基本相似的条件下，在相应的颗粒表层中包含更少的氮或基本不含氮的活性炭吸附剂相比较，在表层中的氮至少部分减少活性炭吸附剂中的碳正离子通过 SO_4（或由 SO_3 获得的离子或其它物质，例如 HSO_3^- 或 SO_3^{2-}）中和。在一些实例中，与在基本相似的条件下，在相应的颗粒表层中包含更少的氮或基本不含氮的活性炭吸附剂相比较，在表层中的氮至少部分阻止活性炭中的碳正离子与 SO_4（或由 SO_3 获得的离子或其它物质，例如 HSO_4^- 或 SO_3^{2-}）形成离子键。

[0041] 在各种活性炭吸附剂中，在污染物捕获例如汞捕获期间可能发生两种问题：1）在碳边缘位点得到高氧化反应性（动力学效应）和 2）防止 / 避免被氧化的汞由于被硫酸盐取代而损失碳结合状态（平衡效应）。气相中的元素汞可在碳边缘表面（阳离子锯齿形位

PAC ET AL. EXHIBIT 1019
Page 1906

点）被氧化，并可被共价结合作为有机汞卤化物。阳离子位点可通过向碳边缘结构添加酸或卤素（X_2）形成，这可产生碳鎓－卤化物离子对。所述氧化可通过负卤化物离子稳定随着汞原子添加至碳鎓原子而在汞原子上发展的正电荷来得到协助。若碳鎓离子的氧化电势（电荷）或其稳定性更高，则所述氧化可更容易发生，其可由存在于碳框架结构和附近环境中的邻近电荷所影响或决定。结构中另外的阳离子官能可使在反应性位点的氧化电势升高（增加正电荷），或可增加在反应性位点的正电荷的稳定性。负基团（例如由 SO_3 获得的离子，如 SO_3^{2-} 和 SO_2^{-}），可稳定并减少总电荷和可获得的碳鎓离子，并因而降低对于汞氧化的反应性和对于汞捕获的可获得性。

[0042] 对于经短接触时间的捕获，例如通过静电除尘器（ESP）的飞行中捕获，长期平衡效应可能不那么重要。但是，在一些情况下，平衡取代问题可能更为重要，如，袋滤室（baghouse）收集或在选择性催化还原（SCR）单元中的 SO_3 注射或形成。因为硫酸盐浓度可随着在碳表面的暴露时间增加而增加，所以它们在长暴露时间里在取代卤化汞进入气相（脱附和穿透）的效应可能是重要的。当 SO_3 相关的化合物和离子例如硫酸、硫酸盐、或相关离子，初始存在于或快速形成于湿表面上时，如，对于 SO_3 注射，平衡取代效应在伴随短接触时间的系统中也可能变得重要。

[0043] 在各种实施方式中，在表层中的氮可稳定或增加碳结构中的正电荷，这可克服由硫酸盐的电荷消耗，且碳边缘可使用卤素／卤化物促进。在一些实施方式中，在碳边缘结构中的阳离子中心（通常存在于卤化的（如溴化的）碳中并有用于快速汞氧化）的收集可被硫酸氢盐离子和由在碳表面的 SO_3 反应形成的其它相关离子的干扰所损害。这些阴离子可中和碳鎓离子的正电荷并降低具有共享电荷的剩余反应性位点的总氧化电势。另外的阳离子中心可通过在活性炭形成期间引入氮原子在碳结构内产生，帮助抗衡该效应并抵消一些电荷，所述电荷可通过与，如 SO_3 或由 SO_3 获得的离子发生离子相互作用或其它相互作用来使用。原子例如氮可以多环结构添加以形成增加的阳离子或以稳定现存的阳离子。

[0044] 在一些实施方式中，在活性炭吸附剂颗粒的表层中的氮增加吸附剂中的阳离子电荷，因为氮保护阳离子中心使其免于 SO_3 和由 SO_3 获得的离子或化合物的影响。氮原子可形成带电笼或在碳边缘结构周围的其它保护性阻塞结构，或为带电笼或碳边缘结构周围的其它保护性阻塞结构的部分，以防止 SO_3 和由 SO_3 获得的离子或化合物，例如阴离子硫酸盐基团进入，但是允许汞原子扩散进入纳米结构以到达氧化或吸附（sorbtion）的活性中心。

[0045] 在一些实施方式中，无机基质载体例如粘土可帮助阻止 SO_3 和由 SO_3 获得的离子或化合物进入活性阳离子中心，或帮助稳定或增加在活性炭吸附剂中的阳离子电荷。

[0046] 在一些实施方式中，向活性炭添加酸或酸性物质改善了性能。在各种实施方式中，可在碳使用之前通过将酸性溶液浸渍进入碳来添加酸或酸性物质，或可在使用期间将其作为溶液或气体添加至吸附床。改性碳可使用酸性物质浸渍，例如约 1 wt％或更少或约 2 wt％、3、4、5、6、7、8、9、10、15 或约 20 wt％或更多或酸性物质，例如 HBr、HCl、H_2SO_4 等。

[0047] 降低包含污染物的气体中的污染物含量的方法。

[0048] 在各种实施方式中，本发明提供了使用活性炭吸附剂的方法。所述方法可为任何合适的方法。例如，一些实施方式提供了降低包含污染物的气体中的污染物含量的方法。在一些实例中，包含污染物的气体可至少包含一些氧。所述方法可包括获得或提供包含活性炭吸附剂颗粒的活性炭吸附剂，在表层或吸附剂颗粒中包含氮。在一些实施方式中，在吸

PAC ET AL. EXHIBIT 1019
Page 1907

附剂颗粒的表层中的氮的浓度可高于在吸附剂颗粒的核中的氮的浓度。活性炭吸附剂可为在此描述的任何含氮的活性炭吸附剂。在一些实例中，含氮的活性炭吸附剂可为促进的含氮活性炭吸附剂。在一些实例中，含氮的活性炭吸附剂可为无机基体负载的或纳米复合材料含氮活性炭吸附剂。在一些实例中，活性炭吸附剂可为促进的含氮活性炭吸附剂和无机基体负载的或纳米复合材料含氮活性炭吸附剂二者。在一些实施方式中，活性炭吸附剂可为促进的但不包含无机基体载体。在一些实施方式中，活性炭吸附剂可既不是促进的，也不是无机基体负载的。活性炭吸附剂可包含结合位点，其可与包含污染物的气体中的污染物中的至少一种和污染物的氧化种类结合，以形成污染物－吸附剂组合物。活性炭吸附剂中的至少一部分结合位点可与污染物中的至少一种和污染物的氧化种类反应，以形成污染物－吸附剂组合物。

[0049] 降低包含污染物的气体中的污染物含量的方法可包括使包含污染物的气体与活性炭吸附剂接触。所述接触形成污染物－吸附剂组合物。所述接触可为任何合适的接触。在一些实施方式中，包含污染物的气体与活性炭吸附剂接触可包括将活性炭吸附剂添加或注射进入含污染物的气体。例如，所述接触可发生于气体中。在另一实施方式中，所述接触可发生于水性液体中。在另一实例中，所述接触可发生于气体中，且随后接触也可发生于水相例如洗涤器中。

[0050] 在一些实施方式中，在包含污染物的气体与活性炭吸附剂接触期间，活性炭吸附剂可在任何合适的结构中以便其接触包含污染物的气体。例如，在接触期间，活性炭吸附剂可为以下中的至少一种：在固定结构中例如在固定床中、在活动结构中例如在活动床中、在洗涤器中、在过滤器中（如固定过滤器或移动的/活动的过滤器）或悬浮在包含污染物的气体中。

[0051] 污染物－吸附剂组合物可为任何合适的组合物，其包括污染物或污染物的氧化形式或另外的化学转化形式和活性炭吸附剂。在一些实施方式中，汞以其元素形式被吸附剂吸收；汞－吸附剂组合物可包括吸附剂和汞的元素形式。在一些实施方式中，汞通过化学反应，例如氧化，被吸附剂转化，以使得来自气体的汞转化成为包含结合汞的活性炭的碳框架的有机汞化合物，其可在与合适的酸反应之后作为汞(II)化合物释放，以产生其盐。在一些实施方式中，汞－吸附剂组合物可包含元素汞、有机汞化合物、和Hg(II)化合物中的至少一种。

[0052] 在一些实例中，元素汞或经转化的汞可保持被吸收至吸附剂，直至汞－吸附剂组合物在后续分离步骤中被除去。例如，元素汞或经转化的汞可被吸收或反应并吸收进入吸附剂组合物中或在吸附剂组合物上，以使得在从包含污染物的气体中分离出污染物－吸附剂组合物之后，分离的气体具有约1%或更少、3%、5%、10%、20%、30%、40%、50%、60%、70%、80%、90%、95%、96%、97%、98%、99%、99.9%、99.99%、或约99.999%或更多的初始存在于包含污染物的气体中的汞。在一些实施方式中，元素汞或经转化的汞可从汞－吸附剂组合物中释放；例如，少于约1 wt%、3 wt%、5 wt%、10 wt%、20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%、90 wt%、95 wt%、或少于约99 wt%的汞可在从气体中分离汞－吸附剂组合物之前从汞－吸附剂组合物中释放。在一些实例中，大部分被吸收的元素汞或经转化的汞可保持部分汞－吸附剂组合物，直至汞－吸附剂组合物在后续分离步骤中被除去。在一些实例中，从汞－吸附剂组合物中释放的经转化的汞可通过分离步骤或另一步骤被后续从气体中除去。

PAC ET AL. EXHIBIT 1019
Page 1908

在一些实例中，已从汞-吸附剂组合物中释放的元素汞或经转化的汞可接触活性炭吸附剂以形成汞-吸附剂组合物，通过分离步骤被后续除去。

[0053] 降低包含污染物的气体中污染物含量的方法可包括从包含污染物的气体中分离至少一些污染物-吸附剂组合物，以得到分离气体。在一些实施方式中，从包含污染物的气体中分离至少一些污染物-吸附剂组合物包括在微粒分离器中分离。所述微粒分离器可为任何合适的微粒分离器，例如静电除尘器(ESP)、袋滤室、湿式洗涤器、过滤器、旋风分离器、织物分离器(fabric separator)、或它们的任意组合。在一些实施方式中，可使用静电除尘器，接着是洗涤器。在其它实施方式中，可使用没有洗涤器的静电除尘器，或可使用另一微粒分离器。可用作微粒分离器的一些设备也可具有其它功能，例如洗涤器也可除去SO_2或SO_3。在包括使汞与吸附剂在水相中，如在洗涤器中接触的实施方式中，通过汞与吸附剂在水相中的反应或相互作用发生在水相内的汞从气体中的除去可被认为是汞-吸附剂组合物从气体中分离。

[0054] 在一些实例中，通过从含汞气体中分离微粒，至少约20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%、90 wt%、95 wt%、96 wt%、97 wt%、98 wt%、99 wt%、99.9 wt%、99.99 wt%、或约99.999 wt%或更多汞可从含汞气流中被除去。如在此所讨论的，汞可以元素汞的形式、或以经转化的汞的形式被除去，所述经转化的汞例如包含结合活性炭的碳框架的汞的有机汞化合物或以与合适的抗衡离子复合的Hg(II)。

[0055] 在一些实施方式中，接触和分离中的至少一者发生在含水洗涤器中。所述含水洗涤器可为任何合适的含水洗涤器。例如，洗涤器可包含含活性炭吸附剂的水性浆料。

[0056] 在一些实施方式中，所述方法除去约1%或更少、或约2%、3、4、5、10、20、30、40、50、60、70、80、85、90、91、92、93、94、95、96、97、98、99、99.5、99.9、99.99、99.999、或约99.9999%或更多的存在于含汞气体中的汞(如用汞的最终浓度除以汞的初始浓度)。在一些实施方式中，活性炭吸附剂结合约50-100 wt%的存在于含汞气体中的汞，或约60-90 wt%、60-80 wt%、70-80 wt%、80-90 wt%、90-100 wt%、或约95-100 wt%或存在于含汞气体中的汞。

[0057] 在一些实施方式中，在含汞气体中的硫(VI)(如来自SO_3、H_2SO_4等)的浓度为大于约3 ppm (摩尔浓度)，及第一量的活性炭吸附剂以第一汞吸附速率形成汞-吸附剂组合物，其中所述第一吸附速率高于在基本类似条件下，第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种a)在相应表层更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体。在一些实施方式中，在包含污染物的气体中，处于其中包含污染物的气体接触吸附剂的位置或靠近所述位置的SO_3的浓度为约1 ppm至约100,000 ppm、2-10,000 ppm、3 ppm-1000 ppm、3-100 ppm、3-50 ppm、3-10 ppm、或约3-6 ppm或更多、或在包含污染物的气体中，处于其中包含污染物的气体接触吸附剂的位置或靠近所述位置的硫(VI)(如来自SO_3、H_2SO_4等)的浓度为约1 ppm至约100,000 ppm、2-10,000 ppm、3 ppm-1000 ppm、3-100 ppm、3-50 ppm、3-10 ppm、或约3-6 ppm或更多，其中ppm指百万分之一摩尔。所述浓度可为瞬时浓度，或随时间流逝的平均浓度。与在基本相似的条件下，在相应表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在活性炭吸附剂颗粒的表层中的氮可通过SO_3^{2-}和HSO_3^-中的至少一种减少活性炭中的碳正离子的中和。与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮相应活性炭吸附剂相比较，在活性炭吸附剂颗粒的表层中的氮可至少部分阻止活性

PAC ET AL. EXHIBIT 1019
Page 1909

炭中的碳正离子受 HSO_3^- 或 SO_3^{2-} 中的至少一种的影响。

[0058] 在一些实施方式中，降低包含污染物的气体中污染物含量的方法包括在接触期间或在接触之前的至少一种情况下，将碱性组分添加或注射进入包含污染物的气体中。所述碱性组分可为任何合适的碱性组分，例如碱元素、碱土元素或碱土元素的氧化物、氢氧化物、碳酸盐或磷酸盐、和包括其的化合物或材料。在各种实例中，碱性组分单独添加或与碳吸附剂一起添加可得到改善的汞捕获。各种因素可影响碱添加的有效性，诸如，例如烟道气污染物、烟道气组分（如 SO_2、NO_x、Se、HCl 等）、操作温度、汞形式和汞浓度。在一些实例中，可调节碱与活性炭的比例以优化给定系列的现场条件（site condition）。

[0059] 在一些实施方式中，活性炭包含稳定剂。在一些实例中，稳定剂可包括 S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5 中的至少一种、或它们的混合物。所述稳定剂可在促进之前或之后添加。

[0060] 在各种实施方式中，除汞速率可随温度升高和随汞的载量增加而逐步降低，其至少部分归因于逆反应速率的增加。在一些实例中，最高速率可在约 100 至 150 ° C、50-200 ° C、或约 50-250 ° C 下发生。在一些实例中，在 400° C 下，逆反应可为热力学上高度有利的。在一些实例中，活性炭可通过用水洗以除去在其上的硫酸得以再生，例如在美国专利第 8,173,566 号中所描述的。

[0061] 在一些实施方式中，降低包含污染物的气体中污染物含量的方法可包括使污染物-吸附剂组合物再生以得到再生的活性炭吸附剂。所述再生可为允许再生的活性炭吸附剂重新用于从包含污染物的气体中除去污染物的任何合适的再生。所述方法可包括使用再生的活性炭吸附剂从包含污染物的气体中除去污染物。

[0062] 制备含氮活性炭的方法。

[0063] 在一些实施方式中，包含含氮活性炭颗粒的活性炭从市场上获得。在其它实施方式中，含氮活性炭是合成的。例如，降低包含污染物的气体中污染物含量的方法可包括制备含氮活性炭。

[0064] 例如，在降低包含污染物的气体中污染物含量的方法中，获得或提供活性炭吸附剂 可包括获得或提供含氮碳前体。所述方法也可包括处理（如加热）碳前体，以提供活性炭吸附剂。所述处理可包括任何合适的处理。在包括加热碳前体的方法中，所述方法除了加热，可包括任何其它合适的任选的步骤，例如洗涤、化学处理或振动。在一些实施方式中，碳前体包含含碳的含碳物质和含氮的含氮物质。所述加热可包括加热至约 100 °C 至 15,000 °C、200 °C 至 10,000 °C、300 °C 至 9000 °C、或约 400 °C 至 8000 °C。

[0065] 含碳物质可为任何合适的含碳物质。例如，含碳物质可为有机化合物。在一些实例中，含碳物质包括以下物质中的至少一种：黄糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜、糖蜜萃余液（糖废品）、葡聚糖、半乳聚糖、木聚糖、和糖废品。在一些实例中，含碳物质包括粉末状活性炭、颗粒状活性炭、碳黑、碳纤维、碳蜂窝或平面结构、气凝胶碳膜、热解炭、或活性炭或再生的活性炭，其具有大于要处理的烟道气流中的飘尘的质量平均颗粒尺寸。氮可从任何合适的含氮物质获得或部分可为任何合适的含氮物质。例如，含氮物质可为含氮有机化合物，例如含氮杂环。在一些实例中，含氮物质包括吲哚、喹喔啉、咔唑、异喹啉、哌嗪、喹诺酮、喹喔啉、二氮杂二环辛烷、聚丙烯腈、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮-醋酸乙烯酯共聚物、乙烯基吡咯烷酮-丙烯酸共聚物、乙烯基吡咯烷酮-马来酸共聚物、聚氮丙啶、

PAC ET AL. EXHIBIT 1019
Page 1910

氨基酸（如丙氨酸、精氨酸、天冬酰胺、天冬氨酸、半胱氨酸、谷氨酰胺、谷氨酸、甘氨酸、组氨酸、异亮氨酸、亮氨酸、赖氨酸、蛋氨酸、苯丙氨酸、脯氨酸、丝氨酸、苏氨酸、色氨酸、酪氨酸、或缬氨酸）、苯胺、硝基苯、羟胺、尿素、肼、氨基磺酸、腈类、氨基甲酸酯类、异氰酸酯类、尿烷类、或它们的混合物。含氮物质可为任何合适的铵盐，例如由脂肪族含氮化合物、芳香族含胺化合物或杂环含氮化合物获得的铵盐；在实施方式中，其中含氮物质是卤化物盐，含氮活性炭等同于促进的物质进行作用且促进步骤可略去或减少。在一些实例中，含氮物质可为以下物质中的至少一种：氨、溴化铵、氯化铵、硝酸、亚硝酸、二氧化氮、包含 NO_3 的化合物、包含 NO_2 的化合物等。

[0066] 在一个实例中，包含含氮活性炭吸附剂颗粒的活性炭可通过任意种类的活性炭或炭的表面改性来制备，所述表面改性通过向现存的碳或较低温度的炭施加含氮聚合物涂层或浸渍，并重新碳化经浸渍的碳。所述涂层或浸渍可包括含有氮杂环的聚合物或共聚物，例如聚合的乙烯基吡咯烷酮。在该类型碳的一个实例中，使用聚乙烯基吡咯烷酮、乙烯基吡咯烷酮－马来酸共聚物或乙烯基吡咯烷酮－醋酸乙烯酯共聚物涂布碳表面。在加热或重新碳化之后，经浸渍的混合物可在颗粒上形成含氮活性炭表层。在含氮活性炭的表层中的氮浓度可高于在使用氮进行表面改性或浸渍之前的物质的氮浓度。

[0067] 在一个实例中，含氮活性炭可通过氧化炭的表面改性来制备，所述表面改性通过使用合适的含氮化合物例如氨或尿素处理炭，接着是浸渍氮的物质的活化。

[0068] 在一个实例中，含氮活性炭可通过将含氮化合物浸渍进入炭，接着通过常规方法对经浸渍的炭进行碳化和活化来制备。该类型碳的一个实例为胺或氨基酸与碳水化合物的组合，该组合在加热时经历美拉德（Maillard）缩合反应以形成含氮杂环的碳表面。

[0069] 在一个实例中，含氮活性炭可通过将含氮化合物浸渍进入煤、褐煤、或风化褐煤，紧接着进行碳化和活化来制备。

[0070] 促进的含氮活性炭吸附剂。

[0071] 在一些实施方式中，包含含氮活性炭吸附剂颗粒的活性炭包含促进的含氮活性炭吸附剂。用在降低包含污染物的气体中污染物含量的方法中的含氮活性炭吸附剂可为促进的活性炭吸附剂，并可包含氮。所述方法可包括促进未促进的活性炭吸附剂，或促进的吸附剂可从市场上获得。

[0072] 例如，降低包含污染物的气体中污染物含量的方法可包括获得或提供未促进的碳吸附剂。所述未促进的碳吸附剂可为任何合适的未促进的含氮吸附剂，并可被合成获得或从市场上获得。所述方法可包括获得或提供促进剂。所述方法可包括通过将未促进的吸附剂的一部分与促进剂接触（如化学反应）来促进至少一部分未促进的吸附剂，以形成活性炭吸附剂。

[0073] 所述促进剂可为任何合适的促进剂，以使得形成促进的吸附剂，其有效用于从包含污染物的气体中除去污染物，例如汞。例如，所述促进剂可包括卤素或卤化物促进剂。所述卤素或卤化物可为氟或氟化物、氯或氯化物、溴或溴化物、或碘或碘化物。在一些实例中，所述促进剂可包括以下物质中的至少一种：卤素、第 V 主族卤化物、第 VI 主族卤化物、卤化氢、卤化铵、碱土金属卤化物（alkali earth metal halide）和碱土金属卤化物（alkaline earth metal halide）。因此，在一些实施方式中活性炭可为以下情况中的至少一种：卤素促进、第 V 主族卤化物促进、第 VI 主族卤化物促进、卤化氢促进、卤化铵促进、碱土金属卤化

PAC ET AL. EXHIBIT 1019
Page 1911

物促进和碱土金属卤化物促进。所述促进剂可包括以下物质中的至少一种：HI、IBr、ICl、NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$和 HCl。在一些实例中，所述促进剂是 NH_4Br，并可在导管中被注射进入温热区域，例如单独注射或与活性炭吸附剂一起注射。在一些实例中，可在燃烧过程期间将任何合适的含卤素或卤化物的物质，例如 NaCl、$CaCl_2$、NaBr 或 $CaBr_2$与煤一起注射，这可使碳活化。在各种实施方式中，含卤素或卤化物的物质可转化成为活化促进剂，例如活性溴化物或氯化物化合物，如 HCl、HBr、xCl 或 xBr。在一些实例中，所述促进剂是包括以下中的至少一种的形式：蒸汽形式、在溶剂中、作为液体、作为固体、和它们的组合。在一些实施方式中，所述促进可发生于含水洗涤器中，其中所述洗涤器包含含促进剂的水性浆料。

[0074] 所述吸附剂材料的促进可发生于添加或注射进入气流之前、添加或注射进入气流期间、添加或注射进入气流之后、或它们的组合，其中所述气流可为含汞气流、输送流、或它们的组合。在一些实例中，所述促进剂可在促进剂和吸附剂反应之前添加至吸附剂，以使得促进剂添加进入其中的气流的加热引起吸附剂的促进。例如，所述促进剂可作为气体、作为溶解于液体中的气体、或作为固体例如盐、或溶解于液体（如水）中的其它物质（如酸），例如氢溴酸被添加。在其中促进剂以液体例如水被添加的实例中，可允许干燥水，这可允许促进剂附着于活性炭吸附剂、浸渍活性炭吸附剂、或与活性炭吸附剂反应，或它们的组合。在一些实例中，预添加的促进剂可为铵盐，例如氯化铵、溴化铵、或碘化铵，包括，例如一烷基卤化铵、二烷基卤化铵、三烷基卤化铵、或四烷基卤化铵、或卤化铵盐。在一些实例中，可在接近促进时间或在促进时间向吸附剂添加促进剂；例如，所述促进剂可与吸附剂一起添加至气流或以使得其在经加热的气流内接触吸附剂，所述经加热的气流例如含汞气流或进料气流。在一些实例中，所述促进剂可为 NH_4Br。

[0075] 在一些实施方式中，促进剂前体转化成为卤素或卤化物促进剂，其与活性炭吸附剂反应以得到活性炭材料。所述促进剂前体可为可转化成为卤素或卤化物促进剂的任何合适的前体。在一些实施方式中，所述促进剂前体可为在未促进的吸附剂上的和与未促进的吸附剂一起添加或注射中的至少一种。在一些实施方式中，所述促进剂可为 HBr，且在一些实例中，HBr 可借由促进剂前体例如溴化铵、溴化钠、或溴化钙的分解或反应提供。所述促进剂可为 HCl，且在一些实例中，HCl 可借由促进剂前体例如氯化铵、氯化钠、或氯化钙的分解或反应提供。所述促进剂可为 HF，且在一些实例中，HF 可借由促进剂前体例如氟化铵、氟化钠、或氟化钙的分解或反应提供。在一些实例中，促进剂（如 HBr 或 HCl）或促进剂前体（如 NH_4Br、NaBr、$CaBr_2$、NH_4Cl、NaCl、$CaCl_2$）可与活性炭吸附剂分开或与活性炭吸附剂一起在烟道气中添加或注射（如，可应用于吸附剂预注射、在同样的位置同时添加或注射、或在不同位置同时添加或注射）。在一些实例中，NaCl、$CaCl_2$、NaBr 或 $CaBr_2$可与未燃烧的物质例如未燃烧的煤一起添加。

[0076] 无机基体载体或纳米复合材料。

[0077] 在一些实施方式中，包含含氮活性炭颗粒的活性炭包含无机基体载体或是纳米复合材料。在降低包含污染物的气体中污染物含量的方法中使用的含氮活性炭可包含无机基体载体或可为纳米复合材料。所述方法可包括向活性炭添加无机基体载体或使用未负载的含氮活性炭制备纳米复合材料，或所述方法可包括从市场上获得基体负载的活性炭或纳米复合材料活性炭。在各种实施方式中，所述无机基质载体包括硅藻土、粘土、沸石或矿物中

PAC ET AL. EXHIBIT 1019
Page 1912

的至少一种。

[0078] 例如，降低包含污染物的气体中的污染物含量的方法可包括获得或提供基质材料。所述基质材料可为任何合适的基质。例如，所述基质可为硅藻土、粘土、沸石或矿物中的至少一种。所述方法可包括使碳前体和基质材料接触，以提供吸附剂原材料。所述接触可以任何合适的方式发生。所述接触使碳前体和基质材料混合，以使得当混合体经加热（或经受任何其它合适的能量来源）时，形成碳纳米复合材料吸附剂或负载的吸附剂。所述接触可进行以使得碳前体接近均匀分布在基质上。在一些实例中，可添加水或另一溶剂以帮助碳前体在基质上分布。在碳前体和基质的混合物中包含水的实例中，混合体可在加热之前被干燥。所述干燥可以任何常规的方式（如对流方式、传导方式、微波方式等）发生，包括在环境压力下、在压力下、或在真空下通过在接近或高于溶剂沸点下进行加热，在水的情况中（如 50° C-120° C 或更高）。

[0079] 所述基质可包括任何合适的多孔材料。例如，所述基质材料可为硅藻土、沸石、多孔矿物（如粘土）包括，例如，蒙脱石（如蒙脱土、膨润土、绿脱石、皂石）、高岭土、伊利石、绿泥石、海泡石、或凹凸棒石。在一些实例中，所述基体可包括聚合物、非金属、金属、准金属、陶瓷或混合物、和共混物、以及复合材料及其合金。所述材料可为合成的或天然存在的或天然获得的材料。合成聚合物的实例包括任何普通的热塑性和热固性材料。金属的实例包括铝、钛、铜、钢和不锈钢。陶瓷的实例包括氧化铝、氧化锆、二氧化钛和二氧化硅的任何形式。天然存在或天然获得的材料的实例包括木材、木材复合材料、纸、纤维素醋酸酯、和地质形成物(geologic formations)例如花岗岩或石灰石。非金属的实例包括各种形式的碳，例如石墨或碳。准金属的实例包括硅或锗。所述多孔材料可为建筑材料，例如混凝土或沥青。

[0080] 在一些实例中，对于碳纳米复合材料吸附剂，所述基质材料可以原材料的约 1 wt%至约 99 wt%、约 20 wt%至约 80 wt%、或约 40 wt%至约 60 wt%存在。本段中的 Wt%是指基于碳前体和基质材料的总重量的重量百分数。

[0081] 所述方法可包括处理（如加热、振动、超声处理、微波、或以其它方式将能量添加至）吸附剂原材料，以提供活性炭吸附剂。碳前体和基质的接触组合物可随后经处理（如加热、振动、超声、微波、或其它合适的能量添加）以形成碳纳米复合材料吸附剂或无机基体负载的吸附剂。所述处理可在任何合适的温度下发生，以使得吸附剂充分形成，例如加热至约 50° C、100° C、200° C、300° C、400° C、500° C、600° C、700° C、800° C、900° C、1000° C、1100° C 或约 1200° C 或更高。所述处理可发生持续任何合适的时间，以使得碳纳米复合材料充分形成，例如，持续大于约 1 min、2 min、5 min、10 min、30 min、1 h、1.5 h、2 h、3 h、4 h、5 h、10 h 或大于约 24 h。所述加热可在任何合适的装置中发生，例如，在充分排除氧的单元中，如，其允许经加热的惰性气体空气在正在经加热的混合物周围流动。在一个实例中，所述加热发生于在其中具有惰性气体环境的炉子中。取决于装置和纳米复合材料或负载的材料，可加速或延长所述处理。

[0082] 在一些实施方式中，加热吸附剂原材料可提供第二吸附剂原材料。所述方法可进一步包括使第二吸附剂原材料与酸性物质或碱性物质反应，以提供活性炭吸附剂。所述酸性物质或碱性物质可为任何合适的酸性物质或碱性物质，例如 HBr、HCl、H_2SO_4、KOH、NaOH 等。在一些实施方式中，使用酸性物质或碱性物质处理可制备用于使用促进剂处理的活性

PAC ET AL. EXHIBIT 1019
Page 1913

炭或可制备以使得获得与汞或另一污染物的充分反应性或吸收的材料。

[0083] 制备含氮活性炭吸附剂的方法。

[0084] 在各种实施方式中，本发明提供了制备包含含氮活性炭吸附剂颗粒的活性炭吸附剂的方法。本发明的实施方式可包括由所述方法制备的任何含氮活性炭吸附剂。所述方法包括获得或提供未促进的含氮吸附剂。所述未促进的含氮吸附剂可为任何合适的含氮活性炭吸附剂，例如在此描述的任何含氮活性炭吸附剂。所述未促进的含氮吸附剂可从市场上获得或可合成。所述方法可包括促进至少一部分未促进的吸附剂。所述促进可包括使该部分未促进的吸附剂与促进剂接触（如化学反应），以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂。

[0085] 在一些实例中，所述未促进的含氮吸附剂可包括无机基体载体或可为纳米复合材料。例如，制备含氮活性炭吸附剂的方法可包括获得或提供含氮碳前体。所述方法可包括获得或提供基质材料。所述方法可包括使碳前体和基质材料接触，以提供吸附剂原材料。所述方法还可包括加热吸附剂原材料，以提供未促进的含氮碳吸附剂。所述未促进的含氮吸附剂可包含含氮活性炭吸附剂颗粒。

[0086] 在一些实施方式中，制备含氮活性炭吸附剂的方法可包括从含碳物质和含氮物质合成含氮碳前体。例如，所述方法可包括获得或提供含碳的含碳物质和含氮的含氮物质。所述方法可包括适当地接触和处理含碳物质和含氮物质以提供含氮碳前体，其中处理可包括以下中的至少一种：加热、微波、超声处理、振动等。

实施例

[0087] 可参考通过举例方式提供的以下实施例更好地理解本发明。本发明不限于在此给出的实施例。

[0088] 实施例 1. 氮前体浸渍进入炭，紧接着对经浸渍的炭进行碳化和活化。

[0089] 实施例 1a. 碳前体。

[0090] 将通过褐煤焦 (lignite char) 的蒸汽活化制备的碳 (20 X 60 目) 与右旋糖和乙醇胺的水溶液以 1 份碳比 0.016 份乙醇胺和 0.034 份右旋糖的比例一起搅拌。通过旋转蒸发 (rotovaporation) 除去水溶剂，并使经浸渍的碳经空气干燥。经干燥的材料在 750° C、在氮流下再活化 2 小时。

[0091] 实施例 1b. 炭前体。

[0092] 将通过在 400° C 下加热褐煤制备的炭 (20 X 60 目) 与右旋糖和乙醇胺的水溶液以 1 份碳比 0.016 份乙醇胺和 0.034 份右旋糖的一起搅拌。通过旋转蒸发除去水溶剂，并使经浸渍的碳进行空气干燥。经干燥的材料在 750° C、在氮流下活化 2 小时。

[0093] 实施例 1c. 木炭前体。

[0094] 将通过木炭的蒸汽活化制备的碳 (20 X 60 目) 与右旋糖和乙醇胺的水溶液以 1 份碳比 0.016 份乙醇胺和 0.034 份右旋糖的比例一起搅拌。通过旋转蒸发除去水溶剂，并使经浸渍的碳经空气干燥。经干燥的材料在 750° C、在氮流下再活化 2 小时。

[0095] 实施例 1d. 木炭 - 丙氨酸。

[0096] 将通过木炭的蒸汽活化制备的碳 (20 X 60 目) 与右旋糖和丙氨酸的水溶液以 1 份碳比 0.016 份乙醇胺和 0.034 份丙氨酸的比例一起搅拌。通过旋转蒸发除去水溶剂，并

PAC ET AL. EXHIBIT 1019
Page 1914

使经浸渍的碳经空气干燥。经干燥的材料在 750° C、在氮流下再活化 2 小时。

[0097] 实施例 2. 管式反应器试验。

[0098] 将如在实施例 1a-d 中所述获得的分子筛碳使用 5 wt% 的硫酸浸渍。随后将经浸渍的碳在 110° C 的炉中干燥。将碳 (0.100 g) 装填入 3 mm 直径的派热克斯玻璃管 (pyrex tube) 中并通过在两端的玻璃纤维塞将其保持在原位。在派热克斯玻璃管中出口端处的收缩防止塞子喷出。反应器管在作为恒温设备的处于 150° C ± 0.50 的 GC 炉中加热。汞蒸汽包含在 100 cm^3/min 的空气流中，以 429-447 mg/m^3 的浓度经过反应器管，所述浓度使用连续汞蒸汽监控器进行测定。

[0099] 汞源为温度校准的渗透管。将渗透管在具有循环热硅油系统的双夹套玻璃冷凝器中加热。来自反应器管的流出空气流中的浓度使用连续冷蒸汽紫外汞蒸汽监控器 (EPM) 进行监测。在各碳试验之前进行空白试验以测定汞浓度。使用空气流通过大的碘化碳过滤器进行仪器调零。该装置因此给出未由碳床除去的汞的百分数 (出口中的汞浓度除以进口中的汞浓度，乘以 100)。对于含氮分子筛碳 (实施例 1-4)，经数小时的时期，仅 1% 的汞蒸汽未由碳床除去。

[0100] 实施例 3. 过滤床试验。

[0101] 将如实施例 1e 进行预处理的吸附剂碳磨成约 200 目，并引入管中，其中其可由降低的压力被吸引到保持在不锈钢固定器中的特氟龙或石英过滤器上。随后在空气流下将经碳浸渍的过滤器和固定器置于炉中并如实施例 2 中所述对其进行试验。

[0102] 实施例 4. 含氮聚合物浸渍进入活性炭或炭，紧接着对经浸渍的材料进行碳化和活化。

[0103] 实施例 4a. 乙烯基吡咯烷酮 - 丙烯酸共聚物。

[0104] 将通过褐煤的蒸汽活化制备的碳与乙烯基吡咯烷酮 - 丙烯酸共聚物的水溶液一起搅拌持续 30 min。聚合物的量经选择以提供 1 重量 % 至 30 重量 % 的载量。在 50° C 下通过旋转蒸发蒸去溶剂，并在 110° C 的炉中进一步干燥。经浸渍的碳通过在 750° C、在氮流中加热 2 小时来再活化。接近 40% 的聚合物重量转化为表面涂层，60% 挥发。

[0105] 实施例 4b. 乙烯基吡咯烷酮 - 醋酸乙烯酯共聚物。

[0106] 使用溶解于二氯甲烷中的乙烯基吡咯烷酮 - 醋酸乙烯酯共聚物浸渍活性炭。蒸发掉溶剂并将经浸渍的碳在 110° C 的炉中干燥。随后经浸渍的碳通过在 750° C、在氮流中加热 2 小时来活化。

[0107] 实施例 4c. 聚乙烯基吡咯烷酮。

[0108] 活性炭使用聚乙烯基吡咯烷酮和在实施例 4a-b 中所描述的共聚物中的一种进行浸渍并如在实施例 4a 中所描述的进行活化。

[0109] 实施例 4d. 聚乙烯基吡咯烷酮。

[0110] KOH- 活化的褐煤使用聚乙烯基吡咯烷酮和在实施例 4a-4b 中所描述的共聚物中的一种进行浸渍并如在实施例 4a 中所描述的进行活化。

[0111] 实施例 4e. 木材衍生的木炭。

[0112] 木材衍生的木炭使用聚乙烯基吡咯烷酮和在实施例 4a-4b 中所描述的共聚物中的一种进行浸渍并如在实施例 4a 中所描述的进行活化。

[0113] 实施例 4f. 褐煤的碳化 (假设实施例)。

PAC ET AL. EXHIBIT 1019
Page 1915

[0114] 炭由褐煤的碳化产生，其使用聚乙烯基吡咯烷酮和在实施例 4a-4b 中所描述的共聚物中的一种进行浸渍，并如在实施例 4a 中所描述的进行活化。作为替代，可使用蒸汽活化。

[0115] 实施例 4g. 蒸汽活化。

[0116] 使用经含氮聚合物浸渍的碳材料的蒸汽活化执行实施例 4a-4e，以产生有效的吸附剂。

[0117] 实施例 5. 氮前体浸渍进入煤、褐煤或风化褐煤，紧接着对经浸渍的材料进行碳化和活化。

[0118] 实施例 5a. 1,4- 二氮杂二环 [2.2.2] 辛烷 (DABCO)。

[0119] 褐煤（如接受时一样）与 DABCO 的水溶液以 1 份煤比 0.02 份 DABCO 的比例一起搅拌。通过过滤除去水溶剂，并使经浸渍的煤经空气干燥。经干燥的材料在 400° C 下碳化，并在 750° C、在氮流下活化 2 小时。

[0120] 实施例 5b. 氨基磺酸。

[0121] 褐煤（如接受时一样）与氨基磺酸的水溶液以 1 份煤比 0.02 份氨基磺酸的比例一起搅拌。通过过滤除去水溶剂，并使经浸渍的煤经空气干燥。经干燥的材料经碳化，并在 750° C、在氮流下活化 2 小时。

[0122] 实施例 5c. 经碳化的褐煤。

[0123] 褐煤在 400°C 下碳化 30 分钟，且得到的炭通过如在实施例 5b 中所描述，与氨基磺酸溶液一起搅拌来处理。随后将经处理的炭如在实施例 5b 中所描述进行活化。

[0124] 实施例 5d. 蒸汽活化。

[0125] 经 DABCO 浸渍的炭或经氨基磺酸浸渍的炭的蒸汽活化在产生汞吸附剂碳中也是有效的。

[0126] 实施例 6. 含氮沥青的制备。

[0127] 含氮沥青使用由 Mochida 等人 (Mochida, I.; An, K.H.; Korai, Y. Carbon 1995, 33, 1069) 报道的步骤制备。制备总结在表 1 中。作为实施例，将异喹啉 (26 g, 0.2 摩尔）、无水三氯化铝 (13.3 g, 0.25 摩尔）和硝基苯 (7.68 g, 0.06 摩尔）的混合物置于配备回流冷凝器和氮进口管的二颈烧瓶中。将混合物在 280° C 下回流 4 小时。使用 0.1 N 盐酸萃取残留物并过滤。使用 0.1 N 盐酸洗残留物。进一步使用甲醇萃取残留物以除去任何单体。将不溶于甲醇的沥青在真空下干燥。沥青的产率为 49%。如在实施例 7 中所描述，使用步骤 A 或 B 在氮流中碳化部分含氮沥青。

[0128] 表 1. 含氮沥青的制备。* 表示反应在 300-mL 帕尔 (Parr) 反应器中进行。** 表示乙二胺。

PAC ET AL. EXHIBIT 1019
Page 1916

基质 (g, 摩尔)	催化剂 (g, 摩尔)	助催化剂 (g, 摩尔)	温度 (°C)	时间 (hr)	产率 (g,%)	可溶的 (%)
吲哚 (10, 0.77)	无	无	253*	4	9.6 (96%)	甲醇 (100)
喹喔啉 (26, 0.2)	$AlCl_3$ (13.3, 0.1)	硝基苯 (7.68, 0.06)	225*	4	13.5 (52%)	EDA**
吖啶 (16.7, 0.1)	$AlCl_3$ (27.7, 0.2)	硝基苯 (3.6, 0.03)	25	12	59.1 (92%)	EDA**
异喹啉 (26, 0.2)	$AlCl_3$ (13.3, 0.1)	硝基苯 (7.68, 0.06)	280	4	6.5 (25%)	EDA**

[0129] 对于喹啉聚合，利用所述方法的数种修改。除烧瓶法以外，反应使用了帕尔反应器，并改变了温度和反应时间。产率报道在表 2 中。在该步骤中，64.5 g 喹啉和 33.25 g 三氯化铝置于 300-mL 帕尔高压釜中。将反应器在氮气下密封并于 280° C 持续加热 4 小时。使用 0.1 N 盐酸萃取硬质黑色块，紧接着使用甲醇萃取并在真空中干燥。为测定聚合物的溶解度，将该黑色块的 10-g 部分使用 100 mL 乙醇萃取。萃取数据显示 27 wt% 的产物溶解于乙醇。

[0130] 表 2. 含氮沥青的制备。* 表示反应在 300-mL 帕尔反应器中进行。** 表示 10 g 沥青使用乙醇萃取。

喹啉 (g)	$AlCl_3$ (g)	温度 (°C)	时间 (hr)	产率 (g,%)	乙醇-S (g)	乙醇-I (g)
64.5	33.25	280	12	57.7 (89%)	-	-
64.5*	33.25	175	12	0 (0%)	-	-
64.5*	33.25	280	12	59.1 (92%)	-	-
64.5*	33.25	280	4	56.8 (88%)	7.3** (73%)	2.7 (27%)

[0131] 实施例 7. 经氮浸渍的碳的制备。

[0132] 进行浸渍和再碳化以研究前体浓度、活化过程和吸附剂颗粒尺寸对于汞吸附的影响。前体基碳，颗粒状活性炭 (Calgon F400 或 Gascoyne AC, 20 x 60) 使用下述的初湿法用各种含氮聚合物和沥青进行浸渍。对于在烟道气组合物中的细颗粒吸附剂试验，将 Calgon 碳在浸渍之前磨成约 400 目的尺寸。氮聚合物例如乙烯基吡咯烷酮聚合物和共聚物是市场上可获得的。类似地制备尿素、丙氨酸－右旋糖、哌嗪－右旋糖和聚氮丙啶－右旋糖组合物。

[0133] 在用于初湿法的典型步骤中，将溶解于适当溶剂中的所需量的聚合物或沥青缓慢添加至碳，伴随彻底混合。干燥糊状物以除去溶剂。将干燥产物装填入不锈钢管中并使用步骤 A 或步骤 B 在温和的氮流中活化。

[0134] 步骤 A 包括：以 10° C/min 从 25° C 加热至 400° C；在 400° C 下保持 30 min；以 20° C/min 从 400° 加热至 750° C；并在 750° C 下保持 4 hr。

[0135] 步骤 B 包括：以 15° C/min 从 25° C 加热至 225° C；以 1 ° C/min 从 225° C 加热至 270° C；在 270° C 下保持 1 hr；冷却至室温；以 15° C/min 加热升至 750° C；并在 750° C 下保持 4 hr。

[0136] 实施例 8. 从不溶性部分制备含氮的碳。

PAC ET AL. EXHIBIT 1019
Page 1917

[0137] 通过使用如上所述的步骤B在温和的氮流中加热使在表1中描述的沥青的不溶性部分转化成为含氮的碳。得到的碳是类似于焦炭的多孔玻璃状材料。

[0138] 实施例9. 使用实施例6-7的含氮物质制备的用于汞捕获的吸附剂的初步筛分。

[0139] 实施例9a. 硫酸聚集的模拟。

[0140] 借助初湿法，通过添加5 wt% 硫酸来模拟在热烟道气流中含氮的碳表面上的SO_3捕获和随后的硫酸形成。将经酸浸渍的碳在110 ° C下干燥。

[0141] 实施例9b. 填充床试验。

[0142] 空气流中的填充床试验在颗粒状碳产物上进行以评估表面改性的影响。汞吸附在直通式管状反应器系统中试验，配备来自床的流出物的连续在线汞分析，以测定汞除去速率随时间的变化。漏出容量的积分允许测定每单位质量碳的汞吸附 (mg/g)。使具有56或81μg/m^{3}的元素汞浓度的空气穿过经加热的 (150° C) 反应器。为获得该浓度，将汞源置于双夹套玻璃冷凝器中并通过抽取热油经过冷凝器将其加热至所需温度。

[0143] 使用具有收缩和玻璃棉塞的玻璃管作为用于汞吸附试验的反应器。使用气相色谱 (GC) 炉作为用于反应器的恒温 (150° C) 室。在实际试验之前，进行空白试验。将玻璃管连在所述源上，汞分析器由特氟龙管连接。将用空气稀释的汞蒸汽（在检测器末端测量为2000-4000 cm^3/min或4-8 scfh）穿过管。将汞分析器（环境和过程监控 [EPM] 连续蒸汽监控器）连接至Hydra和个人电脑 (PC) 以记录数据。对于填充床试验，使用经浸渍的活性炭 (20 x 60目尺寸)。在实际试验中，将约0.2-0.6 g的吸附剂装填入玻璃管并由在两端的玻璃棉塞固定。使用150° C的源温度、150° C的炉温度和等于4或8 scfh (4000 cm^3/min) 的空气流进行试验。使用通过将各种氯化合物、聚合物和沥青浸渍进入Calgon基碳来制备的碳在4000 cm^3/min (8 scfh) 下进行众多试验（表3和4）。这些条件产生对于吸附剂的部分穿透并允许它们的动力学活性的比较。

[0144] 表3. 经表面处理的碳在8 scfh用于汞除去的吸附剂试验。空气流 = 4000 cm^3/min (8 scfh)、结束温度 = 150 ° C、汞浓度 = 81 μg/m^3。*表示在实施例4a中制备的活性炭。

PAC ET AL. EXHIBIT 1019
Page 1918

碳源	重新碳化方法	H_2SO_4 浸渍	除去的%Hg(时间, min)		
			初始	50%	试验结束
空白		-	0 (0)	<1	-
Calgon		5%	87 (0)	50 (171)	38 (304)
Calgon/尿素	A	5%	95 (0)	50 (305)	49 (306)
EERC*/尿素	A	5%	100 (0)	50 (575)	38 (1221)
Calgon/2% 氨基磺酸	A	5%	92 (0)	50 (226)	39 (1303)
Calgon/5% PVP	A	5%	94 (0)	50 (2217)	42 (2574)
Calgon/10% PVP	A	5%	88 (0)	50 (150)	55 (253)
Calgon/10% PVP	A	5%	90 (0)	50 (300)	65 (1098)
Calgon/5% PVP	A	5%	98 (0)	50 (3315)	43 (4010)
Calgon/2% PVP	A	5%	79 (0)	50 (312)	49 (320)
Calgon/10% PVP	A	5%	85 (0)	50 (424)	30 (1114)
Calgon/5%乙烯基吡咯烷酮-醋酸乙烯酯共聚物	A	5%	90 (0)	50 (84)	39 (180)
Calgon/5%乙烯基吡咯烷酮-丙烯酸共聚物	A	5%	90 (0)	50 (76)	29 (362)
Calgon/5%乙烯基吡咯烷酮-丙烯酸共聚物	A	5%	98 (0)	50 (223)	50 (223)
Calgon/聚氮丙啶	A	5%	88 (0)	50 (373)	22 (1147)
Calgon/右旋糖-聚氮丙啶	A	5%	88 (0)	50 (51)	35 (350)
Calgon/右旋糖+丙氨酸	A	5%	88 (0)	50 (76)	53 (216)
Calgon/右旋糖+哌嗪	A	5%	65 (0)	50 (35)	25 (942)

[0145] 表 4. 经含氮沥青浸渍的碳用于汞捕获的吸附剂试验。对于所有样品均使用重新碳化步骤 B。吸附剂 = 0.20 g、颗粒尺寸 = 20 X 50 目、空气流 = 8 scfh (4000 mL/min)、源温度 = 150 °C、炉温度 = 150 °C。*表示由在帕尔反应器中加热喹诺酮和三氯化铝获得的沥青溶解于乙醇并浸渍在 Calgon 碳上。** 表示由喹诺酮与三氯化铝的回流获得的沥青溶解于 EDA 并浸渍在 Calgon 碳上。

PAC ET AL. EXHIBIT 1019
Page 1919

文件名	吸附剂(g)	H_2SO_4 (wt%)	汞浓度 ($\mu g/m^3$)	除去的%Hg的时间, min)		
				初始	50%	终了
RKS32	无	-	31	-	50 <1	-
RKS35	Calgon/5 wt% 喹诺酮 *	5%	-	89 (0)	50 (306)	49 (302)
RKS23	Calgon/5 wt% 喹诺酮 *	5%	-	91 (0)	50 (204)	46 (292)
RKS37	Calgon/5 wt% 喹噻啉	5%	-	90 (0)	50 (632)	25 (1300)
RKS31	Calgon/5 wt% 异喹啉	5%	-	98 (0)	54 (584)	34 (1214)
RKS75	Calgon/5 wt% 吲哚	5%	-	98 (0)	50 (1403)	49 (1473)

[0146] 实施例 9c. 试验结果。

[0147] 通过将尿素或氨基磺酸浸渍进入 Calgon 基碳并进行重新碳化制备的碳分别产生 95% 或 92% 的初始捕获率。这些结果显著优于使用未改性的 Calgon 碳所观察到的那些。在较低温度 (75° C) 下试验尿素碳产生 100% 的初始捕获。通过含氮聚合物的浸渍制备的碳在这些试验中是高度活性的。通过 5 wt% PVP 的浸渍来制备并使用步骤 A(快加热速率) 进行活化的吸附剂证明优异的活性。初始除去为 94%,降低至 50% 除去需要 2217 min。因此该吸附剂比尿素碳远更长时间地保留其高活性。使用 10% PVP 制备的吸附剂 (还是步骤 A) 活性较低 (初始 88% 除去,在 150min 降低至 50%)。

[0148] 使用步骤 B(较慢的加热速率) 在 10% PVP 浓度水平产生活性更高的吸附剂。使用步骤 B 制备具有不同浓度的另一系列的碳。再一次,使用 5% 浓度 PVP 的浸渍产生高活性 (初始 98% 除去,在 3315 mm 降低至 50%)。再一次地,10% PVP 活性较低,且 2% PVP 浓度活性最低。

[0149] 还制备并评估了从 PVP 的共聚物制备的碳。具有醋酸乙烯酯的共聚物 (PVP-VA 共聚物) 以 5% 浓度浸渍 (步骤 A) 产生具有相对低活性的吸附剂。5% 的乙烯基吡咯烷酮 - 丙烯酸共聚物 (PVP-AA 共聚物) 也产生低活性的吸附剂。使用步骤 B 用于活化略微改善了活性。

[0150] 使用聚氮丙啶制备另一类型的经 N- 聚合物浸渍的碳。不同于 PVP,其中氮连接于碳链骨架上,该聚合物前体在聚合物骨架中含有氮。活性与 10% PVP 聚合物的类似。

[0151] 通过浸渍右旋糖和胺的混合物制备数种碳。这些碳在这些试验中都不展现高活性。之前的试验显示经右旋糖 + 丙氨酸浸渍的碳 (步骤 B) 是相当活性的。因为在本研究中使用了步骤 A,活性的降低可能与使用的快加热速率有关。在从这些前体制备吸附剂时,缓慢进行反应可能是相当有益的。

[0152] 通过由各种杂环的聚合制备的含氮沥青的浸渍制备的吸附剂都是相当活性的 (表 4),但是观察到活性的显著差异。从喹喔啉沥青的浸渍制备的 N- 碳的活性是喹啉衍生的 N- 碳的活性的 2-3 倍。异喹啉衍生的碳的活性也非常高。吲哚衍生的碳的高活性也引起了人们很大的兴趣。这是一个重要的引导,因为吲哚比喹喔啉前体更容易获得。

[0153] 还在由含氮沥青的不溶性部分制备的碳化沥青上进行了试验。所述碳化沥青的活性非常差。初始漏出是相当大的,伴随 21% 至 54% 的除去百分数,其可能与碳化沥青的玻璃

PAC ET AL. EXHIBIT 1019
Page 1920

质有关。尽管表面积未经测定，但是它们可能非常低，因为所述材料不像活性炭，反而却像焦炭。

[0154] 已使用的术语和表述用作描述而非限制的术语，且在此类术语和表述的使用中不意欲排除所示和所述的特征或其部分的任何等价物，但是人们意识到在要求保护的本发明范围之内的各种修改是可能的。因此，应当理解尽管本发明已通过优选的实施方式和任选的特征具体公开，但是本领域技术人员可采用在此公开的概念的修改和改变，且此类修改和改变被认为是在由所附权利要求所定义的本发明的范围之内。

[0155] 另外的实施方式。

[0156] 本发明提供了以下示例性的实施方式，其编号不解释为指定重要性级别：

实施方式 1 提供了降低包含污染物的气体中污染物含量的方法，所述方法包括：获得或提供包含活性炭吸附剂颗粒的活性炭吸附剂，在所述吸附剂颗粒的表层包含氮；使包含污染物的气体与活性炭吸附剂接触，以形成污染物 - 吸附剂组合物；并从包含污染物的气体中分离出至少一些污染物 - 吸附剂组合物，以产生分离的气体。

[0157] 实施方式 2 提供了实施方式 1 的方法，其中污染物包含汞，且包含污染物的气体是含汞气体。

[0158] 实施方式 3 提供了实施方式 1-2 中任一种的方法，其中在吸附剂颗粒的表层中的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

[0159] 实施方式 4 提供了实施方式 2-3 中任一种的方法，其中活性炭吸附剂结合至少约 70 wt% 的存在于含汞气体中的汞。

[0160] 实施方式 5 提供了实施方式 2-4 中任一种的方法，其中含汞气体进一步包括硫 (VI) 的浓度，且含汞气体中硫 (VI) 的摩尔浓度为大于约 3 ppm，且相对于相应活性炭吸附剂，所述活性炭吸附剂以更高的吸收速率形成汞 - 吸附剂组合物，所述相应活性炭吸附剂包含以下至少一种 a) 在相应颗粒表层中更少的氮或基本无氮，b) 更少或基本无卤化物或卤素促进，其中包含活性炭吸附剂颗粒的活性炭吸附剂是卤化物或卤素促进的，和 c) 更少或基本无无机基体载体，其中包含活性炭吸附剂颗粒的活性炭吸附剂是无机基体负载的。

[0161] 实施方式 6 提供了实施方式 1-5 中任一种的方法，其中包含污染物的气体进一步包括一定浓度的硫 (VI)，且包含污染物的气体中硫 (VI) 的浓度为约 3 ppm - 2000 ppm。

[0162] 实施方式 7 提供了实施方式 1-6 中任一种的方法，其中氮基本上均匀分布在活性炭吸附剂颗粒的核中。

[0163] 实施方式 8 提供了实施方式 1-7 中任一种的方法，其中与在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在表层中的氮减少活性炭中的碳正离子通过 SO_3^{2-} 和 HSO_3^{-} 中的任一种的中和。

[0164] 实施方式 9 提供了实施方式 1-8 中任一种的方法，其中与在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在表层中的氮至少部分阻止活性炭中的碳正离子受到 SO_3^{2-} 和 HSO_3^{-} 中的至少一种的影响。

[0165] 实施方式 10 提供了实施方式 1-9 中任一种的方法，进一步包括：获得或提供未促进的碳吸附剂；获得或提供促进剂；并通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成活性炭吸附剂。

[0166] 实施方式 11 提供了实施方式 10 的方法，其中促进剂包括卤素或卤化物促进剂。

PAC ET AL. EXHIBIT 1019
Page 1921

[0167] 实施方式 12 提供了实施方式 10-11 中任一种的方法，其中促进剂包括以下物质中的至少一种：卤素、第 V 主族卤化物、第 VI 主族卤化物、卤化氢、卤化铵、碱土金属卤化物、和碱土金属卤化物。

[0168] 实施方式 13 提供了实施方式 10-12 中任一种的方法，其中促进剂包括以下物质中的至少一种：HI、IBr、ICl、NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$和 HCl。

[0169] 实施方式 14 提供了实施方式 10-13 中任一种的方法，其中促进剂是包括以下中的至少一种的形式：蒸汽形式、在溶剂中、作为液体、作为固体、和它们的组合。

[0170] 实施方式 15 提供了实施方式 10-14 中任一种的方法，其中促进发生于含水洗涤器中，其中洗涤器包含含促进剂的水性浆料。

[0171] 实施方式 16 提供了实施方式 1-15 中任一种的方法，其中使包含污染物的气体与活性炭吸附剂接触包括向包含污染物的气体中添加活性炭吸附剂。

[0172] 实施方式 17 提供了实施方式 1-16 中任一种的方法，其中活性炭吸附剂为至少以下中的一种：在固定床中、在活动床中、在洗涤器中、在过滤器中或悬浮在包含污染物的气体中。

[0173] 实施方式 18 提供了实施方式 1-17 中任一种的方法，其中活性炭吸附剂颗粒的核包含约 0 wt% - 约 99 wt% 的氮。

[0174] 实施方式 19 提供了实施方式 1-18 中任一种的方法，其中活性炭吸附剂颗粒的核包含约 1 wt% - 约 6 wt% 的氮。

[0175] 实施方式 20 提供了实施方式 1-19 中任一种的方法，其中活性炭吸附剂颗粒的表层包含约 0.001 wt% - 约 99 wt% 的氮。

[0176] 实施方式 21 提供了实施方式 1-20 中任一种的方法，其中活性炭吸附剂颗粒的表层包含约 5 wt% - 约 80 wt% 的氮。

[0177] 实施方式 22 提供了实施方式 1-21 中任一种的方法，其中活性炭吸附剂的表层包含在颗粒表面的层，其具有颗粒半径的约 0.001% 至约 99% 的厚度。

[0178] 实施方式 23 提供了实施方式 1-22 中任一种的方法，其中活性炭吸附剂颗粒的表层包含在颗粒表面的层，其具有颗粒半径的约 0.001% 至约 50% 的厚度。

[0179] 实施方式 24 提供了实施方式 1-23 中任一种的方法，其中活性炭吸附剂颗粒具有约 0.1 μm 至约 1000 μm 的平均直径。

[0180] 实施方式 25 提供了实施方式 1-24 中任一种的方法，其中吸附剂颗粒的表层是连续的表层。

[0181] 实施方式 26 提供了实施方式 1-25 中任一种的方法，其中获得或提供活性炭吸附剂包括：获得或提供含氮碳前体；并使用加热、微波和辐照中的至少一种方法处理碳前体，以提供活性炭吸附剂。

[0182] 实施方式 27 提供了实施方式 26 的方法，其中碳前体包括含碳的含碳物质和含氮的含氮物质。

[0183] 实施方式 28 提供了实施方式 27 的方法，其中含碳物质包括以下物质中的至少一种：黄糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜、葡聚糖、半乳聚糖、木聚糖和糖废品。

[0184] 实施方式 29 提供了实施方式 27-28 中任一种的方法，其中含氮物质包括含氮有机化合物或含氮无机化合物。

PAC ET AL. EXHIBIT 1019
Page 1922

[0185] 实施方式 30 提供了实施方式 27-29 中任一种的方法，其中含氮物质包括氮杂环、含氮聚合物或共聚物、腈、氨基甲酸酯、氨基酸、硝基苯、羟胺、尿素、肼、氨基磺酸、或它们的组合。

[0186] 实施方式 31 提供了实施方式 26-30 中任一种的方法，进一步包括：获得或提供基质材料；使碳前体和基质材料接触，以提供吸附剂原材料；及使用加热、微波和辐照中的至少一种方法处理吸附剂原材料，以提供活性炭吸附剂。

[0187] 实施方式 32 提供了实施方式 31 的方法，其中加热吸附剂原材料提供第二吸附剂原材料，进一步包括使第二吸附剂原材料与酸性物质或碱性物质反应，以提供活性炭吸附剂。

[0188] 实施方式 33 提供了实施方式 31-32 中任一种的方法，其中基质包括硅藻土、粘土、沸石或矿物中的至少一种。

[0189] 实施方式 34 提供了实施方式 31-33 中任一种的方法，其中加热吸附剂原材料包括加热至约 100 ° C - 约 1200 ° C。

[0190] 实施方式 35 提供了实施方式 31-34 中任一种的方法，其中活性炭吸附剂包括碳纳米复合材料吸附剂。

[0191] 实施方式 36 提供了实施方式 1-35 中任一种的方法，其中活性炭吸附剂包含一个或更多个结合位点。

[0192] 实施方式 37 提供了实施方式 36 的方法，其中活性炭吸附剂中的至少一部分结合位点与至少一种污染物和污染物的氧化种类反应，以形成污染物 - 吸附剂组合物。

[0193] 实施方式 38 提供了实施方式 1-37 中任一种的方法，其中从包含污染物的气体中分离至少一些污染物 - 吸附剂组合物包括在微粒分离器中分离。

[0194] 实施方式 39 提供了实施方式 38 的方法，其中微粒分离器包括静电除尘器 (ESP)、袋滤室、湿式洗涤器、过滤器、旋风分离器、织物分离器、或它们的任意组合。

[0195] 实施方式 40 提供了实施方式 10-39 中任一种的方法，其中促进剂前体转化成为卤素或卤化物促进剂，其随后与活性炭吸附剂反应以产生活性炭材料。

[0196] 实施方式 41 提供了实施方式 40 的方法，其中促进剂前体为在未促进的吸附剂上和与未促进的吸附剂一起添加中的至少一种。

[0197] 实施方式 42 提供了实施方式 1-41 中任一种的方法，进一步包括在接触期间或在接触之前的至少一种情况下，将碱性组分添加进入包含污染物的气体中。

[0198] 实施方式 43 提供了实施方式 42 的方法，其中碱性组分包括以下物质中的至少一种：碱元素、碱土元素或碱土元素的氧化物、氢氧化物、碳酸盐或磷酸盐、和包括其的化合物或材料。

[0199] 实施方式 44 提供了实施方式 1-43 中任一种的方法，其中活性炭吸附剂包含稳定剂，所述稳定剂包括 S、Se 中的至少一种、或它们的混合物。

[0200] 实施方式 45 提供了实施方式 1-44 中任一种的方法，其中活性炭吸附剂包含稳定剂，所述稳定剂包括 H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5中的至少一种、或它们的混合物。

[0201] 实施方式 46 提供了实施方式 1-45 中任一种的方法，进一步包括使污染物 - 吸附剂组合物再生以产生再生的活性炭吸附剂。

[0202] 实施方式 47 提供了实施方式 1-46 中任一种的方法，其中活性炭吸附剂是再生的

PAC ET AL. EXHIBIT 1019
Page 1923

活性炭吸附剂。

[0203] 实施方式 48 提供了实施方式 1-47 中任一种的方法，其中接触和分离中的至少一者发生于含水洗涤器中。

[0204] 实施方式 49 提供了实施方式 48 的方法，其中洗涤器包含含活性炭吸附剂的水性浆料。

[0205] 实施方式 50 提供了降低含汞气体的汞含量的方法，所述方法包括：获得或提供含氮碳前体；获得或提供基质材料；使碳前体和基质材料接触，以提供无机基体负载的吸附剂原材料；加热无机基体负载的吸附剂原材料，以提供未促进的吸附剂；通过使未促进的吸附剂的一部分与促进剂发生化学反应来促进至少一部分未促进的吸附剂，以形成包含活性炭吸附剂颗粒的促进的无机基体负载的活性炭吸附剂，在吸附剂颗粒的表层包含氮；使含汞气体与活性炭吸附剂接触，以形成汞 - 吸附剂组合物；并从含汞气体中分离出至少一些汞 - 吸附剂组合物，以产生分离的气体；其中含汞气体具有约 3 - 2000 ppm 摩尔浓度的硫 (VI)，且第一量的活性炭吸附剂以第一汞吸附速率形成汞 - 吸附剂组合物，其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种 a) 在相应颗粒表层中更少的氮或基本无氮，b) 更少或基本无卤化物或卤素促进，和 c) 更少或基本无无机基体载体。

[0206] 实施方式 51 提供了制备活性炭吸附剂的方法，包括：获得或提供未促进的含氮碳吸附剂；通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂，其中在吸附剂颗粒的表层中的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

[0207] 实施方式 52 提供了实施方式 51 的方法，进一步包括：获得或提供含氮碳前体；获得或提供基质材料；使碳前体和基质材料接触，以提供吸附剂原材料；和处理吸附剂原材料，以提供未促进的含氮碳吸附剂。

[0208] 实施方式 53 提供了实施方式 52 的方法，其中获得或提供含氮碳前体包括：获得或提供含碳的含碳物质和含氮的含氮物质；及使含碳物质和含氮物质接触并加热，以提供含氮碳前体。

[0209] 实施方式 54 提供了制备活性炭吸附剂的方法，包括：使含碳物质和含氮物质接触，以提供未促进的含氮碳吸附剂；通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂，其中在吸附剂颗粒中的氮的浓度高于在含碳物质中的氮的浓度。

[0210] 实施方式 55 提供了通过实施方式 51-54 中任一种的方法制备的活性炭吸附剂。

[0211] 实施方式 56 提供了活性炭吸附剂，包含：卤素或卤化物促进的活性炭，所述活性炭包含活性炭吸附剂颗粒，在吸附剂颗粒的表层含有氮。

[0212] 实施方式 57 提供了实施方式 56 的活性炭吸附剂，其中在吸附剂颗粒的表层中的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

[0213] 实施方式 58 提供了实施方式 56-57 中任一种的活性炭吸附剂，其中活性炭吸附剂颗粒具有约 0.1 μm 至约 1000 μm 的平均直径。

[0214] 实施方式 59 提供了实施方式 56-58 中任一种的活性炭吸附剂，其中活性炭为以下情况中的至少一种：卤素促进、第 V 主族卤化物促进、第 VI 主族卤化物促进、卤化氢促进、

PAC ET AL. EXHIBIT 1019
Page 1924

卤化铵促进、碱土金属卤化物促进、和碱土金属卤化物促进。

[0215] 实施方式60提供了实施方式56-59中任一种的活性炭吸附剂，其中活性炭吸附剂是无机基体负载的，所述无机基质载体包括硅藻土、粘土、沸石或矿物中的至少一种。

[0216] 实施方式61提供了实施方式56-60中任一种的活性炭吸附剂，其中氮基本上均匀分布在活性炭吸附剂颗粒的核中。

[0217] 实施方式62提供了实施方式56-61中任一种的活性炭吸附剂，其中与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在颗粒的表层中的氮至少部分减少活性炭吸附剂中的碳正离子通过 HSO_3^- 或 SO_3^{2-} 的中和。

[0218] 实施方式63提供了实施方式56-62中任一种的活性炭吸附剂，其中与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在颗粒表层中的氮至少部分阻止活性炭中的碳正离子与 HSO_3^- 或 SO_3^{2-} 形成离子键。

[0219] 实施方式64提供了实施方式56-63中任一种的活性炭吸附剂，其中第一量的活性炭吸附剂以第一汞吸附速率在含汞气体组合物中形成汞-吸附剂组合物，其中在该气体组合物中硫(VI)的摩尔浓度约为3 - 2000 ppm，且其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含以下至少一种 a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体，其中所述活性炭吸附剂是无机基体负载的。

[0220] 实施方式65提供了实施方式56-64中任一种的活性炭吸附剂，其中氮从含氮有机化合物或含氮无机化合物获得。

[0221] 实施方式66提供了实施方式56-65中任一种的活性炭吸附剂，其中氮从以下物质获得：吲哚、喹喔啉、咔唑、异喹啉、硝基苯、尿素、氨基磺酸、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮-醋酸乙烯酯共聚物、乙烯基吡咯烷酮-丙烯酸共聚物、乙烯基吡咯烷酮-马来酸共聚物、聚氨丙啶、丙氨酸、哌嗪、喹诺酮、喹喔啉、二氮杂二环辛烷、氨基酸、铵盐、或它们的组合。

[0222] 实施方式67提供了用于从含汞气体中除去汞的活性炭吸附剂，所述吸附剂包含：卤素或卤化物促进的含有活性炭颗粒的活性炭，所述颗粒在表层中含有氮，在表层中的氮浓度足够以达到以下目的中的至少之一：a)与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，减少活性炭吸附剂中的碳正离子通过 HSO_3^- 或 SO_3^{2-} 的中和，和b)与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，至少部分阻止活性炭中的碳正离子与 HSO_3^- 或 SO_3^{2-} 形成离子键。

[0223] 实施方式68提供了实施方式1-67的任一种或任意组合的装置或方法，其任选地被配置以使得所述的所有元素或选项都能够供使用或供从中选择。

PAC ET AL. EXHIBIT 1019
Page 1925

Espacenet

Bibliographic data: CN107661744 (A) — 2018-02-06

ACTIVATED CARBON SORBENT INCLUDING NITROGEN AND METHODS OF USING THE SAME

Inventor(s): E.S.奥尔森, ; J.H.帕夫利什

Applicant(s): 能源及环境研究中心基金会

Classification: - international: *B01D53/02; B01J20/20; B01J20/32*
- cooperative: **B01D53/02**; **B01D53/64**; **B01D53/81**; **B01J20/20**; **B01J20/28004**; **B01J20/3204**; **B01J20/3208**; **B01J20/3234**; **B01J20/3236**; **B01J20/324**; **B01J20/3255**; **B01J20/327**; **B01J20/3276**; **B01J20/3293**; **C01B32/336**; **C01B32/354**; B01D2253/102; B01D2253/25; B01D2253/304; B01D2257/602; B01D2258/0283; B01D53/025; B01D53/04; B01D53/10; B01D53/8665

Application number: CN20171951091 20140303 Global Dossier

Priority number(s): US201361773549P 20130306 : CN2014825701 20140303

Also published as: CA2904039 (A1) CN105188910 (A) EP2964376 (A2) US2014255279 (A1) US2017239644 (A1) more

Abstract not available for CN107661744 (A)
Abstract of corresponding document: US2014255279 (A1)

The present invention relates to activated carbon sorbents including nitrogen. In various embodiments, the present invention provides an activated carbon sorbent including a halogen- or halide-promoted activated carbon, the activated carbon sorbent particles including nitrogen in a surface layer of the sorbent particles. In various embodiments, the present invention provides a method of reducing the pollutant content in a pollutant-containing gas using the activated carbon sorbent. In various embodiments, the activated carbon sorbent can remove mercury from a mercury-containing gas that includes sulfur(VI) such as SO3 more efficiently than other sorbents.

PAC ET AL. EXHIBIT 1019
Page 1926

(19)中华人民共和国国家知识产权局

(12)发明专利申请

(10)申请公布号 CN 107661744 A
(43)申请公布日 2018.02.06

(21)申请号 201710951091.0
(22)申请日 2014.03.03
(30)优先权数据
61/773549 2013.03.06 US
(62)分案原申请数据
201480025701.9 2014.03.03
(71)申请人 能源及环境研究中心基金会
地址 美国北达科他州
(72)发明人 E.S.奥尔森 J.H.帕夫利什
(74)专利代理机构 中国专利代理(香港)有限公司 72001
代理人 周蓉 黄念
(51)Int.Cl.
B01J 20/20(2006.01)
B01J 20/32(2006.01)
B01D 53/02(2006.01)

权利要求书4页 说明书25页

(54)发明名称

含氮活性炭吸附剂和使用其的方法

(57)摘要

本发明涉及含氮的活性炭吸附剂。在各种实施方式中，本发明提供了包含卤素或卤化物促进的活性炭的活性炭吸附剂，活性炭吸附剂颗粒在吸附剂颗粒的表层包含氮。在各种实施方式中，本发明提供了使用活性炭吸附剂来降低包含污染物的气体中污染物含量的方法。在各种实施方式中，所述活性炭吸附剂可比其它吸附剂更有效地从包含硫(VI)例如SO_3的含汞气体中除去汞。

CN 107661744 A

1.卤素或卤化物促进的在其表层包含氮的活性炭吸附剂颗粒，所述氮源自铵盐。

2.根据权利要求1所述的促进的包含氮的活性炭吸附剂颗粒，其中在所述吸附剂颗粒的表层中的氮的浓度高于在所述吸附剂颗粒的核中的氮的浓度。

3.根据权利要求1或2中任一项所述的促进的包含氮的活性炭吸附剂颗粒，其中所述活性炭吸附剂颗粒的核是约0 wt%至约99 wt%氮。

4.根据权利要求1-3中任一项所述的促进的包含氮的活性炭吸附剂颗粒，其中所述活性炭吸附剂颗粒的表层是约0.001 wt%至约99 wt%氮。

5.根据权利要求1-4中任一项所述的促进的包含氮的活性炭吸附剂颗粒，其中所述活性炭吸附剂颗粒的表层包含在所述颗粒的表面的层，所述层独立地具有所述颗粒的半径的约0.001%至约99%的厚度。

6.根据权利要求1-5中任一项所述的促进的包含氮的活性炭吸附剂颗粒，其中所述活性炭吸附剂颗粒的表层包含在所述颗粒的表面的层，所述层具有所述颗粒的半径的约0.001%至约50%的厚度。

7.根据权利要求1-6中任一项所述的促进的包含氮的活性炭吸附剂颗粒，其中所述活性炭吸附剂颗粒具有约0.1 μm至约1000 μm的平均直径。

8.降低含汞气体中的汞含量的方法，所述方法包括：

使含汞气体与权利要求1所述的促进的包含氮的活性炭吸附剂颗粒接触，以形成汞-吸附剂组合物；和

从所述含汞气体中分离至少一些所述汞-吸附剂组合物，以产生分离的气体。

9.根据权利要求8所述的方法，其中所述含汞气体还包含一定浓度的硫(VI)并且在所述含汞气体中硫(VI)的摩尔浓度为大于或等于约1 ppm，且相对于相应促进的活性炭吸附剂，所述促进的活性炭吸附剂颗粒以更高的吸收速率形成汞-吸附剂组合物，所述相应促进的活性炭吸附剂包含以下至少一种a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进。

10.根据权利要求8所述的方法，进一步包括：

促进未促进的包含氮的活性炭吸附剂颗粒，以便提供卤素或卤化物促进的活性炭吸附剂颗粒。

11.根据权利要求10所述的方法，其中所述促进包括使未促进的活性炭吸附剂颗粒与促进剂或转化成促进剂的促进剂前体接触。

12.根据权利要求11所述的方法，其中所述促进剂包括以下物质中的至少一种：卤素、第V主族卤化物、第VI主族卤化物、卤化氢、卤化铵、碱土金属卤化物和碱土金属卤化物。

13.根据权利要求11或12中任一项所述的方法，其中

所述促进剂包括以下物质中的至少一种：F_2、F^-、Cl_2、Cl^-、Br_2、Br^-、I_2、I^-、HI、IBr、ICl、NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$和HCl，

所述促进剂前体包括以下物质中的至少一种：NH_4Br、NaBr、$CaBr_2$、NH_4I、NaI、CaI_2、KBr、Ki、KCl、NH_4Cl、NaCl、$CaCl_2$、NH_4F、NaF和CaF_2，或

它们的组合。

14.根据权利要求10-13中任一项所述的方法，其中所述促进在含汞气体中进行。

15.根据权利要求14所述的方法，其中所述促进包括使未促进的包含氮的活性炭吸附

PAC ET AL. EXHIBIT 1019
Page 1928

剂颗粒与促进剂或促进剂前体接触，所述促进剂或促进剂前体作为气体、液体、固体或其组合加入到含汞气体流、燃烧区中的至少一者，并加入到一部分被燃烧以形成所述含汞气体流的煤中。

16.根据权利要求15所述的方法，其中所述燃烧区位于炉子内。

17.根据权利要求10-15中任一项所述的方法，进一步包括：

加工包含碳前体和铵盐或其分解产物的混合物，以便提供未促进的活性炭吸附剂颗粒。

18.根据权利要求16所述的方法，其中所述加工包括加热至约100 °C至约15000 °C、微波处理和辐照中的至少一种。

19.根据权利要求16或17中任一项所述的方法，其中所述加工在含汞气体中进行。

20.根据权利要求17或18中任一项所述的方法，其中所述铵盐或其降解分解产物被单独加入含汞气体中。

21.制备包含氮的活性炭吸附剂颗粒的方法，所述方法包括：

将包含碳前体和铵盐或其降解产物的混合物加热，以便提供包含氮的活性炭吸附剂颗粒。

22.根据权利要求21所述的制备包含氮的活性炭吸附剂颗粒的方法，其中所述碳前体选自含碳物质、活性炭、焦炭、木炭、或其混合物。

23.制备权利要求1-7中任一项所述的促进的活性炭吸附剂颗粒的方法，所述方法包括：

将包含碳前体和铵盐或其降解产物的混合物加热，以便提供未促进的活性炭吸附剂颗粒，和

促进所述未促进的活性炭吸附剂颗粒，以便提供卤素-或卤化物-促进的活性炭吸附剂颗粒。

24.从含汞气体流中分离汞的方法，所述方法包括：

使含汞气体流与包含促进的铵盐保护的活性炭吸附剂颗粒与未促进的铵盐保护的活性炭吸附剂颗粒中的至少一者的活性炭吸附剂接触，以便形成汞-吸附剂组合物；和

从所述含汞气体流中分离至少一些所述汞-吸附剂组合物，以产生分离的气体。

25.根据权利要求24所述的方法，其中所述活性炭吸附剂在固定床中、在移动床中、在涤气器中、在过滤器中、悬浮在含汞气体流中、或它们的组合。

26.根据权利要求24或25中任一项所述的方法，进一步包括：

将吸附剂注射入含汞气体流，其中所述被注射的吸附剂是包含促进的铵盐保护的活性炭吸附剂颗粒的活性炭吸附剂，所述被注射的吸附剂是包含促进的铵盐保护的活性炭吸附剂颗粒的活性炭吸附剂的前体，所述卤化物促进、铵盐保护或其组合发生在所述前体的注射之后，或其组合。

27.根据权利要求24-26中任一项所述的方法，其中所述活性炭吸附剂包含选自下组的汞稳定剂：S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5和它们的组合。

28.根据权利要求24-27中任一项所述的方法，其中所述促进的铵盐保护的活性炭包含氨、铵盐、或它们的组合。

29.根据权利要求24-28中任一项所述的方法，其中所述未促进的铵盐保护的活性炭包

PAC ET AL. EXHIBIT 1019
Page 1929

含氮、铵盐、或它们的组合。

30.根据权利要求24-28中任一项所述的方法，其中所述促进的铵盐保护的活性炭包含铵盐的阴离子平衡离子。

31.根据权利要求24-30中任一项所述的方法，其中所述未促进的铵盐保护的活性炭包含铵盐的阴离子平衡离子。

32.根据权利要求24-30中任一项所述的方法，进一步包括用促进剂促进前体活性炭吸附剂颗粒以便形成卤素或卤化物促进的活性炭吸附剂颗粒。

33.根据权利要求32所述的方法，其中所述前体活性炭吸附剂颗粒的促进发生于以下情况中的至少一种，在注射在含汞气体流中之前、在加入含汞气体流过程中和在含汞气体流内。

34.根据权利要求32所述的方法，其中所述前体活性炭吸附剂颗粒的促进发生于含汞气体流中或含汞气体流的注射/传输系统中。

35.根据权利要求32-34中任一项所述的方法，进一步包括燃烧包含所述促进剂、促进剂前体或其组合的煤。

36.根据权利要求32-35中任一项所述的方法，进一步包括燃烧煤和在燃烧过程中添加所述促进剂、促进剂前体或它们的组合。

37.根据权利要求32-36中任一项所述的方法，其中所述促进剂包含卤化物。

38.根据权利要求32所述的方法，其中所述促进剂是HCl、HBr、HI、Br_2、Cl_2、I_2、BrCl、IBr、ICl、ClF、PBr_3、PCl_5、SCl_2、$CuCl_2$、$CuBr_2$、Al_2Br_6、FeI_x (x=1，2，3 或4)、$FeBr_y$ (y=1，2，3或4)、$FeCl_z$ (z=1，2，3或4)、$MnBr_2$、$MnCl_2$、$NiBr_2$、$NiCl_2$、NiI_2、$ZnBr_2$、$ZnCl_2$、ZnI_2、NHBr、NH_4Cl、NH_4I、NH_4F或它们的组合。

39.根据权利要求32-38中任一项所述的方法，进一步包括从促进剂前体形成促进剂。

40.根据权利要求39所述的方法，其中所述促进剂前体是溴化氢、溴化铵、溴化钠、溴化钙、氯化氢、氯化铵、氯化钙、氟化氢、氟化铵、氟化钠、氟化钙、氯化钙、碘化铵、碘化钙、碘化钠、溴化钾、碘化钾或氯化钾。

41.根据权利要求39或40中任一项所述的方法，其中所述促进剂前体是NaBr、NaCl、NaI、Br^-、Cl^-、I^-、KI、KCl、LiCl、LiBr、$CuCl_2$、$CuBr_2$、AgCl、AgBr、CHI_3、CH_3Br、AuBr、FeI_x (x=1，2，3或4)、$FeBr_y$ (y=1，2，3或4)、$FeCl_z$ (z=1，2，3或4)、$MgBr_2$、$MgCl_2$、$MnBr_2$、$MnCl_2$、$NiBr_2$、$NiCl_2$、NiI_2、$ZnBr_2$、$ZnCl_2$、ZnI_2、CaI_2、$CaBr_2$、$CaCl_2$、或它们的组合。

42.根据权利要求24-41中任一项所述的方法，进一步包括用铵盐保护促进的活性炭吸附剂颗粒，以形成促进的铵盐保护的活性炭吸附剂颗粒，或用铵盐保护未促进的活性炭吸附剂颗粒以形成未促进的铵盐保护的活性炭吸附剂颗粒，并促进所述未促进的铵盐保护的活性炭吸附剂颗粒，以便形成促进的铵盐保护的活性炭吸附剂颗粒，或其组合。

43.根据权利要求32-42中任一项所述的方法，其中所述前体活性炭吸附剂颗粒的促进发生于以下情况中的至少一种，在注射在含汞气体流中之前、在加入含汞气体流过程中和在含汞气体流内。

44.根据权利要求42所述的方法，其中所述促进的或未促进的活性炭吸附剂颗粒的铵盐保护发生于含汞气体流中、含汞气体流的注射/传输系统中、或其组合。

45.根据权利要求42所述的方法，其中所述铵盐是卤化铵、甲基卤化铵、或其组合。

PAC ET AL. EXHIBIT 1019
Page 1930

46.根据权利要求42所述的方法，其中所述铵盐是卤化铵、甲基卤化铵、第VI主族元素的含氧酸的铵盐、第V主族元素的含氧酸的铵盐、或它们的组合。

47.根据权利要求42所述的方法，其中所述铵盐选自衍生自脂族含氮化合物、芳族含胺化合物、杂环含氮化合物的铵盐，和卤化物盐。

48.根据权利要求42所述的方法，其中所述铵盐是溴化铵、碘化铵、氯化铵、具有式CH_3NH_3X（其中X是Cl、Br或I）的有机卤化物、硫酸铵、硫酸氢铵、亚硫酸铵、亚硫酸氢铵、过硫酸铵、焦硫酸铵、硫代硫酸铵、连二亚硫酸铵、铵铝矾、硫酸铁铵、氨基磺酸铵、磷酸铵、磷酸氢二铵、磷酸氢铵、磷酸二氢铵、硫代磷酸铵、硝酸铵、亚硝酸铵、碳酸铵、硫氰酸铵、硫化铵、氢硫化铵、乙酸铵、氨基甲酸铵、碳酸铵、氯酸铵、铬酸铵、氟化铵、甲酸铵、氢氧化铵、高氯酸铵、或它们的组合。

49.包含与汞原子结合的活性位点的铵盐保护的活性炭吸附剂颗粒，其中所述活性位点在至少其表层中包含结合到促进剂阴离子、和氨、铵盐或它们的组合的碳正离子。

50.制备权利要求49所述的铵盐保护的活性炭颗粒的方法，所述方法包括：使包含前体活性炭吸附剂和铵盐的混合物经受加热、微波处理、辐照、或它们的组合，以便形成包含铵盐保护的活性炭吸附剂颗粒的活性炭吸附剂。

51.从含汞气体流分离汞的方法，所述方法包括：使含汞气体流与包含促进的或未促进的活性炭吸附剂颗粒的活性炭吸附剂与氨接触，以便形成汞-吸附剂组合物；和从所述含汞气体流中分离至少一些所述汞-吸附剂组合物，以产生分离的气体。

PAC ET AL. EXHIBIT 1019
Page 1931

含氮活性炭吸附剂和使用其的方法

[0001] 本申请是申请日为2014年03月03日、申请号为201480025701.9(国际申请号为PCT/US2014/019916)、发明名称为"含氮活性炭吸附剂和使用其的方法"的中国专利申请的分案申请。

[0002] 相关申请的交叉引用

本申请要求2013年3月6号提交的美国临时专利申请系列号61/773,549的优选权的权益,其公开内容在此经引用以其全部内容并入本文。

技术领域

[0003] 本发明涉及活性炭吸附剂、制备活性炭吸附剂的方法、减少包含污染物的气体中的污染物含量的方法。

背景技术

[0004]

因为汞的毒性和生物累积的能力,汞(Hg)排放已成为健康和环境问题。美国国家环境保护局(U.S. Environmental Protection Agency) (EPA)已颁布法规用于控制来自废物再生能源(waste-to-energy)、水泥生产和烧煤发电厂的汞排放。来自工业来源(如发电厂)的烟道气中的汞可被吸附剂例如活性炭捕获,所述吸附剂随后可由微粒分离设备除去。供应市场需要大量的标准吸附剂(如活性炭)。标准吸附剂不总是有效的,且随着使用的量增大变得更加昂贵。

[0005] 当硫(VI) (如SO_3,H_2SO_4)存在于气流中时,可发生通过活性炭吸附剂从气流中捕获汞的抑制作用,在更高的浓度下,抑制作用增强。硫(VI)摩尔浓度在3 ppm以上的汞捕获受到限制。许多公用工程希望在约5-6 ppm的最小值操作SO_3注射系统以改善灰分可回收性。但是,约6 ppm的硫(VI)浓度可使元素汞捕获减少约25%-50%或更多。介于这种减少,经济节约地获得所需的汞水平变得困难,如果不是不可能的话。当硫(VI)浓度增加如此小的量时,存在汞吸附的严重抑制的原因的科学理解是有限的。

发明内容

[0006]

在各种实施方式中,本发明提供了活性炭吸附剂。所述活性吸附剂包含卤素或卤化物促进的碳。所述活性炭包含含氮的活性炭吸附剂颗粒。在吸附剂颗粒表层中的氮的浓度至少是以下情况之一1)高于在吸附剂颗粒核中的氮的浓度和2)高于在从其中获得吸附剂颗粒的碳材料中的氮的浓度。

[0007] 在各种实施方式中,本发明提供了制备活性炭吸附剂的方法。所述方法包括使含碳物质与含氮物质接触,以提供含氮的未促进的碳吸附剂。所述方法还包括通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂,以形成包含含氮的活性炭吸附剂颗粒的活性炭吸附剂,其中在吸附剂颗粒中的氮的浓度高于在含碳物质中的氮

PAC ET AL. EXHIBIT 1019
Page 1932

的浓度。

[0008] 在各种实施方式中，本发明提供了用于从含汞气体中除去汞的活性炭吸附剂。所述活性炭吸附剂包括卤素或卤化物促进的无机活性炭颗粒，在吸附剂颗粒的表层包含氮。氮原子以足够的浓度在活性炭吸附剂颗粒的表层以达到以下目的中的至少之一：a) 与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，减少活性炭吸附剂中的碳正离子通过HSO_3^-或SO_3^{2-}的中和，和b) 与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，至少部分阻止活性炭中的碳正离子与HSO_3^-或SO_3^{2-}形成离子键。

[0009] 在各种实施方式中，本发明提供了减少包含污染物的气体中的污染物含量的方法。所述方法包括获得或提供包括活性炭吸附剂颗粒的活性炭吸附剂，在吸附剂颗粒表层包含氮。所述方法包括使包含污染物的气体与活性炭吸附剂接触。所述接触形成污染物-吸附剂组合物。所述方法还包括从包含污染物的气体中分离出至少一些污染物-吸附剂组合物。所述分离产生分离的气体。

[0010] 在各种实施方式中，本发明提供了用于降低含汞气体的汞含量的方法。所述方法包括获得或提供碳前体。所述碳前体包含氮。所述方法包括获得或提供基质材料。所述方法包括使碳前体与基质材料接触。所述接触提供无机基体负载的吸附剂原材料。所述方法包括加热无机基体负载的吸附剂原材料。所述加热提供未促进的吸附剂。所述方法包括通过使未促进的吸附剂的一部分与促进剂接触(如化学反应)来促进至少一部分未促进的吸附剂，以形成促进的无机基体负载的活性炭吸附剂。所述活性炭吸附剂包括活性炭吸附剂颗粒，在吸附剂颗粒的表层包含氮。所述方法包括使含汞气体与活性炭吸附剂接触。所述接触形成汞-吸附剂组合物。所述方法还包括从含汞气体中分离至少一些汞-吸附剂组合物。所述分离产生分离的气体。硫(VI)在含汞气体中的摩尔浓度约为3-1000 ppm。第一量的活性炭吸附剂以第一汞吸附速率形成汞-吸附剂组合物。第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种a) 在相应颗粒表层中更少的氮或基本无氮，b) 更少或基本无卤化物或卤素促进，和c) 更少或基本无无机基体载体。

[0011] 在各种实施方式中，本发明提供了制备活性炭吸附剂的方法。所述方法包括获得或提供未促进的含氮的碳吸附剂。所述方法包括通过使未促进的吸附剂的一部分与促进剂接触(如化学反应)来促进至少一部分未促进的吸附剂，以形成包含活性炭吸附剂颗粒的活性炭吸附剂，在吸附剂颗粒的表层包含氮。

[0012] 本发明的各种实施方式提供了某些超越其它活性炭吸附剂和使用其的方法的优势，其中至少一些是意想不到的。在一些实施方式中，活性炭吸附剂能比其它方法更有效地分离物质(如污染物)，从包括那种物质的气体中。在各种实施方式中，活性炭的除汞效率超过或匹配常规方法的效率，而伴随附加的益处，例如成本降低。本发明的各种实施方式的方法和材料可比其它除汞方法更加有效地操作。在一些实施方式中，与其它方法相比较，各种实施方式的方法和材料可用更少量的财务支出除去给定量的汞。例如，与其它除汞方法相比较，包括与包含碳吸附剂的其它除汞方法相比较，对于给定质量的碳，各种实施方式的方法和材料可除去更大量的汞。

[0013] 例如，在一些实施方式中，给定质量的含氮活性炭吸附剂可以高于相同质量的相

PAC ET AL. EXHIBIT 1019
Page 1933

应活性炭吸附剂的速率从含汞气流中吸收汞，所述含汞气流包含硫(VI) (如SO_3、H_2SO_4等)，例如大于约3 ppm硫(VI)，例如约3-200 ppm硫(VI)，3-1000 ppm硫(VI)，或约3-10 ppm硫(VI)，所述相应活性炭吸附剂包含更少的氮或不含氮，例如在相应颗粒表层中包含更低浓度的氮或无氮。在一些实施方式中，活性炭吸附剂中的碳正离子比其它活性炭吸附剂，例如在相应颗粒表层包含更少的氮或基本不含氮的其它活性炭吸附剂，更少地被来自SO_3的离子，例如 SO_3^{2-}或HSO_3^{1-}中和。在一些实施方式中，活性炭吸附剂中的碳正离子比在其它活性炭吸附剂中，例如在相应颗粒表层包含更少的氮或基本不含氮的其它活性炭吸附剂中，更多地至少部分阻止来自SO_3的离子，例如 SO_3^{2-}或HSO_3^{1-}。

[0014] 在一些实施方式中，吸附剂可再生和再利用，减少了废吸附剂的处理并降低除汞成本。在一些实施方式中，活性炭吸附剂的制备和促进可有利地现场发生。现场制备和促进可具有优势，包括例如：分离制备设施或位置的设备成本和操作成本的降低或消除、运输成本的降低或消除、更新鲜的和反应性更高的吸附剂、处理的减少、组合物的现场定制(例如当改变燃料或减少载量时)。

[0015] 在一些实施方式中，与无机组分可能阻碍污染物在活性炭上的吸附的传统教导相反，吸附剂中的无机基体载体可增强污染物在活性炭中的吸附，例如在最接近的和氧化反应性的碳石墨烯层上。在各种实施方式中，无机基体载体可稳定阳离子位点在最接近的石墨烯碳结构上的发展，所述碳结构可氧化污染物例如汞。在包括通过从相应卤化铵的降解或反应获得的卤化氢化合物促进的无机基体负载的纳米复合材料的实施方式中，无机部分的另一有利的作用可以是为由二者择一的铵盐的分解或反应所释放的氨提供结合位点。结合的氨可形成具有碱性特征的复合物，其可与包含污染物的气体中的SO_2或 SO_3反应，并可阻止它们干扰污染物(例如汞)在活性炭上的活性位点中或接近活性炭上的活性位点的吸附。

[0016] 粘土常常难以从水性介质中过滤或分离。在一些包括粘土作为无机基体载体的实施方式中，粘土有利地被稳定以分散在水性介质中，并可容易地经过滤从水性介质中分离。

具体实施方式

[0017]

现在将详细参考本公开主题的某些实施方式。尽管本公开主题将结合枚举的权利要求来描述，但是将理解例示的主题不意欲将权利要求限制于本公开主题。

[0018] 以范围格式表述的值应当以灵活方式解释为不仅包括如范围限制明确所述的数值，而且包括在那个范围之内的所有个体数值或子范围，如同各数值和子范围被明确所述一样。例如，“约0.1%至约5%”或“约0.1%至5%”的范围应当解释为不仅包括约0.1%至约5%，而且包括在所表明范围之内的个体值(如1%、2%、3%和4%) 和子范围 (如0.1%至0.5%、1.1%至2.2%、3.3%至4.4%)。“约X至Y”的陈述与“约X至约Y”具有相同的意义，除非另外表明。类似地，“约X、Y或约Z”的陈述与“约X、约Y、或约Z”具有相同的意义，除非另外表明。

[0019] 在本文件中，术语“一”或“所述”用于包括一或多于一，除非上下文另外清楚地规定。术语“或”用于指非排他性的“或”，除非另外表明。另外，要理解在此使用且未另外定义的措辞或术语仅用于描述目的，而非限制目的。段落标题的任何使用意欲帮助文件阅读而不解释为限制；与段落标题相关的信息可能出现在那个具体段落之内或以外。此外，在本文

PAC ET AL. EXHIBIT 1019
Page 1934

件中参考的所有出版物、专利和专利文献均在此经引用以它们的全部内容并入，如同单独经引用并入一样。在本文件和如此经引用并入的那些文件之间存在不一致的用法的情况中，在并入的参考中的用法应认为是对于本文件的补充；对于不可调和的不一致，以本文件中的用法为准。

[0020] 在在此描述的制备方法中，可以不偏离本发明原理的任何顺序进行步骤，除非在明确叙述暂时顺序或操作顺序时。此外，特定的步骤可同时进行，除非明确的权项语言叙述它们分开进行。例如，做X的要求保护的步骤和做Y 的要求保护的步骤可在单一操作之内同时进行，且所得的过程将落在要求保护的过程的字面范围内。

[0021] 定义

在此使用的术语"约"可允许在值或范围中变化的程度，例如，在所述值或所述范围的限制的10%之内、5%之内或1%之内。

[0022] 在此使用的术语"基本上"是指大多数、或多半，如在至少约50%、60%、70%、80%、90%、95%、96%、97%、98%、99%、99.5%、99.9%、99.99%，或至少约99.999%或更多中。

[0023] 在此使用的术语"数均分子量"是指样品中个体分子的分子量的普通算术平均值。其定义为用样品中所有分子的总重量除以样品中分子的总数目。在实验上，数均分子量(M_n)通过以下分析测定：通过公式$M_n = \Sigma M_i n_i / \Sigma n_i$，样品分成种类i的分子量部分，所述种类i具有$n_i$个分子量$M_i$的分子。数均分子量可通过各种各样熟知的方法包括凝胶渗透色谱法、光谱端基分析(spectroscopic end group analysis)和渗透压力测定法来测量。

[0024] 在此使用的术语"重均分子量"指(M_w)，其等于$\Sigma M_i^2 n_i / \Sigma M_i n_i$，其中$n_i$是分子量$M_i$的分子的数目。在各种实例中，重均分子量可使用光散射、小角中子散射、X-射线散射和沉降速率测定。

[0025] 在此使用的术语"溶剂"是指可溶解固体、液体或气体的液体。溶剂的非限制性实例是硅氧烷、有机化合物、水、醇、离子液体和超临界流体。

[0026] 在此使用的术语"空气"是指气体混合物，其具有与取自大气，通常在地平面的气体的天然组成近似相同的组成。在一些实例中，空气取自周围环境。空气具有包括接近78%的氮、21%的氧、1%的氩和0.04%的二氧化碳，以及少量的其它气体的组成。

[0027] 在此使用的术语"室温"是指约15℃至28℃的温度。

[0028] 在此使用的"矿物"是指天然存在的固态化学物质，其通过生物地球化学过程形成，具有，例如，特有的化学组成、高度有序的原子结构和特殊的物理性质。

[0029] 描述

在各种实施方式中，本发明提供了用于降低汞含量的活性炭吸附剂和相关方法，用于在燃烧系统中使用，在所述燃烧系统的烟道气中固有地具有高水平的硫(VI)（如SO_3，或可从其获得的相关化合物，例如H_2SO_4或其它硫酸盐），和用于在使用SO_3 注射用于灰分调节用于改善的灰分收集的工厂中使用。在一些实例中，通过克服能在高SO_3 或高硫酸盐(如高硫(VI))系统中抑制汞捕获的动力学效应和平衡效应，所述方法可在高硫(VI)含量的烟道气中获得高的汞捕获率。所述活性炭吸附剂包含活性炭吸附剂颗粒。在吸附剂颗粒的表层的氮的浓度可高于在吸附剂颗粒的核中的氮的浓度。在一些实例中，所述活性炭吸附剂可为促进的。

[0030] 在各种实施方式中，活性炭吸附剂和相关方法可在中等温度下(如约25-330℃，或

PAC ET AL. EXHIBIT 1019
Page 1935

约50-500℃)，有效除去空气或烟道气流中的元素汞蒸汽。在一些实例中，活性炭不掺杂硫或金属卤化物，其在更高温度下可以是不稳定的。

[0031] 在一些实施方式中，除去过程不包括像在低温下发生的那种元素汞的吸附，但是可包括汞与氧化剂的催化反应，以形成包括结合到活性炭表面的汞的有机汞化合物，其中汞可通过如与酸的反应被释放，以提供具有低蒸汽压的汞(II)种类，例如硫酸汞、溴化汞或氯化汞。离子汞(II)形式可为氧化物或用于所述过程中的任选的酸的盐(例如来自硫酸的硫酸盐)，其可具有更低的挥发性。活性炭可展现归因于，例如，众多活性催化位点的高速率的氧化催化活性，且同时具有用于有机汞化合物产生的大的表面积并因此快速产生转化的汞(II)盐。

[0032] 含氮的活性炭吸附剂。

[0033] 在各种实施方式中，本发明提供了活性炭吸附剂。所述活性炭吸附剂可包含卤素或卤化物促进的活性炭颗粒；在其它实施方式中，所述活性炭吸附剂是未促进的。在一些实例中，所述活性炭可具有无机基体载体。

[0034] 所述活性炭吸附剂可包含活性炭吸附剂颗粒。在吸附剂颗粒的表层的氮的浓度可至少是以下情况之一1)高于在吸附剂颗粒的核中的氮的浓度和2)高于在从其中获得活性炭吸附剂颗粒的活性炭材料中的氮的浓度。各颗粒的表层可独立地为连续的(如未破坏的，具有最小的间隙或没有间隙)或非连续的。所述表层可能在颗粒的外表面。各颗粒的表层可独立地具有任意合适的厚度。所述表层可具有可变的厚度，或可具有基本一致的厚度。在一些实施方式中，所述表层可具有颗粒半径的约0.000,001%至约99.99%的厚度，颗粒半径的0.001%至99%、0.001%至约50%、1%至约50%、0.1%至25%、或约25%至50%的厚度。若颗粒是非球形的，则半径可估算为约颗粒的最大尺寸的一半。

[0035] 在一些实施方式中，各活性炭颗粒可在表层中独立地包含比在核中高约1.001倍的氮浓度，或更低，或在表层中包含比在核中高约1.01、1.1、1.2、1.4、1.6、1.8、2、3、4、5、6、7、8、9、10、15、20、50、100倍，或约1000倍的氮浓度。在一些实施方式中，在表层中的氮的浓度可为约0.000,001 wt%或更少的氮，或约0.001 wt%、0.01 wt%、0.1 wt%、1 wt%、2 wt%、3 wt%、4 wt%、5 wt%、10 wt%、15 wt%、20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%，或约90 wt%或更多的氮。在一些实例中，在表层中的氮的浓度可为约0.001 wt% - 99 wt%氮，5 wt% - 80 wt%，或约 5-60 wt%。在各种实施方式中，在核中的氮的浓度可为约0 wt%、0.000,001 wt%，或约0.001 wt%、0.01 wt%、0.1 wt%、1 wt%、2 wt%、3 wt%、4 wt%、5 wt%、10 wt%、15 wt%、20 wt%、50 wt%、或90 wt%或更多。在一些实例中，在核中的氮的浓度可为约0.001 wt% - 99 wt%氮，0.1 wt% - 20 wt%或约1 wt% - 6 wt%。

[0036] 所述活性炭吸附剂可为任意合适的形式。例如，活性炭可为颗粒状或细颗粒。所述活性炭可具有任何合适的形状，例如球形或不规则的。所述活性炭可具有约0.1 nm或更小的平均直径，或约1 nm、10 nm、100 nm、1 μm、10 μm、100 μm、1 mm、或约10 mm或更大的平均直径。在一些实例中，活性炭具有约0.01 μm或更小的直径，或约 0.1 μm、1 μm、2 μm、3 μm、4 μm、5 μm、10 μm、20 μm、30 μm、40 μm、50 μm、60 μm、70 μm、80 μm、90 μm、100 μm、1000 μm或更大的直径。在一些实例中，颗粒的直径约为0.1-1000 μm，或1-100 μm，或约 1-30 μm。若颗粒是非球形的，直径可估算为颗粒的最长尺寸。含汞的活性炭吸附剂的吸收容量可为约0.000,1 mg汞每克吸附剂或更少，或约0.001 mg/g、0.01、0.1、1、2、3、4、5、10、15、20、25、

PAC ET AL. EXHIBIT 1019
Page 1936

PAC ET AL. EXHIBIT 1019
Page 1937

30、35、40、45、50、55、60、65、70、75、80、85、90、95、100、110、120、150、200、300、400、500、750、或约1 g汞每克吸附剂或更多。

[0037] 在一些实施方式中，活性炭中的至少一些碳是碳的石墨烯(graphene)形式。在一些实施方式中，石墨烯形式的碳可包括更高浓度的适合作为活性位点的位置。在一些实例中，石墨烯碳的某些部分可具有最高浓度的适合作为活性位点的位置：在一些实例中在边缘处，在一些实例中在非边缘位置。如在此所描述的，此类适合作为活性位点的位置可通过使用卤化物或卤素处理来活化。在各种实施方式中，活性炭吸附剂中的碳可为至少约1 wt%、2 wt%、3 wt%、4 wt%、5 wt%、10 wt%、20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%、90 wt%、95 wt%、96 wt%、97 wt%、98 wt%、99 wt%、99.9 wt%、99.99 wt%、或大于约99.999 wt%的石墨烯形式的碳。

[0038] 在一些实施方式中，氮基本上遍及活性炭颗粒均匀分布。在一些实施方式中，氮基本上均匀分布在活性炭吸附剂颗粒的核中；在其它实施方式中，氮在核中可具有任意合适的分布。在一些实施方式中，氮基本上均匀分布在活性炭吸附剂颗粒的表层。在一些实施方式中，氮在表层中不是均匀分布的；如，氮可具有梯度，最高浓度在表层外部和较低浓度在表层内部。

[0039] 氮在活性炭内可为任意合适的形式。在一些实例中，氮可为氮原子，其结合一个或更多个氢原子或一个或更多个其它原子，所述其它原子是，例如，为活性炭框架的部分的含碳基团(如活性炭骨架或其附件)，或结合有机基团。在一些实例中，例如，氮可为中性的或可带有正电荷(如铵)或负电荷。氮可具有任意合适的氧化态，例如0或1。氮可结合4个、3个、2个、1个或0个氢原子。氮可在0、1、2、3或4个位置结合一个或更多个活性炭框架。在一些实施方式中，氮可包括与活性炭的碳框架或与其它官能团结合的一个或两个双键或一个三键，如此使得氮结合1、2或3个碳原子。

[0040] 活性炭中的氮可由任意含氮化合物，例如含氮的有机或无机化合物，例如通过热解或碳化获得。在一些实例中，氮由任意含氮杂环获得或是所述任意含氮杂环的部分，或由任意其它含氮化合物获得。例如，氮可由以下物质获得：吲哚、喹喔啉、咔唑、异喹啉、哌嗪、喹诺酮、喹噁啉、二氮杂二环辛烷、聚丙烯腈、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮-醋酸乙烯酯共聚物、乙烯基吡咯烷酮-丙烯酸共聚物、乙烯基吡咯烷酮-马来酸共聚物、聚氨丙啶、氨基酸(如丙氨酸、精氨酸、天冬酰胺、天冬氨酸、半胱氨酸、谷氨酰胺、谷氨酸、甘氨酸、组氨酸、异亮氨酸、亮氨酸、赖氨酸、蛋氨酸、苯丙氨酸、脯氨酸、丝氨酸、苏氨酸、色氨酸、酪氨酸、或缬氨酸)、苯胺(analine)、硝基苯、羟胺、尿素、肼、氨基磺酸、腈类、氨基甲酸酯类、异氰酸酯类、尿烷类、或它们的组合。在一些实例中，活性炭中的氮可由含氮无机化合物获得或是所述含氮无机化合物的部分，所述含氮无机化合物例如氨、溴化铵、氯化铵、硝酸、亚硝酸、二氧化氮、含NO_3的化合物、含NO_2的化合物等。

[0041] 在各种实施方式中，含氮活性炭吸附剂可在给定浓度的硫(VI)中以比其它吸附剂更高的速率吸收污染物，例如汞。在一些实例中，第一量的活性炭吸附剂以第一汞吸附速率在含汞气体组合物中形成汞-吸附剂组合物，其中硫(VI)在气体组合物中的摩尔浓度约为3 - 2000 ppm，其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种 a)在相应颗粒表层中更少(如更低浓度)的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体。

[0042] 活性炭吸附剂的操作原理不意欲受限于在此提出的任何特定的操作理论。在一些实施方式中，与在基本相似的条件下，在相应的颗粒表层中包含更少的氮或基本不含氮的活性炭吸附剂相比较，在表层中的氮至少部分减少活性炭吸附剂中的碳正离子通过SO_3(或由SO_3获得的离子或其它物质，例如HSO_3^{1-}或SO_3^{2-})中和。在一些实例中，与在基本相似的条件下，在相应的颗粒表层中包含更少的氮或基本不含氮的活性炭吸附剂相比较，在表层中的氮至少部分阻止活性炭中的碳正离子与SO_3(或由SO_3获得的离子或其它物质，例如HSO_3^{1-}或SO_3^{2-})形成离子键。

[0043] 在各种活性炭吸附剂中，在污染物捕获例如汞捕获期间可能发生两种问题：1) 在碳边缘位点得到高氧化反应性(动力学效应)和 2)防止/避免被氧化的汞由于被硫酸盐取代而损失碳结合状态(平衡效应)。气相中的元素汞可在碳边缘表面(阳离子锯齿形位点)被氧化，并可被共价结合作为有机汞卤化物。阳离子位点可通过向碳边缘结构添加酸或卤素(X_2)形成，这可产生碳鎓-卤化物离子对。所述氧化可通过负卤化物离子稳定随着汞原子添加至碳鎓原子而在汞原子上发展的正电荷来得到协助。若碳鎓离子的氧化电势(电荷)或其稳定性更高，则所述氧化可更容易发生，其可由存在于碳框架结构和附近环境中的邻近电荷所影响或决定。结构中另外的阳离子官能可使在反应性位点的氧化电势升高(增加正电荷)，或可增加在反应性位点的正电荷的稳定性。负基团(例如由SO_3获得的离子，如SO_3^{2-}和SO_2^{1-})，可稳定并减少总电荷和可获得的碳鎓离子，并因而降低对于汞氧化的反应性和对于汞捕获的可获得性。

[0044] 对于经短接触时间的捕获，例如通过静电除尘器(ESP)的飞行中捕获，长期平衡效应可能不那么重要。但是，在一些情况下，平衡取代问题可能更为重要，如，袋滤室(baghouse)收集或在选择性催化还原(SCR)单元中的SO_3注射或形成。因为硫酸盐浓度可随着在碳表面的暴露时间增加而增加，所以它们在长暴露时间里在取代卤化汞进入气相(脱附和穿透)的效应可能是重要的。当SO_3相关的化合物和离子例如硫酸、硫酸盐、或相关离子，初始存在于或快速形成于湿表面上时，如，对于SO_3注射，平衡取代效应在伴随短接触时间的系统中也可能变得重要。

[0045] 在各种实施方式中，在表层中的氮可稳定或增加碳结构中的正电荷，这可克服由硫酸盐的电荷消耗，且碳边缘可使用卤素/卤化物促进。在一些实施方式中，在碳边缘结构中的阳离子中心(通常存在于卤化的(如溴化的)碳中并有用于快速汞氧化)的收集可被硫酸氢盐离子和由在碳表面的SO_3反应形成的其它相关离子的干扰所损害。这些阴离子可中和碳鎓离子的正电荷并降低具有共享电荷的剩余反应性位点的总氧化电势。另外的阳离子中心可通过在活性炭形成期间引入氮原子在碳结构内产生，帮助抗衡该效应并抵消一些电荷，所述电荷可通过与，如SO_3或由SO_3获得的离子发生离子相互作用或其它相互作用来使用。原子例如氮可以多环结构添加以形成增加的阳离子或以稳定现存的阳离子。

[0046] 在一些实施方式中，在活性炭吸附剂颗粒的表层中的氮增加吸附剂中的阳离子电荷，因为氮保护阳离子中心使其免于SO_3 和由SO_3获得的离子或化合物的影响。氮原子可形成带电笼或在碳边缘结构周围的其它保护性阻塞结构，或为带电笼或碳边缘结构周围的其它保护性阻塞结构的部分，以防止SO_3和由SO_3获得的离子或化合物，例如阴离子硫酸盐基团进入，但是允许汞原子扩散进入纳米结构以到达氧化或吸附(sorbtion)的活性中心。

[0047] 在一些实施方式中，无机基质载体例如粘土可帮助阻止SO_3和由SO_3获得的离子或

PAC ET AL. EXHIBIT 1019
Page 1938

化合物进入活性阳离子中心，或帮助稳定或增加在活性炭吸附剂中的阳离子电荷。

[0048] 在一些实施方式中，向活性炭添加酸或酸性物质改善了性能。在各种实施方式中，可在碳使用之前通过将酸性溶液浸渍进入碳来添加酸或酸性物质，或可在使用期间将其作为溶液或气体添加至吸附床。改性碳可使用酸性物质浸渍，例如约1 wt%或更少或约2 wt%、3、4、5、6、7、8、9、10、15或约20 wt%或更多或酸性物质，例如 HBr、HCl、H_2SO_4等。

[0049] 降低包含污染物的气体中的污染物含量的方法。

[0050] 在各种实施方式中，本发明提供了使用活性炭吸附剂的方法。所述方法可为任何合适的方法。例如，一些实施方式提供了降低包含污染物的气体中的污染物含量的方法。在一些实例中，包含污染物的气体可至少包含一些氧。所述方法可包括获得或提供包含活性炭吸附剂颗粒的活性炭吸附剂，在表层或吸附剂颗粒中包含氮。在一些实施方式中，在吸附剂颗粒的表层中的氮的浓度可高于在吸附剂颗粒的核中的氮的浓度。活性炭吸附剂可为在此描述的任何含氮的活性炭吸附剂。在一些实例中，含氮的活性炭吸附剂可为促进的含氮活性炭吸附剂。在一些实例中，含氮的活性炭吸附剂可为无机基体负载的或纳米复合材料含氮活性炭吸附剂。在一些实例中，活性炭吸附剂可为促进的含氮活性炭吸附剂和无机基体负载的或纳米复合材料含氮活性炭吸附剂二者。在一些实施方式中，活性炭吸附剂可为促进的但不包含无机基体载体。在一些实施方式中，活性炭吸附剂可既不是促进的，也不是无机基体负载的。活性炭吸附剂可包含结合位点，其可与包含污染物的气体中的污染物中的至少一种和污染物的氧化种类结合，以形成污染物-吸附剂组合物。活性炭吸附剂中的至少一部分结合位点可与污染物中的至少一种和污染物的氧化种类反应，以形成污染物-吸附剂组合物。

[0051] 降低包含污染物的气体中的污染物含量的方法可包括使包含污染物的气体与活性炭吸附剂接触。所述接触形成污染物-吸附剂组合物。所述接触可为任何合适的接触。在一些实施方式中，包含污染物的气体与活性炭吸附剂接触可包括将活性炭吸附剂添加或注射进入含污染物的气体。例如，所述接触可发生于气体中。在另一实施方式中，所述接触可发生于水性液体中。在另一实例中，所述接触可发生于气体中，且随后接触也可发生于水相例如洗涤器中。

[0052] 在一些实施方式中，在包含污染物的气体与活性炭吸附剂接触期间，活性炭吸附剂可在任何合适的结构中以便其接触包含污染物的气体。例如，在接触期间，活性炭吸附剂可为以下中的至少一种：在固定结构中例如在固定床中、在活动结构中例如在活动床中、在洗涤器中、在过滤器中(如固定过滤器或移动的/活动的过滤器)或悬浮在包含污染物的气体中。

[0053] 污染物-吸附剂组合物可为任何合适的组合物，其包括污染物或污染物的氧化形式或另外的化学转化形式和活性炭吸附剂。在一些实施方式中，汞以其元素形式被吸附剂吸收；汞-吸附剂组合物可包括吸附剂和汞的元素形式。在一些实施方式中，汞通过化学反应，例如氧化，被吸附剂转化，以使得来自气体的汞转化成为包含结合汞的活性炭的碳框架的有机汞化合物，其可在与合适的酸反应之后作为汞(II)化合物释放，以产生其盐。在一些实施方式中，汞-吸附剂组合物可包含元素汞、有机汞化合物、和Hg(II)化合物中的至少一种。

[0054] 在一些实例中，元素汞或经转化的汞可保持被吸收至吸附剂，直至汞-吸附剂组合

PAC ET AL. EXHIBIT 1019
Page 1939

物在后续分离步骤中被除去。例如，元素汞或经转化的汞可被吸收或反应并吸收进入吸附剂组合物中或在吸附剂组合物上，以使得在从包含污染物的气体中分离出污染物-吸附剂组合物之后，分离的气体具有约1%或更少、3%、5%、10%、20%、30%、40%、50%、60%、70%、80%、90%、95%、96%、97%、98%、99%、99.9%、99.99%、或约99.999%或更多的初始存在于包含污染物的气体中的汞。在一些实施方式中，元素汞或经转化的汞可从汞-吸附剂组合物中释放；例如，少于约1 wt%、3 wt%、5 wt%、10 wt%、20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%、90 wt%、95 wt%、或少于约99 wt%的汞可在从气体中分离汞-吸附剂组合物之前从汞-吸附剂组合物中释放。在一些实例中，大部分被吸收的元素汞或经转化的汞可保持部分汞-吸附剂组合物，直至汞-吸附剂组合物在后续分离步骤中被除去。在一些实例中，从汞-吸附剂组合物中释放的经转化的汞可通过分离步骤或另一步骤被后续从气体中除去。在一些实例中，已从汞-吸附剂组合物中释放的元素汞或经转化的汞可接触活性炭吸附剂以形成汞-吸附剂组合物，通过分离步骤被后续除去。

[0055] 降低包含污染物的气体中污染物含量的方法可包括从包含污染物的气体中分离至少一些污染物-吸附剂组合物，以得到分离气体。在一些实施方式中，从包含污染物的气体中分离至少一些污染物-吸附剂组合物包括在微粒分离器中分离。所述微粒分离器可为任何合适的微粒分离器，例如静电除尘器(ESP)、袋滤室、湿式洗涤器、过滤器、旋风分离器、织物分离器(fabric separator)、或它们的任意组合。在一些实施方式中，可使用静电除尘器，接着是洗涤器。在其它实施方式中，可使用没有洗涤器的静电除尘器，或可使用另一微粒分离器。可用作微粒分离器的一些设备也可具有其它功能，例如洗涤器也可除去SO_2或SO_3。在包括使汞与吸附剂在水相中，如在洗涤器中接触的实施方式中，通过汞与吸附剂在水相中的反应或相互作用发生在水相内的汞从气体中的除去可被认为是汞-吸附剂组合物从气体中分离。

[0056] 在一些实例中，通过从含汞气体中分离微粒，至少约20 wt%、30 wt%、40 wt%、50 wt%、60 wt%、70 wt%、80 wt%、90 wt%、95 wt%、96 wt%、97 wt%、98 wt%、99 wt%、99.9 wt%、99.99 wt%、或约 99.999 wt%或更多汞可从含汞气流中被除去。如在此所讨论的，汞可以元素汞的形式、或以经转化的汞的形式被除去，所述经转化的汞例如包含结合活性炭的碳框架的汞的有机汞化合物或以与合适的抗衡离子复合的Hg(II)。

[0057] 在一些实施方式中，接触和分离中的至少一者发生在含水洗涤器中。所述含水洗涤器可为任何合适的含水洗涤器。例如，洗涤器可包含含活性炭吸附剂的水性浆料。

[0058] 在一些实施方式中，所述方法除去约1%或更少、或约2%、3、4、5、10、20、30、40、50、60、70、80、85、90、91、92、93、94、95、96、97、98、99、99.5、99.9、99.99、99.999、或约99.9999%或更多的存在于含汞气体中的汞(如用汞的最终浓度除以汞的初始浓度)。在一些实施方式中，活性炭吸附剂结合约50-100 wt%的存在于含汞气体中的汞，或约60-90 wt%、60-80 wt%、70-80 wt%、80-90 wt%、90-100 wt%、或约95-100 wt%或存在于含汞气体中的汞。

[0059] 在一些实施方式中，在含汞气体中的硫(VI)(如来自SO_3、H_2SO_4等)的浓度为大于约3 ppm (摩尔浓度)，及第一量的活性炭吸附剂以第一汞吸附速率形成汞-吸附剂组合物，其中所述第一吸附速率高于在基本类似条件下，第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种a)在相应表层更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体。在一些实施方式中，在包含污染

PAC ET AL. EXHIBIT 1019
Page 1940

物的气体中，处于其中包含污染物的气体接触吸附剂的位置或靠近所述位置的SO_3的浓度为约1 ppm至约100,000 ppm、2-10,000 ppm、3 ppm-1000 ppm、3-100 ppm、3-50 ppm、3-10 ppm、或约3-6 ppm或更多、或在包含污染物的气体中，处于其中包含污染物的气体接触吸附剂的位置或靠近所述位置的硫(VI)(如来自SO_3、H_2SO_4等)的浓度为约1 ppm至约100,000 ppm、2-10,000 ppm、3 ppm-1000 ppm、3-100 ppm、3-50 ppm、3-10 ppm、或约3-6 ppm或更多，其中ppm指百万分之一摩尔。所述浓度可为瞬时浓度，或随时间流逝的平均浓度。与在基本相似的条件下，在相应表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在活性炭吸附剂颗粒的表层中的氮可通过SO_3^{2-}和HSO_3^{1-}中的至少一种减少活性炭中的碳正离子的中和。与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮相应活性炭吸附剂相比较，在活性炭吸附剂颗粒的表层中的氮可至少部分阻止活性炭中的碳正离子受HSO_3^{1-}或SO_3^{2-}中的至少一种的影响。

[0060] 在一些实施方式中，降低包含污染物的气体中污染物含量的方法包括在接触期间或在接触之前的至少一种情况下，将碱性组分添加或注射进入包含污染物的气体中。所述碱性组分可为任何合适的碱性组分，例如碱元素、碱土元素或碱土元素的氧化物、氢氧化物、碳酸盐或磷酸盐、和包括其的化合物或材料。在各种实例中，碱性组分单独添加或与碳吸附剂一起添加可得到改善的汞捕获。各种因素可影响碱添加的有效性，诸如，例如烟道气污染物、烟道气组分(如SO_2、NO_x、Se、HCl等)、操作温度、汞形式和汞浓度。在一些实例中，可调节碱与活性炭的比例以优化给定系列的现场条件(site condition)。

[0061] 在一些实施方式中，活性炭包含稳定剂。在一些实例中，稳定剂可包括S、Se、H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5中的至少一种、或它们的混合物。所述稳定剂可在促进之前或之后添加。

[0062] 在各种实施方式中，除汞速率可随温度升高和随汞的载量增加而逐步降低，其至少部分归因于逆反应速率的增加。在一些实例中，最高速率可在约100至150 °C、50-200 °C、或约50-250 °C下发生。在一些实例中，在400°C下，逆反应可为热力学上高度有利的。在一些实例中，活性炭可通过用水洗以除去在其上的硫酸得以再生，例如在美国专利第 8,173,566号中所描述的。

[0063] 在一些实施方式中，降低包含污染物的气体中污染物含量的方法可包括使污染物-吸附剂组合物再生以得到再生的活性炭吸附剂。所述再生可为允许再生的活性炭吸附剂重新用于从包含污染物的气体中除去污染物的任何合适的再生。所述方法可包括使用再生的活性炭吸附剂从包含污染物的气体中除去污染物。

[0064] 制备含氮活性炭的方法。

[0065] 在一些实施方式中，包含含氮活性炭颗粒的活性炭从市场上获得。在其它实施方式中，含氮活性炭是合成的。例如，降低包含污染物的气体中污染物含量的方法可包括制备含氮活性炭。

[0066] 例如，在降低包含污染物的气体中污染物含量的方法中，获得或提供活性炭吸附剂 可包括获得或提供含氮碳前体。所述方法也可包括处理(如加热)碳前体，以提供活性炭吸附剂。所述处理可包括任何合适的处理。在包括加热碳前体的方法中，所述方法除了加热，可包括任何其它合适的任选的步骤，例如洗涤、化学处理或振动。在一些实施方式中，碳前体包含含碳的含碳物质和含氮的含氮物质。所述加热可包括加热至约 100 °C至15,000

PAC ET AL. EXHIBIT 1019
Page 1941

°C、200 °C至10,000 °C、300 °C至9000 °C、或约400 °C至8000 °C。

[0067] 含碳物质可为任何合适的含碳物质。例如，含碳物质可为有机化合物。在一些实例中，含碳物质包括以下物质中的至少一种：黄糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜、糖蜜萃余液(糖废品)、葡聚糖、半乳聚糖、木聚糖、和糖废品。在一些实例中，含碳物质包括粉末状活性炭、颗粒状活性炭、碳黑、碳纤维、碳蜂窝或平面结构、气凝胶碳膜、热解炭、或活性炭或再生的活性炭，其具有大于要处理的烟道气流中的飘尘的质量平均颗粒尺寸。氮可从任何合适的含氮物质获得或部分可为任何合适的含氮物质。例如，含氮物质可为含氮有机化合物，例如含氮杂环。在一些实例中，含氮物质包括吲哚、喹喔啉、吡唑、异喹啉、哌嗪、喹诺酮、喹喔啉、二氮杂二环辛烷、聚丙烯腈、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮-醋酸乙烯酯共聚物、乙烯基吡咯烷酮-丙烯酸共聚物、乙烯基吡咯烷酮-马来酸共聚物、聚氮丙啶、氨基酸(如丙氨酸、精氨酸、天冬酰胺、天冬氨酸、半胱氨酸、谷氨酰胺、谷氨酸、甘氨酸、组氨酸、异亮氨酸、亮氨酸、赖氨酸、蛋氨酸、苯丙氨酸、脯氨酸、丝氨酸、苏氨酸、色氨酸、酪氨酸、或缬氨酸)、苯胺、硝基苯、羟胺、尿素、肼、氨基磺酸、腈类、氨基甲酸酯类、异氰酸酯类、尿烷类、或它们的混合物。含氮物质可为任何合适的铵盐，例如由脂肪族含氮化合物、芳香族含胺化合物或杂环含氮化合物获得的铵盐；在实施方式中，其中含氮物质是卤化物盐，含氮活性炭等同于促进的物质进行作用且促进步骤可略去或减少。在一些实例中，含氮物质可为以下物质中的至少一种：氨、溴化铵、氯化铵、硝酸、亚硝酸、二氧化氮、包含NO_3的化合物、包含NO_2的化合物等。

[0068] 在一个实例中，包含含氮活性炭吸附剂颗粒的活性炭可通过任意种类的活性炭或炭的表面改性来制备，所述表面改性通过向现存的碳或较低温度的炭施加含氮聚合物涂层或浸渍，并重新碳化经浸渍的碳。所述涂层或浸渍可包括含有氮杂环的聚合物或共聚物，例如聚合的乙烯基吡咯烷酮。在该类型碳的一个实例中，使用聚乙烯基吡咯烷酮、乙烯基吡咯烷酮-马来酸共聚物或乙烯基吡咯烷酮-醋酸乙烯酯共聚物涂布碳表面。在加热或重新碳化之后，经浸渍的混合物可在颗粒上形成含氮活性炭表层。在含氮活性炭的表层中的氮浓度可高于在使用氮进行表面改性或浸渍之前的物质的氮浓度。

[0069] 在一个实例中，含氮活性炭可通过氧化炭的表面改性来制备，所述表面改性通过使用合适的含氮化合物例如氨或尿素处理炭，接着是浸渍氮的物质的活化。

[0070] 在一个实例中，含氮活性炭可通过将含氮化合物浸渍进入炭，接着通过常规方法对经浸渍的炭进行碳化和活化来制备。该类型碳的一个实例为胺或氨基酸与碳水化合物的组合，该组合在加热时经历美拉德(Maillard)缩合反应以形成含氮杂环的碳表面。

[0071] 在一个实例中，含氮活性炭可通过将含氮化合物浸渍进入煤、褐煤、或风化褐煤，紧接着进行碳化和活化来制备。

[0072] 促进的含氮活性炭吸附剂。

[0073] 在一些实施方式中，包含含氮活性炭吸附剂颗粒的活性炭包含促进的含氮活性炭吸附剂。用在降低包含污染物的气体中污染物含量的方法中的含氮活性炭吸附剂可为促进的活性炭吸附剂，并可包含氮。所述方法可包括促进未促进的活性炭吸附剂，或促进的吸附剂可从市场上获得。

[0074] 例如，降低包含污染物的气体中污染物含量的方法可包括获得或提供未促进的碳吸附剂。所述未促进的碳吸附剂可为任何合适的未促进的含氮吸附剂，并可被合成获得或

PAC ET AL. EXHIBIT 1019
Page 1942

从市场上获得。所述方法可包括获得或提供促进剂。所述方法可包括通过将未促进的吸附剂的一部分与促进剂接触(如化学反应)来促进至少一部分未促进的吸附剂,以形成活性炭吸附剂。

[0075] 所述促进剂可为任何合适的促进剂,以使得形成促进的吸附剂,其有效用于从包含污染物的气体中除去污染物,例如汞。例如,所述促进剂可包括卤素或卤化物促进剂。所述卤素或卤化物可为氟或氟化物、氯或氯化物、溴或溴化物、或碘或碘化物。在一些实例中,所述促进剂可包括以下物质中的至少一种:卤素、第V主族卤化物、第VI主族卤化物、卤化氢、卤化铵、碱土金属卤化物(alkali earth metal halide)和碱土金属卤化物(alkaline earth metal halide)。因此,在一些实施方式中活性炭可为以下情况中的至少一种:卤素促进、第V主族卤化物促进、第VI主族卤化物促进、卤化氢促进、卤化铵促进、碱土金属卤化物促进和碱土金属卤化物促进。所述促进剂可包括以下物质中的至少一种:HI、IBr、ICl、NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$和HCl。在一些实例中,所述促进剂是NH_4Br,并可在导管中被注射进入温热区域,例如单独注射或与活性炭吸附剂一起注射。在一些实例中,可在燃烧过程期间将任何合适的含卤素或卤化物的物质,例如NaCl、$CaCl_2$、NaBr或$CaBr_2$与煤一起注射,这可使碳活化。在各种实施方式中,含卤素或卤化物的物质可转化成为活化促进剂,例如活性溴化物或氯化物化合物,如HCl、HBr、xCl或xBr。在一些实例中,所述促进剂是包括以下中的至少一种的形式:蒸汽形式、在溶剂中、作为液体、作为固体、和它们的组合。在一些实施方式中,所述促进可发生于含水洗涤器中,其中所述洗涤器包含含促进剂的水性浆料。

[0076] 所述吸附剂材料的促进可发生于添加或注射进入气流之前、添加或注射进入气流期间、添加或注射进入气流之后、或它们的组合,其中所述气流可为含汞气流、输送流、或它们的组合。在一些实例中,所述促进剂可在促进剂和吸附剂反应之前添加至吸附剂,以使得促进剂添加进入其中的气流的加热引起吸附剂的促进。例如,所述促进剂可作为气体、作为溶解于液体中的气体、或作为固体例如盐、或溶解于液体(如水)中的其它物质(如酸),例如氢溴酸被添加。在其中促进剂以液体例如水被添加的实例中,可允许干燥水,这可允许促进剂附着于活性炭吸附剂、浸渍活性炭吸附剂、或与活性炭吸附剂反应,或它们的组合。在一些实例中,预添加的促进剂可为铵盐,例如氯化铵、溴化铵、或碘化铵,包括,例如一烷基卤化铵、二烷基卤化铵、三烷基卤化铵、或四烷基卤化铵、或卤化铵盐。在一些实例中,可在接近促进时间或在促进时间向吸附剂添加促进剂;例如,所述促进剂可与吸附剂一起添加至气流或以使得其在经加热的气流内接触吸附剂,所述经加热的气流例如含汞气流或进料气流。在一些实例中,所述促进剂可为NH_4Br。

[0077] 在一些实施方式中,促进剂前体转化成为卤素或卤化物促进剂,其与活性炭吸附剂反应以得到活性炭材料。所述促进剂前体可为可转化成为卤素或卤化物促进剂的任何合适的前体。在一些实施方式中,所述促进剂前体可为在未促进的吸附剂上的和与未促进的吸附剂一起添加或注射中的至少一种。在一些实施方式中,所述促进剂可为HBr,且在一些实例中,HBr可借由促进剂前体例如溴化铵、溴化钠、或溴化钙的分解或反应提供。所述促进剂可为HCl,且在一些实例中,HCl可借由促进剂前体例如氯化铵、氯化钠、或氯化钙的分解或反应提供。所述促进剂可为HF,且在一些实例中,HF可借由促进剂前体例如氟化铵、氟化钠、或氟化钙的分解或反应提供。在一些实例中,促进剂(如HBr或HCl)或促进剂前体(如

PAC ET AL. EXHIBIT 1019
Page 1943

NH_4Br、NaBr、$CaBr_2$、NH_4Cl、NaCl、$CaCl_2$)可与活性炭吸附剂分开或与活性炭吸附剂一起在烟道气中添加或注射(如,可应用于吸附剂预注射、在同样的位置同时添加或注射、或在不同位置同时添加或注射)。在一些实例中,NaCl、$CaCl_2$、NaBr或$CaBr_2$可与未燃烧的物质例如未燃烧的煤一起添加。

[0078] 无机基体载体或纳米复合材料。

[0079] 在一些实施方式中,包含含氮活性炭颗粒的活性炭包含无机基体载体或是纳米复合材料。在降低包含污染物的气体中污染物含量的方法中使用的含氮活性炭可包含无机基体载体或可为纳米复合材料。所述方法可包括向活性炭添加无机基体载体或使用未负载的含氮活性炭制备纳米复合材料,或所述方法可包括从市场上获得基体负载的活性炭或纳米复合材料活性炭。在各种实施方式中,所述无机基质载体包括硅藻土、粘土、沸石或矿物中的至少一种。

[0080] 例如,降低包含污染物的气体中的污染物含量的方法可包括获得或提供基质材料。所述基质材料可为任何合适的基质。例如,所述基质可为硅藻土、粘土、沸石或矿物中的至少一种。所述方法可包括使碳前体和基质材料接触,以提供吸附剂原材料。所述接触可以任何合适的方式发生。所述接触使碳前体和基质材料混合,以使得当混合体经加热(或经受任何其它合适的能量来源)时,形成碳纳米复合材料吸附剂或负载的吸附剂。所述接触可进行以使得碳前体接近均匀分布在基质上。在一些实例中,可添加水或另一溶剂以帮助碳前体在基质上分布。在碳前体和基质的混合物中包含水的实例中,混合体可在加热之前被干燥。所述干燥可以任何常规的方式(如对流方式、传导方式、微波方式等)发生,包括在环境压力下、在压力下、或在真空下通过在接近或高于溶剂沸点下进行加热,在水的情况中(如50°C-120°C或更高)。

[0081] 所述基质可包括任何合适的多孔材料。例如,所述基质材料可为硅藻土、沸石、多孔矿物(如粘土)包括,例如,蒙脱石(如蒙脱土、膨润土、绿脱石、皂石)、高岭土、伊利石、绿泥石、海泡石、或凹凸棒石。在一些实例中,所述基体可包括聚合物、非金属、金属、准金属、陶瓷或混合物、和共混物、以及复合材料及其合金。所述材料可为合成的或天然存在的或天然获得的材料。合成聚合物的实例包括任何普通的热塑性和热固性材料。金属的实例包括铝、钛、铜、钢和不锈钢。陶瓷的实例包括氧化铝、氧化锆、二氧化钛和二氧化硅的任何形式。天然存在或天然获得的材料的实例包括木材、木材复合材料、纸、纤维素醋酸酯、和地质形成物(geologic formations)例如花岗岩或石灰石。非金属的实例包括各种形式的碳,例如石墨或碳。准金属的实例包括硅或锗。所述多孔材料可为建筑材料,例如混凝土或沥青。

[0082] 在一些实例中,对于碳纳米复合材料吸附剂,所述基质材料可以原材料的约1 wt%至约99 wt%、约20 wt%至约80 wt%、或约40 wt%至约60 wt%存在。本段中的Wt%是指基于碳前体和基质材料的总重量的重量百分数。

[0083] 所述方法可包括处理(如加热、振动、超声处理、微波、或以其它方式将能量添加至)吸附剂原材料,以提供活性炭吸附剂。碳前体和基质的接触组合物可随后经处理(如加热、振动、超声、微波、或其它合适的能量添加)以形成碳纳米复合材料吸附剂或无机基体负载的吸附剂。所述处理可在任何合适的温度下发生,以使得吸附剂充分形成,例如加热至约50°C、100°C、200°C、300°C、400°C、500°C、600°C、700°C、800°C、900°C、1000°C、1100°C或约1200°C或更高。所述处理可发生持续任何合适的时间,以使得碳纳米复合材料充分形成,例

PAC ET AL. EXHIBIT 1019
Page 1944

如，持续大于约1 min、2 min、5 min、10 min、30 min、1 h、1.5 h、2 h、3 h、4 h、5 h、10 h或大于约24 h。所述加热可在任何合适的装置中发生，例如，在充分排除氧的单元中，如，其允许经加热的惰性气体空气在正在经加热的混合物周围流动。在一个实例中，所述加热发生于在其中具有惰性气体环境的炉子中。取决于装置和纳米复合材料或负载的材料，可加速或延长所述处理。

[0084] 在一些实施方式中，加热吸附剂原材料可提供第二吸附剂原材料。所述方法可进一步包括使第二吸附剂原材料与酸性物质或碱性物质反应，以提供活性炭吸附剂。所述酸性物质或碱性物质可为任何合适的酸性物质或碱性物质，例如HBr、HCl、H_2SO_4、KOH、NaOH等。在一些实施方式中，使用酸性物质或碱性物质处理可制备用于使用促进剂处理的活性炭或可制备以使得获得与汞或另一污染物的充分反应性或吸收的材料。

[0085] 制备含氮活性炭吸附剂的方法。

[0086] 在各种实施方式中，本发明提供了制备包含含氮活性炭吸附剂颗粒的活性炭吸附剂的方法。本发明的实施方式可包括由所述方法制备的任何含氮活性炭吸附剂。所述方法包括获得或提供未促进的含氮吸附剂。所述未促进的含氮吸附剂可为任何合适的含氮活性炭吸附剂，例如在此描述的任何含氮活性炭吸附剂。所述未促进的含氮吸附剂可从市场上获得或可合成。所述方法可包括促进至少一部分未促进的吸附剂。所述促进可包括使该部分未促进的吸附剂与促进剂接触(如化学反应)，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂。

[0087] 在一些实例中，所述未促进的含氮吸附剂可包括无机基体载体或可为纳米复合材料。例如，制备含氮活性炭吸附剂的方法可包括获得或提供含氮碳前体。所述方法可包括获得或提供基质材料。所述方法可包括使碳前体和基质材料接触，以提供吸附剂原材料。所述方法还可包括加热吸附剂原材料，以提供未促进的含氮碳吸附剂。所述未促进的含氮吸附剂可包含含氮活性炭吸附剂颗粒。

[0088] 在一些实施方式中，制备含氮活性炭吸附剂的方法可包括从含碳物质和含氮物质合成含氮碳前体。例如，所述方法可包括获得或提供含碳的含碳物质和含氮的含氮物质。所述方法可包括适当地接触和处理含碳物质和含氮物质以提供含氮碳前体，其中处理可包括以下中的至少一种：加热、微波、超声处理、振动等。

实施例

[0089] 可参考通过举例方式提供的以下实施例更好地理解本发明。本发明不限于在此给出的实施例。

[0090] 实施例1.氮前体浸渍进入炭，紧接着对经浸渍的炭进行碳化和活化。

[0091] 实施例1a.碳前体。

[0092] 将通过褐煤焦(lignite char)的蒸汽活化制备的碳(20 X 60目)与右旋糖和乙醇胺的水溶液以1份碳比0.016份乙醇胺和0.034份右旋糖的比例一起搅拌。通过旋转蒸发(rotovaporation)除去水溶剂，并使经浸渍的碳经空气干燥。经干燥的材料在750°C、在氮流下再活化2小时。

[0093] 实施例1b. 炭前体。

[0094] 将通过在400°C下加热褐煤制备的炭(20 X 60目)与右旋糖和乙醇胺的水溶液以1

PAC ET AL. EXHIBIT 1019
Page 1945

份碳比0.016份乙醇胺和0.034份右旋糖的一起搅拌。通过旋转蒸发除去水溶剂，并使经浸渍的碳进行空气干燥。经干燥的材料在750°C、在氮流下活化2小时。

[0095] 实施例1c.木炭前体。

[0096] 将通过木炭的蒸汽活化制备的碳(20 X 60目)与右旋糖和乙醇胺的水溶液以1份碳比0.016份乙醇胺和0.034份右旋糖的比例一起搅拌。通过旋转蒸发除去水溶剂，并使经浸渍的碳经空气干燥。经干燥的材料在750°C、在氮流下再活化2小时。

[0097] 实施例1d.木炭-丙氨酸。

[0098] 将通过木炭的蒸汽活化制备的碳(20 X 60目)与右旋糖和丙氨酸的水溶液以1份碳比0.016份乙醇胺和0.034份丙氨酸的比例一起搅拌。通过旋转蒸发除去水溶剂，并使经浸渍的碳经空气干燥。经干燥的材料在750°C、在氮流下再活化2小时。

[0099] 实施例2.管式反应器试验。

[0100] 将如在实施例1a-d中所述获得的分子筛碳使用5 wt%的硫酸浸渍。随后将经浸渍的碳在110°C的炉中干燥。将碳(0.100 g)装填入3 mm直径的派热克斯玻璃管(pyrex tube)中并通过在两端的玻璃纤维塞将其保持在原位。在派热克斯玻璃管中出口端处的收缩防止塞子喷出。反应器管在作为恒温设备的处于150°C ± 0.50的GC 炉中加热。汞蒸汽包含在100 cm^3/min的空气流中，以429-447 mg/m^3的浓度经过反应器管，所述浓度使用连续汞蒸汽监控器进行测定。

[0101] 汞源为温度校准的渗透管。将渗透管在具有循环热硅油系统的双夹套玻璃冷凝器中加热。来自反应器管的流出空气流中的浓度使用连续冷蒸汽紫外汞蒸汽监控器(EPM)进行监测。在各碳试验之前进行空白试验以测定汞浓度。使用空气流通过大的碘化碳过滤器进行仪器调零。该装置因此给出未由碳床除去的汞的百分数(出口中的汞浓度除以进口中的汞浓度，乘以100)。对于含氮分子筛碳(实施例1-4)，经数小时的时期，仅1%的汞蒸汽未由碳床除去。

[0102] 实施例3.过滤床试验。

[0103] 将如实施例1e进行预处理的吸附剂碳磨成约200目，并引入管中，其中其可由降低的压力被吸引到保持在不锈钢固定器中的特氟龙或石英过滤器上。随后在空气流下将经碳浸渍的过滤器和固定器置于炉中并如实施例2中所述对其进行试验。

[0104] 实施例4.含氮聚合物浸渍进入活性炭或炭，紧接着对经浸渍的材料进行碳化和活化。

[0105] 实施例4a.乙烯基吡咯烷酮-丙烯酸共聚物。

[0106] 将通过褐煤的蒸汽活化制备的碳与乙烯基吡咯烷酮-丙烯酸共聚物的水溶液一起搅拌持续30 min。聚合物的量经选择以提供1重量%至30重量%的载量。在50°C下通过旋转蒸发蒸去溶剂，并在110°C的炉中进一步干燥。经浸渍的碳通过在750°C、在氮流中加热2小时来再活化。接近40%的聚合物重量转化为表面涂层，60%挥发。

[0107] 实施例4b.乙烯基吡咯烷酮-醋酸乙烯酯共聚物。

[0108] 使用溶解于二氯甲烷中的乙烯基吡咯烷酮-醋酸乙烯酯共聚物浸渍活性炭。蒸发掉溶剂并将经浸渍的碳在110°C的炉中干燥。随后经浸渍的碳通过在750°C、在氮流中加热2小时来活化。

[0109] 实施例4c.聚乙烯基吡咯烷酮。

PAC ET AL. EXHIBIT 1019
Page 1946

[0110] 活性炭使用聚乙烯基吡咯烷酮和在实施例4a-b中所描述的共聚物中的一种进行浸渍并如在实施例4a中所描述的进行活化。

[0111] 实施例4d.聚乙烯基吡咯烷酮。

[0112] KOH-活化的褐煤使用聚乙烯基吡咯烷酮和在实施例4a-4b中所描述的共聚物中的一种进行浸渍并如在实施例4a中所描述的进行活化。

[0113] 实施例4e.木材衍生的木炭。

[0114] 木材衍生的木炭使用聚乙烯基吡咯烷酮和在实施例4a-4b中所描述的共聚物中的一种进行浸渍并如在实施例4a中所描述的进行活化。

[0115] 实施例4f.褐煤的碳化(假设实施例)。

[0116] 炭由褐煤的碳化产生,其使用聚乙烯基吡咯烷酮和在实施例4a-4b中所描述的共聚物中的一种进行浸渍,并如在实施例4a中所描述的进行活化。作为替代,可使用蒸汽活化。

[0117] 实施例4g.蒸汽活化。

[0118] 使用经含氮聚合物浸渍的碳材料的蒸汽活化执行实施例4a-4e,以产生有效的吸附剂。

[0119] 实施例5.氮前体浸渍进入煤、褐煤或风化褐煤,紧接着对经浸渍的材料进行碳化和活化。

[0120] 实施例5a.1,4-二氮杂二环[2.2.2]辛烷(DABCO)。

[0121] 褐煤(如接受时一样)与DABCO的水溶液以1份煤比0.02份DABCO的比例一起搅拌。通过过滤除去水溶剂,并使经浸渍的煤经空气干燥。经干燥的材料在400°C下碳化,并在750°C、在氮流下活化2小时。

[0122] 实施例5b.氨基磺酸。

[0123] 褐煤(如接受时一样)与氨基磺酸的水溶液以1份煤比0.02份氨基磺酸的比例一起搅拌。通过过滤除去水溶剂,并使经浸渍的煤经空气干燥。经干燥的材料经碳化,并在750°C、在氮流下活化2小时。

[0124] 实施例5c.经碳化的褐煤。

[0125] 褐煤在400°C下碳化30分钟,且得到的炭通过如在实施例5b中所描述,与氨基磺酸溶液一起搅拌来处理。随后将经处理的炭如在实施例5b中所描述进行活化。

[0126] 实施例5d.蒸汽活化。

[0127] 经DABCO浸渍的炭或经氨基磺酸浸渍的炭的蒸汽活化在产生汞吸附剂碳中也是有效的。

[0128] 实施例6.含氮沥青的制备。

[0129] 含氮沥青使用由Mochida等人(Mochida, I.; An, K.H.; Korai, Y. Carbon 1995, 33, 1069)报道的步骤制备。制备总结在表1中。作为实施例,将异喹啉(26 g, 0.2摩尔)、无水三氯化铝(13.3 g, 0.25摩尔)和硝基苯(7.68 g, 0.06摩尔)的混合物置于配备回流冷凝器和氮进口管的二颈烧瓶中。将混合物在280°C下回流4小时。使用0.1 N盐酸萃取残留物并过滤。使用0.1 N盐酸洗残留物。进一步使用甲醇萃取残留物以除去任何单体。将不溶于甲醇的沥青在真空下干燥。沥青的产率为49%。如在实施例7中所描述,使用步骤A或B在氮流中碳化部分含氮沥青。

PAC ET AL. EXHIBIT 1019
Page 1947

[0130] 表1. 含氮沥青的制备。*表示反应在300-mL帕尔(Parr)反应器中进行。**表示乙二胺。

基质 (g, 摩尔)	催化剂 (g, 摩尔)	助催化剂 (g, 摩尔)	温度 (℃)	时间 (hr)	产率 (g, %)	可溶的 (%)
吲哚 (10, 0.77)	无	无	253*	4	9.0 (90%)	甲醇 (100)
喹啉 (26, 0.2)	$AlCl_3$ (13.3, 0.1)	硝基苯 (7.68, 0.06)	225*	4	13.5 (52%)	EDA**
吡啶 (16.7, 0.1)	$AlCl_3$ (27.7, 0.2)	硝基苯 (3.6, 0.03)	25	12	59.1 (92%)	EDA**
异喹啉 (26, 0.2)	$AlCl_3$ (13.3, 0.1)	硝基苯 (7.68, 0.06)	280	4	6.5 (25%)	EDA**

[0131] 对于喹啉聚合，利用所述方法的数种修改。除烧瓶法以外，反应使用了帕尔反应器，并改变了温度和反应时间。产率报道在表2中。在该步骤中，64.5 g喹啉和33.25 g三氯化铝置于300-mL帕尔高压釜中。将反应器在氮气下密封并于280°C持续加热4小时。使用0.1 N盐酸萃取硬质黑色块，紧接着使用甲醇萃取并在真空中干燥。为测定聚合物的溶解度，将该黑色块的10-g部分使用100 mL乙醇萃取。萃取数据显示27 wt%的产物溶解于乙醇。

[0132] 表2. 含氮沥青的制备。*表示反应在300-mL帕尔反应器中进行。**表示10 g沥青使用乙醇萃取。

喹啉 (g)	$AlCl_3$ (g)	温度 (℃)	时间 (hr)	产率 (g, %)	乙醇-S (g)	乙醇-I (g)
64.5	33.25	280	12	57.7 (89%)	-	-
64.5*	33.25	175	12	0 (0%)	-	-
64.5*	33.25	280	12	59.1 (92%)	-	-
64.5*	33.25	280	4	56.8 (88%)	7.3** (73%)	2.7 (27%)

[0133] 实施例7. 经氮浸渍的碳的制备。

[0134] 进行浸渍和再碳化以研究前体浓度、活化过程和吸附剂颗粒尺寸对于汞吸附的影响。前体基碳，颗粒状活性炭(Calgon F400或Gascoyne AC, 20 x 60)使用下述的初湿法用各种含氮聚合物和沥青进行浸渍。对于在烟道气组合物中的细颗粒吸附剂试验，将Calgon碳在浸渍之前磨成约400目的尺寸。氮聚合物例如乙烯基吡咯烷酮聚合物和共聚物是市场上可获得的。类似地制备尿素、丙氨酸-右旋糖、哌嗪-右旋糖和聚氮丙啶-右旋糖组合物。

[0135] 在用于初湿法的典型步骤中，将溶解于适当溶剂中的所需量的聚合物或沥青缓慢添加至碳，伴随彻底混合。干燥糊状物以除去溶剂。将干燥产物装填入不锈钢管中并使用步骤A或步骤B在温和的氮流中活化。

[0136] 步骤A包括：以10°C/min从25°C加热至400°C；在400°C下保持30 min；以20°C/min从400°加热至750°C；并在750°C下保持4 hr。

[0137] 步骤B包括：以15°C/min从25°C加热至225°C；以1 °C/min从225°C加热至270°C；在270°C下保持1 hr；冷却至室温；以15°C/min加热升至750°C；并在750°C下保持4 hr。

PAC ET AL. EXHIBIT 1019
Page 1948

[0138] 实施例8.从不溶性部分制备含氮的碳。

[0139] 通过使用如上所述的步骤B在温和的氮流中加热使在表1中描述的沥青的不溶性部分转化成为含氮的碳。得到的碳是类似于焦炭的多孔玻璃状材料。

[0140] 实施例9. 使用实施例6-7的含氮物质制备的用于汞捕获的吸附剂的初步筛分。

[0141] 实施例9a.硫酸聚集的模拟。

[0142] 借助初湿法,通过添加5 wt% 硫酸来模拟在热烟道气流中含氮的碳表面上的SO_3捕获和随后的硫酸形成。将经酸浸渍的碳在110 °C下干燥。

[0143] 实施例9b. 填充床试验。

[0144] 空气流中的填充床试验在颗粒状碳产物上进行以评估表面改性的影响。汞吸附在直通式管状反应器系统中试验,配备来自床的流出物的连续在线汞分析,以测定汞除去速率随时间的变化。漏出容量的积分允许测定每单位质量碳的汞吸附(mg/g)。使具有56或81μg/m^3的元素汞浓度的空气穿过经加热的(150°C)反应器。为获得该浓度,将汞源置于双夹套玻璃冷凝器中并通过抽取热油经过冷凝器将其加热至所需温度。

[0145] 使用具有收缩和玻璃棉塞的玻璃管作为用于汞吸附试验的反应器。使用气相色谱(GC)炉作为用于反应器的恒温(150°C)室。在实际试验之前,进行空白试验。将玻璃管连在所述源上,汞分析器由特氟龙管连接。将用空气稀释的汞蒸汽(在检测器末端测量为2000-4000 cm^3/min或4-8 scfh)穿过管。将汞分析器(环境和过程监控[EPM]连续蒸汽监控器)连接至Hydra和个人电脑(PC)以记录数据。对于填充床试验,使用经浸渍的活性炭(20 x 60目尺寸)。在实际试验中,将约0.2-0.6 g的吸附剂装填入玻璃管并由在两端的玻璃棉塞固定。使用150°C的源温度、150°C的炉温度和等于4或8 scfh (4000 cm^3/min)的空气流进行试验。使用通过将各种氮化合物、聚合物和沥青浸渍进入Calgon基碳来制备的碳在4000 cm^3/min (8 scfh)下进行众多试验(表3和4)。这些条件产生对于吸附剂的部分穿透并允许它们的动力学活性的比较。

[0146] 表3. 经表面处理的碳在8 scfh用于汞除去的吸附剂试验。空气流 = 4000 cm^3/min (8 scfh)、结束温度 = 150 °C、汞浓度 = 81 μg/m^3。*表示在实施例4a中制备的活性炭。

PAC ET AL. EXHIBIT 1019
Page 1949

[0147]

碳源	重新碳化方法	H_2SO_4浸渍	除去的%Hg(时间、min)		
			初始	50%	试验结束
空白		-	0 (0)	<1	-
Calgon		5%	87 (0)	50 (171)	38 (304)
Calgon/尿素	A	5%	95 (0)	50 (305)	49 (306)
EERC*/尿素	A	5%	100 (0)	50 (575)	38 (1221)
Calgon/2%氨基磺酸	A	5%	92 (0)	50 (226)	39 (1303)
Calgon/3% PVP	A	5%	94 (0)	50 (2217)	42 (2574)
Calgon/10% PVP	A	5%	88 (0)	50 (150)	55 (253)
Calgon/10% PVP	A	5%	90 (0)	50 (300)	65 (1098)
Calgon/5% PVP	A	5%	98 (0)	50 (3315)	43 (4010)
Calgon/2% PVP	A	5%	79 (0)	50 (312)	49 (320)
Calgon/10% PVP	A	5%	85 (0)	50 (424)	30 (1114)
Calgon/5%乙烯基吡咯烷酮-醋酸乙烯酯共聚物	A	5%	90 (0)	50 (84)	39 (180)
Calgon/5%乙烯基吡咯烷酮-丙烯酸共聚物	A	5%	90 (0)	50 (76)	29 (362)
Calgon/5%乙烯基吡咯烷酮-丙烯酸共聚物	A	5%	98 (0)	50 (223)	50 (223)
Calgon/聚氮丙啶	A	5%	88 (0)	50 (373)	22 (1147)
Calgon/右旋糖+聚氮丙啶	A	5%	88 (0)	50 (51)	35 (330)
Calgon/右旋糖+丙氨酸	A	5%	88 (0)	50 (76)	53 (216)
Calgon/右旋糖+哌嗪	A	5%	65 (0)	50 (35)	25 (942)

表 4. 经含氮沥青浸渍的碳用于汞捕获的吸附剂试验。对于所有样品均使用重新碳化步骤B。吸附剂= 0.20 g、颗粒尺寸= 20 X 50目、空气流 = 8 scfh (4000 mL/min)、源温度 = 150 °C、炉温度 = 150 °C。*表示由在帕尔反应器中加热喹诺酮和三氯化铝获得的沥青溶解于乙醇并浸渍在Calgon碳上。**表示由喹诺酮与三氯化铝的回流获得的沥青溶解于EDA并浸渍在Calgon碳上。

PAC ET AL. EXHIBIT 1019
Page 1950

文件名	吸附剂(g)	H_2SO_4 (wt%)	浓度 ($\mu g/m^3$)	除去的%Hg(时间, min)		
				初始	50%	终了
RKS32	无	-	81	-	50 <1	-
RKS35	Calgon/5 wt% 喹诺酮 *	5%	-	89 (0)	50 (306)	49 (308)
RKS23	Calgon/5 wt% 喹诺酮 *	5%	-	91 (0)	50 (204)	46 (292)
RKS37	Calgon/5 wt% 喹唑啉	5%	-	90 (0)	50 (632)	25 (1300)
RKS31	Calgon/5 wt% 异喹啉	5%	-	90 (0)	54 (584)	34 (1214)
RKS75	Calgon/5 wt% 吲哚	5%	-	98 (0)	50 (1403)	40 (1473)

[0148] 实施例9c.试验结果。

[0149] 通过将尿素或氨基磺酸浸渍进入Calgon基碳并进行重新碳化制备的碳分别产生95%或92%的初始捕获率。这些结果显著优于使用未改性的Calgon碳所观察到的那些。在较低温度(75°C)下试验尿素碳产生100%的初始捕获。通过含氮聚合物的浸渍制备的碳在这些试验中是高度活性的。通过5 wt% PVP的浸渍来制备并使用步骤A(快加热速率)进行活化的吸附剂证明优异的活性。初始除去为94%,降低至50%除去需要2217 min。因此该吸附剂比尿素碳远更长时间地保留其高活性。使用10% PVP制备的吸附剂(还是步骤A)活性较低(初始88%除去,在150min降低至50%)。

[0150] 使用步骤B(较慢的加热速率)在10% PVP浓度水平产生活性更高的吸附剂。使用步骤B制备具有不同浓度的另一系列的碳。再一次,使用5%浓度PVP的浸渍产生高活性(初始98%除去,在3315 mm降低至50%)。再一次地,10% PVP活性较低,且2% PVP浓度活性最低。

[0151] 还制备并评估了从PVP的共聚物制备的碳。具有醋酸乙烯酯的共聚物(PVP-VA共聚物)以5%浓度浸渍(步骤A)产生具有相对低活性的吸附剂。5%的乙烯基吡咯烷酮-丙烯酸共聚物(PVP-AA共聚物)也产生低活性的吸附剂。使用步骤B用于活化略微改善了活性。

[0152] 使用聚氮丙啶制备另一类型的经N-聚合物浸渍的碳。不同于PVP,其中氮连接于碳链骨架上,该聚合物前体在聚合物骨架中含有氮。活性与10% PVP聚合物的类似。

[0153] 通过浸渍右旋糖和胺的混合物制备数种碳。这些碳在这些试验中都不展现高活性。之前的试验显示经右旋糖 + 丙氨酸浸渍的碳(步骤B)是相当活性的。因为在本研究中使用了步骤A,活性的降低可能与使用的快加热速率有关。在从这些前体制备吸附剂时,缓慢进行反应可能是相当有益的。

[0154] 通过由各种杂环的聚合制备的含氮沥青的浸渍制备的吸附剂都是相当活性的(表4),但是观察到活性的显著差异。从喹喔啉沥青的浸渍制备的N-碳的活性是喹啉衍生的N-碳的活性的2-3倍。异喹啉衍生的碳的活性也非常高。吲哚衍生的碳的高活性也引起了人们很大的兴趣。这是一个重要的引导,因为吲哚比喹喔啉前体更容易获得。

[0155] 还在由含氮沥青的不溶性部分制备的碳化沥青上进行了试验。所述碳化沥青的活性非常差。初始漏出是相当大的,伴随21%至54%的除去百分数,其可能与碳化沥青的玻璃质有关。尽管表面积未经测定,但是它们可能非常低,因为所述材料不像活性炭,反而却像焦炭。

PAC ET AL. EXHIBIT 1019
Page 1951

[0156] 已使用的术语和表述用作描述而非限制的术语，且在此类术语和表述的使用中不意欲排除所示和所述的特征或其部分的任何等价物，但是人们意识到在要求保护的本发明范围之内的各种修改是可能的。因此，应当理解尽管本发明已通过优选的实施方式和任选的特征具体公开，但是本领域技术人员可采用在此公开的概念的修改和改变，且此类修改和改变被认为是在由所附权利要求所定义的本发明的范围之内。

[0157] 另外的实施方式。

[0158] 本发明提供了以下示例性的实施方式，其编号不解释为指定重要性级别：

实施方式1提供了降低包含污染物的气体中污染物含量的方法，所述方法包括：获得或提供包含活性炭吸附剂颗粒的活性炭吸附剂，在所述吸附剂颗粒的表层包含氮；使包含污染物的气体与活性炭吸附剂接触，以形成污染物-吸附剂组合物；并从包含污染物的气体中分离出至少一些污染物-吸附剂组合物，以产生分离的气体。

[0159] 实施方式2提供了实施方式1的方法，其中污染物包含汞，且包含污染物的气体是含汞气体。

[0160] 实施方式3提供了实施方式1-2中任一种的方法，其中在吸附剂颗粒的表层中的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

[0161] 实施方式4提供了实施方式2-3中任一种的方法，其中活性炭吸附剂结合至少约70wt%的存在于含汞气体中的汞。

[0162] 实施方式5提供了实施方式2-4中任一种的方法，其中含汞气体进一步包括硫(VI)的浓度，且含汞气体中硫(VI)的摩尔浓度为大于约3 ppm，且相对于相应活性炭吸附剂，所述活性炭吸附剂以更高的吸收速率形成汞-吸附剂组合物，所述相应活性炭吸附剂包含以下至少一种a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，其中包含活性炭吸附剂颗粒的活性炭吸附剂是卤化物或卤素促进的，和c)更少或基本无无机基体载体，其中包含活性炭吸附剂颗粒的活性炭吸附剂是无机基体负载的。

[0163] 实施方式6提供了实施方式1-5中任一种的方法，其中包含污染物的气体进一步包括一定浓度的硫(VI)，且包含污染物的气体中硫(VI)的浓度为约3 ppm - 2000 ppm。

[0164] 实施方式7提供了实施方式1-6中任一种的方法，其中氮基本上均匀分布在活性炭吸附剂颗粒的核中。

[0165] 实施方式8提供了实施方式1-7中任一种的方法，其中与在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在表层中的氮减少活性炭中的碳正离子通过SO_3^{2-}和HSO_3^{1-}中的任一种的中和。

[0166] 实施方式9提供了实施方式1-8中任一种的方法，其中与在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在表层中的氮至少部分阻止活性炭中的碳正离子受到SO_3^{2-}和HSO_3^{1-}中的至少一种的影响。

[0167] 实施方式10提供了实施方式1-9中任一种的方法，进一步包括：获得或提供未促进的碳吸附剂；获得或提供促进剂；并通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成活性炭吸附剂。

[0168] 实施方式11提供了实施方式10的方法，其中促进剂包括卤素或卤化物促进剂。

[0169] 实施方式12提供了实施方式10-11中任一种的方法，其中促进剂包括以下物质中的至少一种：卤素、第V主族卤化物、第VI主族卤化物、卤化氢、卤化铵、碱土金属卤化物、和

PAC ET AL. EXHIBIT 1019
Page 1952

碱土金属卤化物。

[0170] 实施方式13提供了实施方式10-12中任一种的方法，其中促进剂包括以下物质中的至少一种：HI、IBr、ICl、NH_4Br、NaBr、$CaBr_2$、HBr、NaCl、$CaCl_2$和HCl。

[0171] 实施方式14提供了实施方式10-13中任一种的方法，其中促进剂是包括以下中的至少一种的形式：蒸汽形式、在溶剂中、作为液体、作为固体、和它们的组合。

[0172] 实施方式15提供了实施方式10-14中任一种的方法，其中促进发生于含水洗涤器中，其中洗涤器包含含促进剂的水性浆料。

[0173] 实施方式16提供了实施方式1-15中任一种的方法，其中使包含污染物的气体与活性炭吸附剂接触包括向包含污染物的气体中添加活性炭吸附剂。

[0174] 实施方式17提供了实施方式1-16中任一种的方法，其中活性炭吸附剂为至少以下中的一种：在固定床中、在活动床中、在洗涤器中、在过滤器中或悬浮在包含污染物的气体中。

[0175] 实施方式18提供了实施方式1-17中任一种的方法，其中活性炭吸附剂颗粒的核包含约0 wt% - 约99 wt%的氮。

[0176] 实施方式19提供了实施方式1-18中任一种的方法，其中活性炭吸附剂颗粒的核包含约1 wt% - 约 6 wt%的氮。

[0177] 实施方式20提供了实施方式1-19中任一种的方法，其中活性炭吸附剂颗粒的表层包含约0.001 wt% - 约99 wt%的氮。

[0178] 实施方式21提供了实施方式1-20中任一种的方法，其中活性炭吸附剂颗粒的表层包含约5 wt% - 约80 wt%的氮。

[0179] 实施方式22提供了实施方式1-21中任一种的方法，其中活性炭吸附剂的表层包含在颗粒表面的层，其具有颗粒半径的约0.001%至约99%的厚度。

[0180] 实施方式23提供了实施方式1-22中任一种的方法，其中活性炭吸附剂颗粒的表层包含在颗粒表面的层，其具有颗粒半径的约0.001%至约50%的厚度。

[0181] 实施方式24提供了实施方式1-23中任一种的方法，其中活性炭吸附剂颗粒具有约0.1 μm至约1000 μm的平均直径。

[0182] 实施方式25提供了实施方式 1-24中任一种的方法，其中吸附剂颗粒的表层是连续的表层。

[0183] 实施方式26提供了实施方式1-25中任一种的方法，其中获得或提供活性炭吸附剂包括：获得或提供含氮碳前体；并使用加热、微波和辐照中的至少一种方法处理碳前体，以提供活性炭吸附剂。

[0184] 实施方式27提供了实施方式26的方法，其中碳前体包括含碳的含碳物质和含氮的含氮物质。

[0185] 实施方式28提供了实施方式27的方法，其中含碳物质包括以下物质中的至少一种：黄糖、麦芽糖、焦糖、蔗糖、玉米糖浆、淀粉、糖蜜、葡聚糖、半乳聚糖、木聚糖和糖废品。

[0186] 实施方式29提供了实施方式27-28中任一种的方法，其中含氮物质包括含氮有机化合物或含氮无机化合物。

[0187] 实施方式30提供了实施方式27-29中任一种的方法，其中含氮物质包括氮杂环、含氮聚合物或共聚物、腈、氨基甲酸酯、氨基酸、硝基苯、羟胺、尿素、肼、氨基磺酸、或它们的组

PAC ET AL. EXHIBIT 1019
Page 1953

合。

[0188] 实施方式31提供了实施方式26-30中任一种的方法，进一步包括：获得或提供基质材料；使碳前体和基质材料接触，以提供吸附剂原材料；及使用加热、微波和辐照中的至少一种方法处理吸附剂原材料，以提供活性炭吸附剂。

[0189] 实施方式32提供了实施方式31的方法，其中加热吸附剂原材料提供第二吸附剂原材料，进一步包括使第二吸附剂原材料与酸性物质或碱性物质反应，以提供活性炭吸附剂。

[0190] 实施方式33提供了实施方式31-32中任一种的方法，其中基质包括硅藻土、粘土、沸石或矿物中的至少一种。

[0191] 实施方式34提供了实施方式31-33中任一种的方法，其中加热吸附剂原材料包括加热至约100 °C -约1200 °C。

[0192] 实施方式35提供了实施方式31-34中任一种的方法，其中活性炭吸附剂包括碳纳米复合材料吸附剂。

[0193] 实施方式36提供了实施方式1-35中任一种的方法，其中活性炭吸附剂包含一个或更多个结合位点。

[0194] 实施方式37提供了实施方式36的方法，其中活性炭吸附剂中的至少一部分结合位点与至少一种污染物和污染物的氧化种类反应，以形成污染物-吸附剂组合物。

[0195] 实施方式38提供了实施方式1-37中任一种的方法，其中从包含污染物的气体中分离至少一些污染物-吸附剂组合物包括在微粒分离器中分离。

[0196] 实施方式39提供了实施方式38的方法，其中微粒分离器包括静电除尘器(ESP)、袋滤室、湿式洗涤器、过滤器、旋风分离器、织物分离器、或它们的任意组合。

[0197] 实施方式40提供了实施方式10-39中任一种的方法，其中促进剂前体转化成为卤素或卤化物促进剂，其随后与活性炭吸附剂反应以产生活性炭材料。

[0198] 实施方式41提供了实施方式40的方法，其中促进剂前体为在未促进的吸附剂上和与未促进的吸附剂一起添加中的至少一种。

[0199] 实施方式42提供了实施方式1-41中任一种的方法，进一步包括在接触期间或在接触之前的至少一种情况下，将碱性组分添加进入包含污染物的气体中。

[0200] 实施方式43提供了实施方式42的方法，其中碱性组分包括以下物质中的至少一种：碱元素、碱土元素或碱土元素的氧化物、氢氧化物、碳酸盐或磷酸盐、和包括其的化合物或材料。

[0201] 实施方式44提供了实施方式1-43中任一种的方法，其中活性炭吸附剂包含稳定剂，所述稳定剂包括S、Se中的至少一种、或它们的混合物。

[0202] 实施方式45提供了实施方式 1-44中任一种的方法，其中活性炭吸附剂包含稳定剂，所述稳定剂包括H_2S、SO_2、H_2Se、SeO_2、CS_2、P_2S_5中的至少一种、或它们的混合物。

[0203] 实施方式46提供了实施方式1-45中任一种的方法，进一步包括使污染物-吸附剂组合物再生以产生再生的活性炭吸附剂。

[0204] 实施方式47提供了实施方式1-46中任一种的方法，其中活性炭吸附剂是再生的活性炭吸附剂。

[0205] 实施方式48提供了实施方式1-47中任一种的方法，其中接触和分离中的至少一者发生于含水洗涤器中。

PAC ET AL. EXHIBIT 1019
Page 1954

[0206] 实施方式49提供了实施方式48的方法，其中洗涤器包含含活性炭吸附剂的水性浆料。

[0207] 实施方式50提供了降低含汞气体的汞含量的方法，所述方法包括：获得或提供含氮碳前体；获得或提供基质材料；使碳前体和基质材料接触，以提供无机基体负载的吸附剂原材料；加热无机基体负载的吸附剂原材料，以提供未促进的吸附剂；通过使未促进的吸附剂的一部分与促进剂发生化学反应来促进至少一部分未促进的吸附剂，以形成包含活性炭吸附剂颗粒的促进的无机基体负载的活性炭吸附剂，在吸附剂颗粒的表层包含氮；使含汞气体与活性炭吸附剂接触，以形成汞-吸附剂组合物；并从含汞气体中分离出至少一些汞-吸附剂组合物，以产生分离的气体；其中含汞气体具有约3 - 2000 ppm摩尔浓度的硫(VI)，且第一量的活性炭吸附剂以第一汞吸附速率形成汞-吸附剂组合物，其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含至少以下一种a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体。

[0208] 实施方式51提供了制备活性炭吸附剂的方法，包括：获得或提供未促进的含氮碳吸附剂；通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂，其中在吸附剂颗粒的表层中的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

[0209] 实施方式52提供了实施方式51的方法，进一步包括：获得或提供含氮碳前体；获得或提供基质材料；使碳前体和基质材料接触，以提供吸附剂原材料；和处理吸附剂原材料，以提供未促进的含氮碳吸附剂。

[0210] 实施方式53提供了实施方式52的方法，其中获得或提供含氮碳前体包括：获得或提供含碳的含碳物质和含氮的含氮物质；及使含碳物质和含氮物质接触并加热，以提供含氮碳前体。

[0211] 实施方式54提供了制备活性炭吸附剂的方法，包括：使含碳物质和含氮物质接触，以提供未促进的含氮碳吸附剂；通过使未促进的吸附剂的一部分与促进剂接触来促进至少一部分未促进的吸附剂，以形成包含含氮活性炭吸附剂颗粒的活性炭吸附剂，其中在吸附剂颗粒中的氮的浓度高于在含碳物质中的氮的浓度。

[0212] 实施方式55提供了通过实施方式51-54中任一种的方法制备的活性炭吸附剂。

[0213] 实施方式56提供了活性炭吸附剂，包含：卤素或卤化物促进的活性炭，所述活性炭包含活性炭吸附剂颗粒，在吸附剂颗粒的表层含有氮。

[0214] 实施方式57提供了实施方式56的活性炭吸附剂，其中在吸附剂颗粒的表层中的氮的浓度高于在吸附剂颗粒的核中的氮的浓度。

[0215] 实施方式58提供了实施方式56-57中任一种的活性炭吸附剂，其中活性炭吸附剂颗粒具有约0.1 μm至约1000 μm的平均直径。

[0216] 实施方式59提供了实施方式 56-58中任一种的活性炭吸附剂，其中活性炭为以下情况中的至少一种：卤素促进、第V主族卤化物促进、第VI主族卤化物促进、卤化氢促进、卤化铵促进、碱土金属卤化物促进、和碱土金属卤化物促进。

[0217] 实施方式60提供了实施方式56-59中任一种的活性炭吸附剂，其中活性炭吸附剂是无机基体负载的，所述无机基质载体包括硅藻土、粘土、沸石或矿物中的至少一种。

PAC ET AL. EXHIBIT 1019
Page 1955

[0218] 实施方式61提供了实施方式56-60中任一种的活性炭吸附剂，其中氮基本上均匀分布在活性炭吸附剂颗粒的核中。

[0219] 实施方式62提供了实施方式56-61中任一种的活性炭吸附剂，其中与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在颗粒的表层中的氮至少部分减少活性炭吸附剂中的碳正离子通过HSO_3^{1-}或SO_3^{2-}的中和。

[0220] 实施方式63提供了实施方式56-62中任一种的活性炭吸附剂，其中与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，在颗粒表层中的氮至少部分阻止活性炭中的碳正离子与HSO_3^{1-}或SO_3^{2-}形成离子键。

[0221] 实施方式64提供了实施方式56-63中任一种的活性炭吸附剂，其中第一量的活性炭吸附剂以第一汞吸附速率在含汞气体组合物中形成汞-吸附剂组合物，其中在该气体组合物中硫(VI)的摩尔浓度约为3 - 2000 ppm，且其中第一吸附速率高于第一量的相应活性炭吸附剂的汞吸收速率，所述相应活性炭吸附剂包含以下至少一种 a)在相应颗粒表层中更少的氮或基本无氮，b)更少或基本无卤化物或卤素促进，和c)更少或基本无无机基体载体，其中所述活性炭吸附剂是无机基体负载的。

[0222] 实施方式65提供了实施方式56-64中任一种的活性炭吸附剂，其中氮从含氮有机化合物或含氮无机化合物获得。

[0223] 实施方式66提供了实施方式56-65中任一种的活性炭吸附剂，其中氮从以下物质获得：吲哚、喹喔啉、咔唑、异喹啉、硝基苯、尿素、氨基磺酸、聚乙烯基吡咯烷酮、乙烯基吡咯烷酮-醋酸乙烯酯共聚物、乙烯基吡咯烷酮-丙烯酸共聚物、乙烯基吡咯烷酮-马来酸共聚物、聚氮丙啶、丙氨酸、哌嗪、喹诺酮、喹喔啉、二氮杂二环辛烷、氨基酸、铵盐、或它们的组合。

[0224] 实施方式67提供了用于从含汞气体中除去汞的活性炭吸附剂，所述吸附剂包含：卤素或卤化物促进的含有活性炭颗粒的活性炭，所述颗粒在表层中含有氮，在表层中的氮浓度足够以达到以下目的中的至少之一：a)与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，减少活性炭吸附剂中的碳正离子通过HSO_3^{1-}或SO_3^{2-}的中和，和b)与在基本相似的条件下，在相应颗粒表层中包含更少的氮或基本不含氮的相应活性炭吸附剂相比较，至少部分阻止活性炭中的碳正离子与HSO_3^{1-}或SO_3^{2-}形成离子键。

[0225] 实施方式68提供了实施方式1-67的任一种或任意组合的装置或方法，其任选地被配置以使得所述的所有元素或选项都能够供使用或供从中选择。

PAC ET AL. EXHIBIT 1019
Page 1956

Espacenet

Bibliographic data: DE3816600 (A1) — 1989-11-23

Process for the regeneration of arsenic-contaminated catalysts and sorbents

Inventor(s):	KAIZIK ALFRED DR [DE]; HOEG HANS-ULRICH DR [DE] ±	
Applicant(s):	HUELS CHEMISCHE WERKE AG [DE] ±	
Classification:	**- International:**	***B01D53/86; B01J21/20; B01J23/92; B01J38/60;*** (IPC1-7): B01D53/34; B01J21/06; B01J21/20; B01J23/18
	- European:	B01D53/86F2C; B01J21/20; B01J23/92; B01J38/60
Application number:	DE19883816600 19880514	
Priority number(s):	DE19883816600 19880514	
Also published as:	DE3816600 (C2)	

Abstract of DE3816600 (A1)

In the selective catalytic removal of nitrogen oxides from flue gases of slag-tap-fired furnaces, in particular those having ash recirculation, the problem occurs that the catalysts based on titanium oxide are rapidly deactivated by arsenic compounds. The catalysts damaged in this way have previously had to be replaced by new ones. On the other hand, there is the possibility of removing the arsenic compounds from the flue gas in advance by a sorbent based on titanium oxide upstream of the catalyst. It is desirable in this case to find a process for the regeneration of arsenic-contaminated catalysts and arsenic-laden sorbents. Arsenic-contaminated catalysts and arsenic-laden sorbents can be regnerated by washing with an inorganic or organic acid. Regeneration of arsenic-contaminated catalysts and arsenic-laden sorbents.

Last updated: 14.03.2012 Worldwide Database 5.7.38; 92p

(19) BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENTAMT

(12) **Offenlegungsschrift**

(11) **DE 38 16 600 A1**

(51) Int. Cl.[4]:
B 01 J 21/20
B 01 J 21/06
B 01 J 23/18
B 01 D 53/34
// B01J 23/30,23/20

(21) Aktenzeichen: P 38 16 600.3
(22) Anmeldetag: 14. 5. 88
(43) Offenlegungstag: 23. 11. 89

DE 38 16 600 A1

(71) Anmelder:
Hüls AG, 4370 Marl, DE

(72) Erfinder:
Kaizik, Alfred, Dr.; Hög, Hans-Ulrich, Dr., 4370 Marl, DE

Prüfungsantrag gem. § 44 PatG ist gestellt

(54) Verfahren zur Regeneration arsenkontaminierter Katalysatoren und Sorbentien

Bei der selektiven katalytischen Stickoxidentfernung aus Rauchgasen von Schmelzkammerfeuerungen, insbesondere von solchen mit Aschenrückführung, trat das Problem auf, daß die Katalysatoren auf Basis Titanoxid durch Arsenverbindungen rasch desaktiviert wurden. Die so geschädigten Katalysatoren mußten bisher durch neue ersetzt werden. Zum anderen besteht die Möglichkeit, die Arsenverbindungen aus dem Rauchgas durch ein dem Katalysator vorgeschaltetes Sorbens auf Basis Titanoxid vorher zu entfernen. Wünschenswert ist es somit, ein Verfahren zur Regeneration von arsenkontaminierten Katalysatoren und von arsenbeladenen Sorbentien zu finden.
Arsenkontaminierte Katalysatoren und arsenbeladene Sorbentien lassen sich durch Waschen mit einer anorganischen oder organischen Säure regenerieren.
Regeneration arsenkontaminierter Katalysatoren und arsenbeladener Sorbentien.

DE 38 16 600 A1

BUNDESDRUCKEREI 10. 89 908 847/392 10/70

PAC ET AL. EXHIBIT 1019
Page 1958

Beschreibung

Die Erfindung betrifft ein Verfahren zur Regeneration arsenkontaminierter Katalysatoren und Sorbentien auf Basis Titanoxid.

Vorzugsweise betrifft die Erfindung ein Verfahren zur Regeneration arsenkontaminierter Katalysatoren auf Basis Titanoxid zur Entfernung von Stickoxiden aus Abgasen und Sorbentien auf Basis Titanoxid zur Entfernung von Arsenverbindungen aus Abgasen.

Die derzeit wichtigste, im großtechnischen Maßstab genutzte Methode zur Minderung des Stickoxidausstoßes von Feuerungsanlagen ist die selektive katalytische Reduktion von Stickoxiden mit Ammoniak, wobei überwiegend Katalysatoren auf Basis von Titandioxid eingesetzt werden. Dieses Verfahren wurde ursprünglich für gas- oder ölbefeuerte Anlagen und für Kohlefeuerungen mit trockenem Ascheabzug entwickelt. Bei der Übertragung auf Schmelzkammerfeuerungen, insbesondere solche mit Ascherückführung, trat das Problem in Erscheinung, daß Spuren von Arsenverbindungen in der Kohle sich im Rauchgas zu einer solchen stationären Konzentration anreichern, daß die Katalysatoren eine rasche Desaktivierung erleiden. Eine Lösung für dieses Problem ist noch unbekannt (Energie Spektrum, November 1986, S. 16).

Ein allgemeines Verfahren zur Entfernung störender Kontaminanten ist die Wäsche mit einem geeigneten Agens. Bislang hat man sich jedoch ausschließlich mit der Entfernung anderer Verunreinigungen als Arsenverbindungen befaßt.

Es sind Verfahren zur Regeneration von Katalysatoren zur Stickoxidminderung in Abgasen von Feuerungsanlagen bekannt, und zwar für die Entfernung der folgenden Kontaminanten, wie

Alkalisalze

durch Wäsche mit Wasser und anschließender Imprägnierung mit einer oxidischen Schwefelverbindung gemäß EP-A 159 959, mit Wasserstoffperoxid gemäß JP-OS 59 127 650 und Chemical Abstracts, Vol. 101, 176, 792 und mit Natriumsulfat- oder Ammoniumsulfat-Lösung gemäß Chem. Letters 1983, S. 515—518, wobei zugleich festgestellt wird, daß früher beschriebene Säurewäschen den Katalysatoren zerstören;

Calciumsulfat

durch Wäsche mit organischen oder anorganischen Säuren gemäß JP-OS 59-0 98 739 und Derwent Sect. E 84-17 90 86/29;

Flugstaub

das heißt anhaftendem Staub, dessen Gehalt an Schwermetallen die unerwünschte SO_2-Oxidation fördert und dessen Gehalt an Natrium- und Kaliumsalzen die NO_x-Minderung beeinträchtigt; durch Wäsche mit einer Oxalsäure-Lösung gemäß EP-A 161 206 und anschließendem Ersatz des herausgelösten Katalysatorbestandteils Wolframoxid durch Nachimprägnierung.

In keiner dieser Veröffentlichungen wird eine Desaktivierung durch Arsenverbindungen als Problem erwähnt, geschweige denn ein Verfahren zur Regeneration von durch Arsenverbindungen desaktivierten Katalysatoren vorgeschlagen.

Zum anderen kann man gemäß Patentanmeldung ... eine Desaktivierung von Katalysatoren durch Arsenverbindungen verhindern, indem dem Katalysator ein Sorbens vorgeschaltet wird, das die Arsenverbindungen aus dem Abgas entfernt. Besonders geeignet für die Entfernung von Arsenverbindungen aus Rauchgasen sind Sorbentien auf Basis Titanoxid, da dieselben auch im Bereich höherer Temperaturen von ca. 300 bis 450°C eingesetzt werden können. Ein Verfahren zur Regeneration von mit Arsenverbindungen beladenen Sorbentien auf Basis Titanoxid ist ebenfalls bisher nicht bekannt.

Somit liegt der Erfindung die Aufgabe zugrunde, ein Verfahren zur Regeneration von Katalysatoren und Sorbentien auf Basis Titanoxid zu finden, die durch Arsenverbindungen desaktiviert bzw. mit denselben beladen sind.

Es wurde nun überraschenderweise gefunden, daß arsenkontaminierte Katalysatoren und mit Arsenverbindungen beladene Sorbentien durch eine Wäsche mit anorganischen oder organischen Säuren ihre ursprüngliche Aktivität wiedererlangen.

Gegenstand der vorliegenden Erfindung ist daher ein Verfahren zur Regeneration arsenkontaminierter Katalysatoren und Sorbentien auf Basis Titanoxid, welches dadurch gekennzeichnet ist, daß die arsenkontaminierten Katalysatoren und mit Arsenverbindungen beladenen Sorbentien mit einer anorganischen oder organischen Säure gewaschen werden.

Vorzugsweise werden die Katalysatoren auf Basis Titanoxid zur Entfernung von Stickoxiden aus Abgasen und die Sorbentien auf Basis Titanoxid zur Entfernung von Arsenverbindungen aus Abgasen eingesetzt.

Insbesondere betrifft die Erfindung bezüglich der Regeneration von Katalysatoren solche auf Basis von Titanoxid, die außerdem zusätzliche katalytisch aktive Komponenten, vorzugsweise Oxide des Vanadiums und/oder Molybdäns und/oder Wolframs enthalten. Des weiteren können noch andere Komponenten, wie z. B. SiO_2, ZrO_2, Al_2O_3 Alumosilikate und Tone im Katalysator vorhanden sein. Beispielhaft sei hierzu auf die DE-PS 24 58 888 verwiesen.

Im Zuge der Entwicklung des erfindungsgemäßen Verfahrens ist bei den Untersuchungen zur Desaktivierung von Katalysatoren zur Stickoxidminderung durch Arsenverbindungen festgestellt worden, daß die schädliche Einwirkung der Arsenverbindungen überwiegend aus der Gasphase erfolgt und beispielsweise durch Arsen-III-Oxid als Spezies herrührt.

Die Form des Katalysators oder Sorbens ist für den Erfolg des Verfahrens unwesentlich. Die Wäsche kann durchgeführt werden mit Waben, Platten, Pellets, Strängen, Tabletten und Pulvern, wobei im letztgenannten Fall die Abtrennung von der Waschlösung durch Filtration oder Zentrifugieren erfolgt.

Beispiele für zum Waschen eingesetzte anorganische Säuren sind Salpetersäure, Salzsäure und Schwefelsäure, für organische Säuren Essigsäure. Komplexierende organische Säuren wie Oxalsäure, Malonsäure oder Zitro-

PAC ET AL. EXHIBIT 1019
Page 1959

nensäure sind nicht geeignet zur Katalysatorregenerierung, da sie zu einer weiteren Verringerung der Aktivität führen. Dagegen eignen sie sich aber zur Regeneration von Sorbentien zur Arsenentfernung, sofern diese keine komplexierbaren Schwermetallkomponenten enthalten. Vorzugsweise werden die mit Arsenverbindungen beladenen Sorbentien mit Oxalsäure gewaschen.

Die Konzentration der zum Waschen verwendeten Säure beträgt vorzugsweise 1 bis 25 Gew.-% in der wäßrigen Lösung, besonders vorzugsweise 8 bis 15 Gew.-%. Konzentrationen außerhalb dieses Bereiches sind ebenfalls anwendbar, doch bedingen kleinere Werte eine unvorteilhafte lange Behandlungsdauer und große Volumina, während höhere Konzentrationen keine Verbesserung mehr mit sich bringen und die Handhabung erschweren. Im Fall der Verwendung von Schwefelsäure zum Waschen ist es vorteilhaft, derselben Wasserstoffperoxid zuzusetzen, so daß der Gehalt an Wasserstoffperoxid, bezogen auf die gesamte Säurelösung, 0,1 bis 2 Gew.-% beträgt.

Die Regeneration geschieht bevorzugt durch Tauchen des Katalysators oder Sorbens in der Säure. Vorteilhaft erfolgt die Behandlung, d. h. die Wäsche mit Säuren, bei erhöhten Temperaturen von 50 bis 90°C und unter Bewegung des Säurebades, beispielsweise durch Umpumpen oder Durchblasen von Luft. Typische Behandlungsdauern liegen zwischen 5 Minuten und 5 Stunden. Anschließend wird mehrfach mit Wasser gewaschen, vorzugsweise auch hier bei erhöhter Temperatur, bei 100 bis 200°C getrocknet und ggf. bei 350 bis 500°C getempert.

Die Erfindung wird durch die folgenden Beispiele näher erläutert:

Beispiel 1

Regeneration von Katalysatoren

Für die Versuche wurden drei handelsübliche Typen von Wabenkatalysatoren für die Stickoxidminderung verwendet, die nach dem Einsatz in kohlebefeuerten Kraftwerken in ihrer Aktivität stark gemindert waren und einen deutlichen Gehalt an Arsen aufwiesen.

Die Katalysatoren bestanden überwiegend, d. h. zu mehr als 80 Gew.-%, aus Titanoxid.

Hierbei enthielt der Katalysator K1 Vom Typ KW 33 221 zusätzlich noch 7 Gew.-% WO_3, der Katalysator K2 von Typ KW 22 120 zusätzlich 7 Gew.-% WO_3 und 0,35 Gew.-% V_2O_5 und der Katalysator K3 vom Typ KW 32 221 zusätzlich 8 Gew.-% WO_3 und 0,7 Gew.-% V_2O_5. Alles sind Katalysatoren der Hüls AG.

Die arsenkontaminierten Katalysatoren wurden nun wie folgt mit einer Säure gewaschen:

Aus den desaktivierten Katalysatorwaben wurden zuerst Stücke von 100 mm Länge und 16.2 mm Kantenlänge mit 2mal 2 Kanälen herausgeschnitten. Anschließend stellte man diese Stücke in ein Glasrohr mit poröser Bodenplatte, in welchem sich 100 ml Säure mit einer Temperatur von 80°C befanden. Unter Durchleiten von Luft wurde zwei Stunden lang behandelt, d. h. mit Säure gewaschen. Anschließend entnahm man die Katalysatorstücke dem Säurebad und tauchte sie dreimal für jeweils zwei Minuten in 50 ml Wasser mit einer Temperatur von 80°C. Nach dem Abtropfen wurde 2 h bei 120°C getrocknet und 16 h bei 450°C getempert.

Die einzelnen Katalysatoren wurden jeweils mit den nachfolgend aufgeführten Säuren der folgenden Konzentrationen gewaschen:

Katalysator K1	mit jeweils 2, 5 und 10gew.-%iger Salzsäure (siehe **Abb.** 1),
Katalysator K2	mit 10gew.-%iger Salzsäure (siehe **Abb.** 2),
	10gew.-%iger Salpetersäure (siehe **Abb.** 3),
	2gew.-%iger Schwefelsäure, die zusätzlich 0,35 Gew.-% H_2O_2, bezogen auf die gesamte Säurelösung, enthielt (siehe **Abb.** 4),
	10gew.-%er Essigsäure (siehe **Abb.** 5) und
	mit 10gew.-%iger Oxalsäure (siehe **Abb.** 6) und
Katalysator K3	mit 10gew.-%iger Salzsäure und
	mit 2gew.-%iger Schwefelsäure, die zusätzlich 0,35 Gew.-% H_2O_2, bezogen auf die gesamte Säurelösung, enthielt (siehe **Abb.** 7).

Bei Katalysator K3 betrug die Waschdauer mit der Säure nur 30 Minuten.

Der Katalysator K1 enthielt vor der Regeneration 0,15 Gew.-% Arsen, berechnet als As, K2 0,26 Gew.-% und K3 0,36 Gew.-%. Nach der Wäsche mit Säure verblieben im Katalysator K1 noch 0,01 Gew.-% Arsen. Aus den Katalysatoren K2 und K3 wurden durch die Säurewäsche, ausgenommen mit Oxalsäure, 20 bis 40% des Arsens sowie bis zu 0,6% des WO_3 und bis zu 3% des V_2O_5, bezogen auf die Ausgangsgehalte, entfernt. Da die Reaktivierung trotz Verbleibs eines großen Teils des Arsens im Katalysator gelang, wird vermutet, daß gezielt die für die Stickoxidminderung verantwortlichen, katalytisch aktiven Zentren von ihrer Blockade durch Arsen befreit wurden. Mit Oxalsäure wurden zwar 50% des Arsens, jedoch auch 23% des WO_3 und 4% des V_2O_5 herausgewaschen, so daß in der Bilanz eine nicht vertretbare Schädigung des Katalysators eintrat.

Aktivitätstestung

Die Katalysatoren K1, K2 und K3 wurden in einem elektrisch beheizten Rohrreaktor bezüglich ihrer Aktivität für die Stickoxidreduktion getestet, und zwar in allen Fällen in jeweils frischem, desaktivierten und regenerierten Zustand. Hierbei leitete man durch ein Wabenstück von 100 mm Länge und 16,6 mm Kantenlänge mit 2 × 2 Kanälen 290 Normliter pro Stunde eines vorgemischten Testgases, das

PAC ET AL. EXHIBIT 1019
Page 1960

5 Vol.-%O_2,
1000 Vol.-ppm NO_x mit mehr als 95% NO,
1000 Vol.-ppm SO_2
1000 Vol.-ppm NH_3 und
94,7 Vol.-ppm N_2

enthielt und registrierte im Temperaturbereich zwischen 200 und 450°C die verbliebene Stickoxidkonzentration im abströmenden Gas mittels Stickoxid-Analysator. Um für die Dauereigenschaften der Katalysatoren ein uncharakteristisches Anfangsverhalten auszuschließen, wurde mit den Messungen erst nach 16stündigem Durchleiten des Testgases bei 350°C begonnen.

Die Versuchsergebnisse werden als prozentualer Stickoxid-Umsatz (NO_x-Umsatz) in Abhängigkeit von der Temperatur in den Abbildungen 1 bis 7 zusammenfassend dargestellt:

—**Abb.** 1 zeigt am Beispiel der Regeneration des Katalysators K1 durch Waschen mit

2gew.-%iger,
5gew.-%iger und
10gew.-%iger Salzsäure

den Einfluß der Säurekonzentration auf das Ausmaß der Regeneration. Überraschenderweise verlieh die Säurewäsche mit 10gew.-%iger Säure dem regenerierten Katalysator K1 eine höhere Aktivität als im frischen Zustand. Vermutlich werden durch die Wäsche neue Brönstedt-Säurezentren geschaffen, die als förderlich für die Stickoxidreduktion angesehen werden.

Legende zur **Abb.** 1:
○ Frischkatalysator
● desaktivierter Katalysator
□ Regenerierung mit 2%iger Salzsäure
■ Regenerierung mit 5%iger Salzsäure
△ Regenerierung mit 10%iger Salzsäure

—**Abb.** 2 bis 5 zeigen den Erfolg der Regeneration des Katalysators K2 durch Wäsche mit 10gew.-%iger Salzsäure (**Abb.** 2), 10gew.-%iger Salpetersäure (**Abb.** 3), 2gew.-%iger Schwefelsäure, die zusätzlich 0,35 Gew.-% H_2O_2, bezogen auf die gesamte Säurelösung, enthält (**Abb.** 4), und mit 10gew.-%iger Essigsäure (**Abb.** 5). Hier ist in allen Fällen die Aktivität des regenerierten Katalysators, vor allem bei höheren Temperaturen, etwas geringer als die des frischen. Ursache dafür ist das Herauslösen eines kleinen Teils des Schwermetallgehaltes. Dieser Effekt kann bei Bedarf in bekannter Weise durch Nachimprägnieren mit Vanadyloxalat- oder Ammoniumvanadat-Lösung rückgängig gemacht werden, ist jedoch im allgemeinen zu dulden.

Legende zu den **Abb.** 2 bis5:
○○ Katalysator frisch
●● Katalysator desaktiviert
△△ Katalysator reaktiviert

—**Abb.** 6 zeigt am Beispiel des Katalysators K2, daß eine Wäsche mit 10gew.-%iger Oxalsäurelösung zu einer deutlichen, weiteren Verschlechterung der Aktivität des Katalysators führt. Ursache dafür ist das Herauslösen erheblicher Teile der Schwermetallkomponenten. Hier wäre ein Nachimprägnieren ebenfalls möglich, jedoch unwirtschaftlich.

Legende zu den **Abb.** 6:
○○ Katalysator frisch
●● Katalysator desaktiviert
△△ Regenerationsversuch

—**Abb.** 7 zeigt die Regeneration des Katalysators K3 mit 10gew.-%iger Salzsäure und mit 2gew.-%iger Schwefelsäure, die zusätzlich 0,35 Gew.-% H_2O_2, bezogen auf die gesamte Säurelösung, enthält. Das Erscheinungsbild entspricht dem bei der Regeneration des Katalysators K2.

Legende zu den **Abb.** 7:
○○ Katalysator frisch
●● Katalysator desaktiviert
△△ Katalysator mit 2gew.-%iger H_2SO_4 mit 0,35 Gew.-% H_2O_2 regeneriert
▲▲ Katalysator mit 10gew.-%iger HCl regeneriert

Beispiel 2

Regeneration eines Sorbens

Kalzinierte Strangpreßlinge aus VKR-611, einer sprühgetrockneten Metatitansäure mit ca. 6 Gew.-% Sulfat-

PAC ET AL. EXHIBIT 1019
Page 1961

gehalt der Firma Sachtleben Chemie, deren Sulfatgehalt vor dem Kalzinieren durch Wäsche mit Ammoniakwasser entfernt worden war und die nach dem Kalzinieren eine BET-Oberfläche von 71 m^2/g besaßen, wurden durch Kontaktieren mit einem Arsen-III-Oxid enthaltenden Gasstrom mit 3,8 Gew.-% Arsen beladen. 15 g der mit Arsen beladenen Strangpreßlinge wusch man auf die gleiche Weise, wie in Beispiel 1 beschrieben, zwei Stunden lang mit 10gew.-%iger Oxalsäure und dann mit Wasser. Anschließend wurden sie für zwei Stunden bei 120°C und für 1 Stunde bei 450°C getrocknet. 50% der Arsenbeladung wurden auf diese Weise entfernt. Bei erneutem Einsatz zur Arsenentfernung aus einem Gasstrom zeigte das Sorbens den entsprechenden Teil seiner früheren Aufnahmekapazität.

Patentansprüche

1. Verfahren zur Regeneration arsenkontaminierter Katalysatoren und Sorbentien auf Basis Titanoxid, **dadurch gekennzeichnet,** daß die arsenkontaminierten Katalysatoren und mit Arsenverbindungen beladenen Sorbentien mit einer anorganischen oder organischen Säure gewaschen werden.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Katalysatoren auf Basis Titanoxid zur Entfernung von Stickoxiden aus Abgasen und die Sorbentien auf Basis Titanoxid zur Entfernung von Arsenverbindungen aus Abgasen eingesetzt werden.
3. Verfahren nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß zum Waschen Salpetersäure, Salzsäure, Schwefelsäure oder Essigsäure eingesetzt werden.
4. Verfahren nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, daß die mit Arsenverbindungen beladenen Sorbentien mit Oxalsäure gewaschen werden.
5. Verfahren nach den Ansprüchen 1 und 4, dadurch gekennzeichnet, daß die Konzentration der zum Waschen verwendeten Säure 1 bis 25 Gew.-% in der wäßrigen Lösung beträgt.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die Konzentration der zum Waschen verwendeten Säure 8 bis 15 Gew.-% in der wäßrigen Lösung beträgt.
7. Verfahren nach den Ansprüchen 1, 2, 3, 5 und 6, dadurch gekennzeichnet, daß die zum Waschen verwendete Schwefelsäure zusätzlich 0,1 bis 2 Gew.-% Wasserstoffperoxid, bezogen auf die gesamte Säurelösung, enthält.
8. Verfahren nach den Ansprüchen 1 und 7, dadurch gekennzeichnet, daß die Wäsche mit Säuren bei Temperaturen von 50 bis 90°C erfolgt.
9. Verfahren nach den Ansprüchen 1 und 8, dadurch gekennzeichnet, daß nach der Wäsche mit Säuren die Katalysatoren und Sorbentien mit Wasser gewaschen, getrocknet ggf. getempert werden.
10. Verfahren nach den Ansprüchen 1, 2, 3 und 5 bis 9, dadurch gekennzeichnet, daß die zu regenerierenden Katalysatoren auf Basis Titanoxid außerdem zusätzlich katalytisch aktive Komponenten enthalten.
11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß die zu regenerierenden Katalysatoren auf Basis Titanoxid als zusätzlich katalytisch aktive Komponenten Oxide des Vanadiums und/oder Molybdäns und/oder Wolframs enthalten.

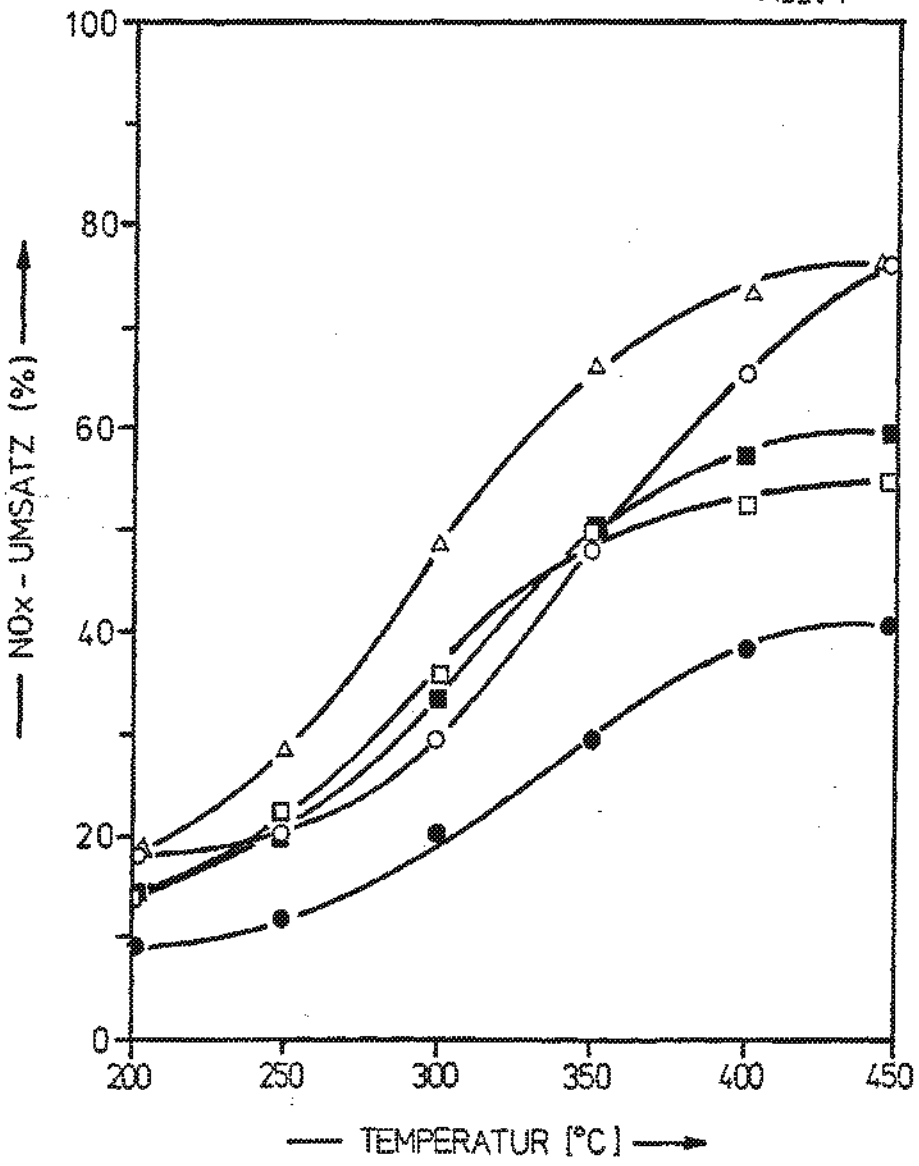
PAC ET AL. EXHIBIT 1019
Page 1962

Nummer: 38 16 600
Int. Cl.⁴: B 01 J 21/20
Anmeldetag: 14. Mai 1988
Offenlegungstag: 23. November 1989

3816600

REGENERATION DES KATALYSATORS K 1
EINFLUSS DER SÄUREKONZENTRATION

Abb. 1

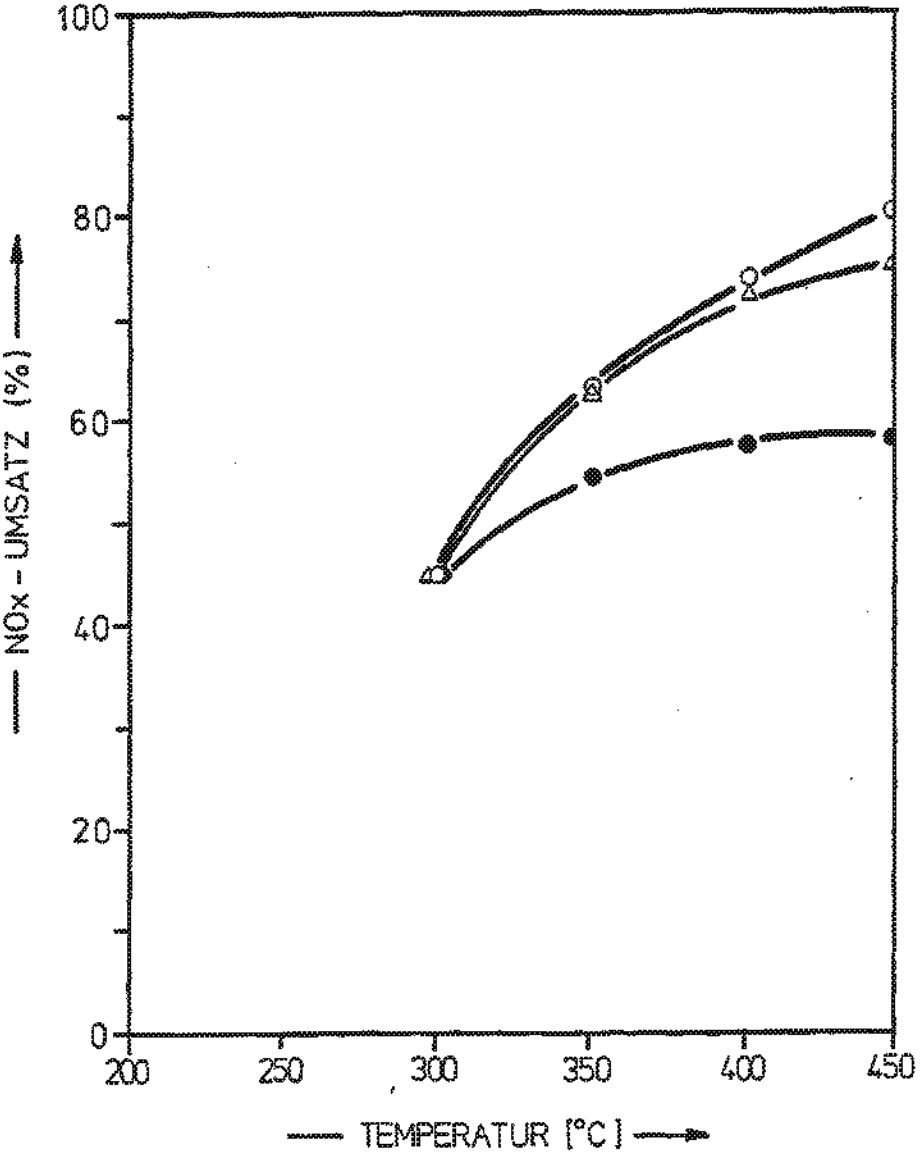


908 847/392

KATALYSATOR K 2

REGENERATION MIT 10%iger SALZSÄURE

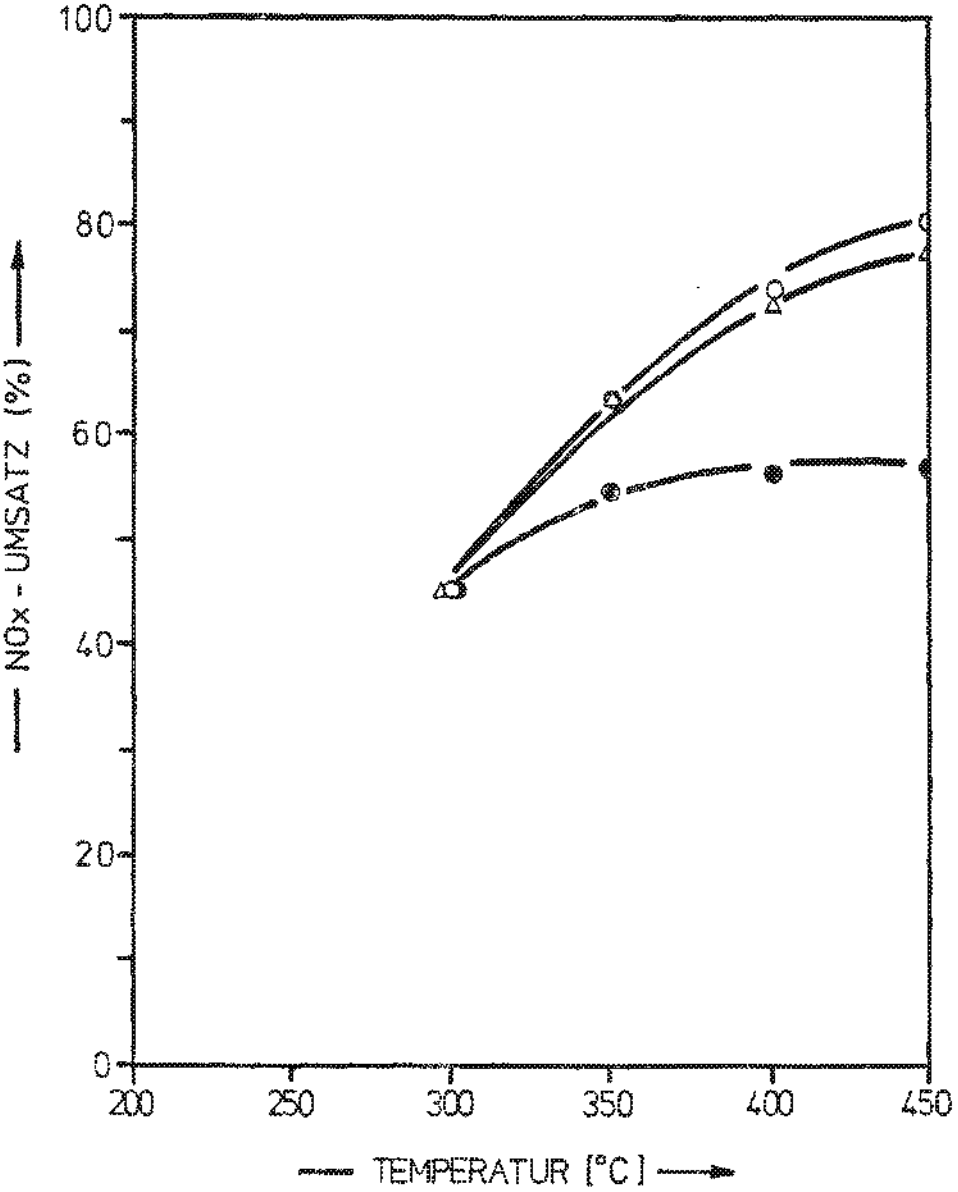
Abb. 2



KATALYSATOR K 2

REGENERATION MIT 10 gew.%iger SALPETERSÄURE

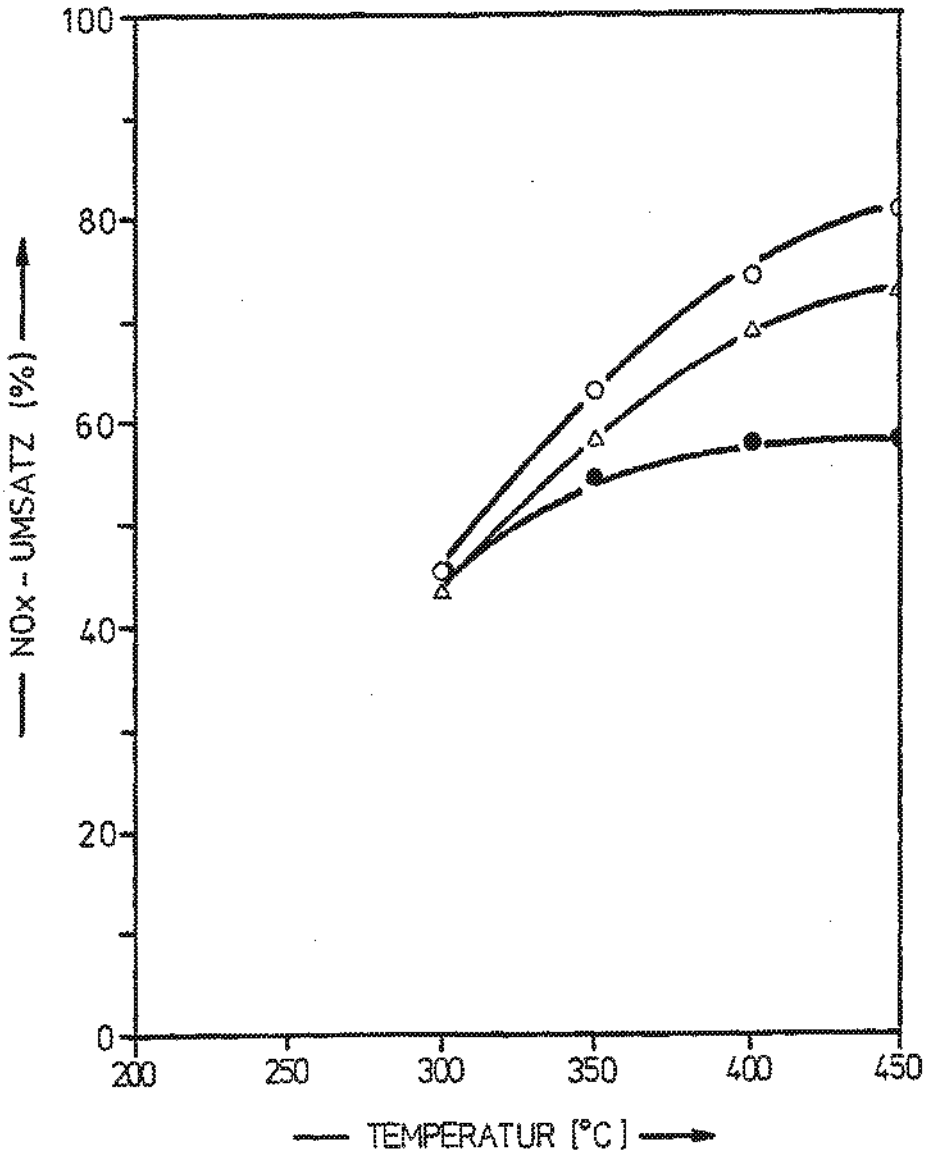
Abb. 3



KATALYSATOR K 2

REGENERATION MIT 2 gew.%iger SCHWEFELSÄURE
MIT 0,35 Gew.% H_2O_2

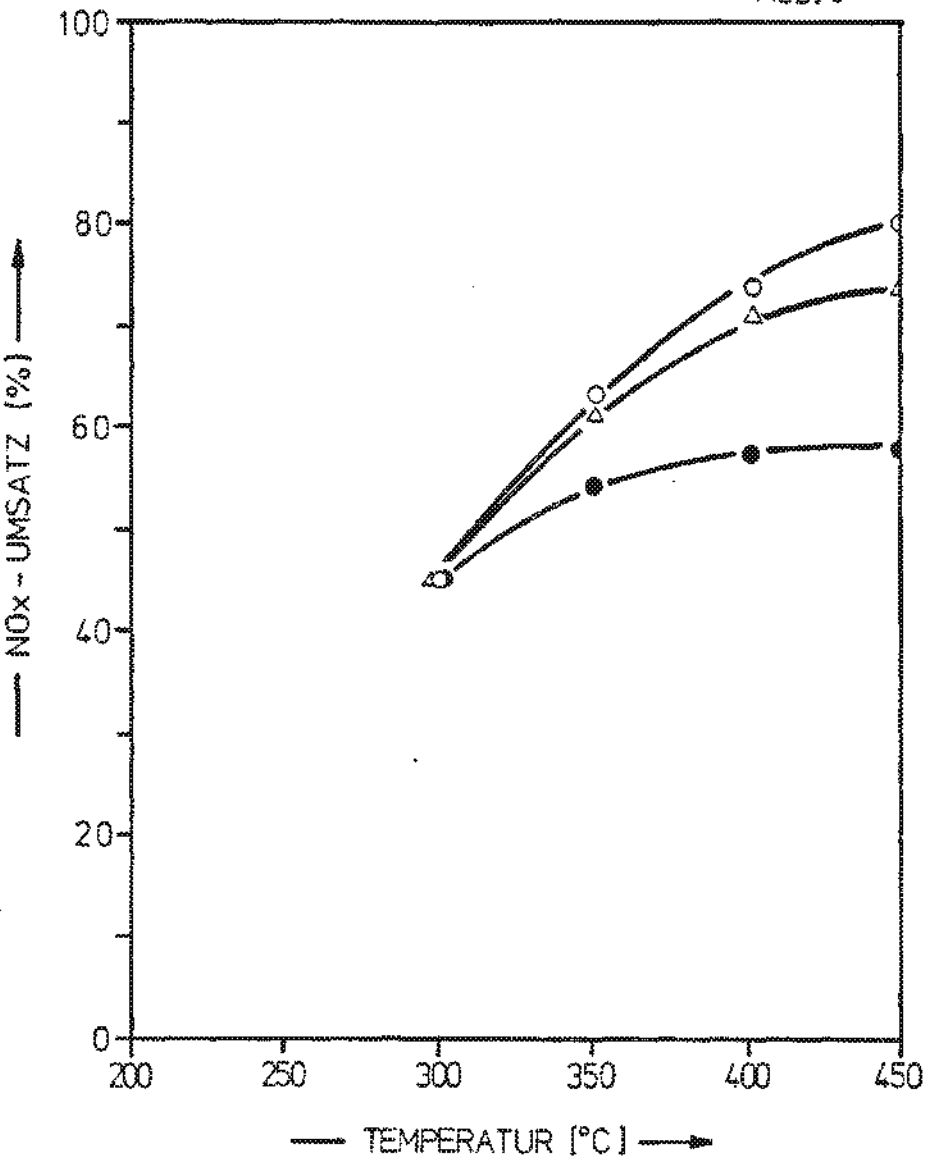
Abb. 4



KATALYSATOR K 2

REGENERATION MIT 10gew.%iger ESSIGSÄURE

Abb. 5

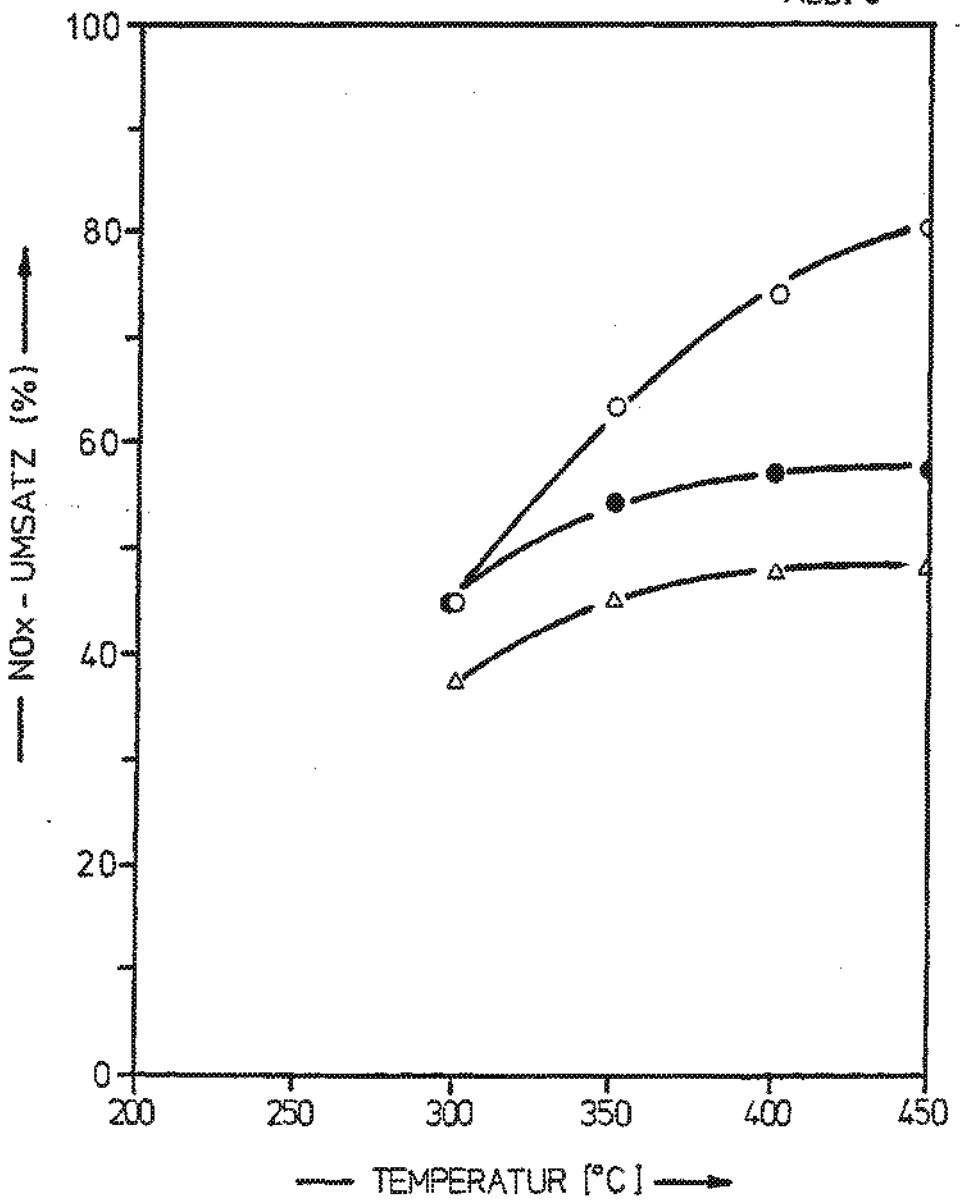


KATALYSATOR K 2

REGENERATIONSVERSUCH

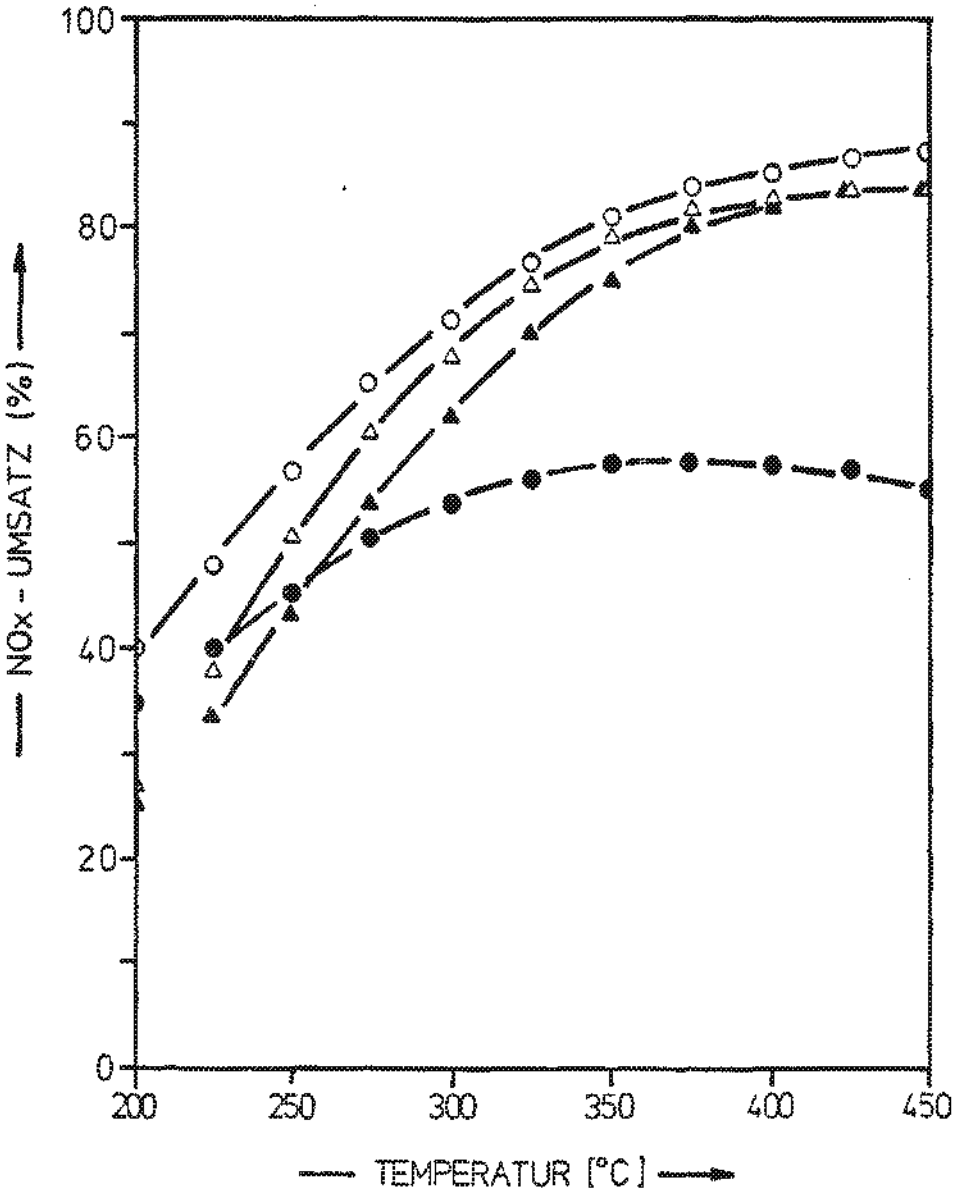
MIT 10gew.%iger OXALSÄURE

Abb. 6



REGENERATION DES KATALYSATORS K3

Abb. 7



Espacenet

Bibliographic data: EP1386655 (A1) — 2004-02-04

Process for removing mercury from flue gases

Inventor(s): VOSTEEN BERNHARD PROF DR [DE]; BEYER JOACHIM [DE]; BONKHOFER THEODOR-GERHARD [DE]; FLETH OLAF [DE]; WIELAND ANDREA [AT]; POHONTSCH ANDREAS [DE]; KANEFKE RICO [DE]; STANDAU EWA [DE]; MUELLER CLAUS [DE]; NOLTE MICHAEL [DE]; KOELSER HEINZ PROF DR-ING HABI [DE] ± (VOSTEEN, BERNHARD, PROF.DR, ; BEYER, JOACHIM, ; BONKHOFER, THEODOR-GERHARD, ; FLETH, OLAF, ; WIELAND, ANDREA, ; POHONTSCH, ANDREAS, ; KANEFKE, RICO, ; STANDAU, EWA, ; MUELLER, CLAUS, ; NOLTE, MICHAEL, ; KOELSER, HEINZ, PROF.DR.-ING.HABIL)

Applicant(s): BAYER AG [DE] ± (BAYER INDUSTRY SERVICES GMBH & CO. OHG)

Classification: - **international:** ***B01D53/34; B01D53/64; B01D53/86; B01J27/06;*** (IPC1-7): B01D53/64
- **cooperative:** **B01D53/64**

Application number: EP20030016026 20030715 Global Dossier

Priority number(s): DE2002133173 20020722

Also published as: EP1386655 (B1) AT383193 (T) AU2003220713 (A1) AU2003220713 (B2) AU2003220713 (B8) more

Abstract of EP1386655 (A1)

Mercury is removed from flue gases of high-temperature plants by feeding bromine and/or a bromine compound to a multi-stage furnace and/or to the flue gas, and subjecting the flue gas to a multi-stage clean-up. The combustion takes place in the presence of a sulfur compound, particularly sulfur dioxide, with or without the addition of sulfur and/or a sulfur compound and/or a mixture of various sulfur compounds. The removal of mercury from flue gases of high-temperature plants, comprises feeding bromine and/or a bromine compound and/or a mixture of various bromine compounds to a multi-stage furnace and/or to the flue gas in a plant section downstream of the furnace, the temperature during the contact of the bromine compound with the flue gas being >= 500[deg]C, preferably >= 800[deg]C. The combustion takes place in the presence of a sulfur compound, particularly sulfur dioxide, with or without the addition

of sulfur and/or a sulfur compound and/or a mixture of various sulfur compounds. The flue gas is subjected to a multi-stage clean-up comprising a wet scrubber and/or a dry clean-up.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 386 655 A1

(12) EUROPÄISCHE PATENTANMELDUNG

(43) Veröffentlichungstag:
04.02.2004 Patentblatt 2004/06

(51) Int Cl.7: **B01D 53/64**

(21) Anmeldenummer: **03016026.1**

(22) Anmeldetag: **15.07.2003**

(84) Benannte Vertragsstaaten:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT RO SE SI SK TR
Benannte Erstreckungsstaaten:
AL LT LV MK

(30) Priorität: **22.07.2002 DE 10233173**

(71) Anmelder: **Bayer Aktiengesellschaft**
51368 Leverkusen (DE)

(72) Erfinder:
- **Vosteen, Bernhard, Prof.Dr.**
  51061 Köln (DE)
- **Beyer, Joachim**
  51515 Kürten (DE)
- **Bonkhofer, Theodor-Gerhard**
  45159 Essen (DE)
- **Fleth, Olaf**
  41515 Grevenbroich (DE)
- **Wieland, Andrea**
  9422 Maria Rojach (AT)
- **Pohontsch, Andreas**
  02694 Grossdubrau (DE)
- **Kanefke, Rico**
  04420 Grosslehna (DE)
- **Standau, Ewa**
  06179 Langenbogen (DE)
- **Müller, Claus**
  51515 Kürten (DE)
- **Nolte, Michael**
  38642 Goslar (DE)
- **Kölser, Heinz, Prof.Dr.-Ing.habil.**
  55218 Ingelheim (DE)

(54) Verfahren zur Abscheidung von Quecksilber aus Rauchgasen

(57) Die Erfindung beschreibt ein Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen, bei dem der, gegebenenfalls mehrstufigen, Feuerung und/oder dem Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil eine bromhaltige Verbindung zugeführt wird, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt. Die Verbrennung erfolgt in Gegenwart einer schwefelhaltigen Verbindung, insbesondere Schwefeldioxid. Im Anschluss an die Feuerung wird das Rauchgas einer, gegebenenfalls mehrstufigen, Reinigung zur Abtrennung von Quecksilber aus dem Rauchgas unterzogen, welche eine Nasswäsche und/oder eine Trockenreinigung umfasst.

EP 1 386 655 A1

Printed by Jouve, 75001 PARIS (FR)

Beschreibung

[0001] Die Erfindung betrifft ein Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen.

[0002] Aufgrund der hohen Toxizität von Quecksilber, insbesondere von organisch gebundenem Quecksilber, das direkt oder indirekt über die Nahrungskette auch vom Menschen aufgenommen wird, existieren strenge Grenzwerte für die gesetzlich zulässige Emission von Quecksilber z.B. aus Verbrennungsanlagen und Kraftwerken. Trotz der heute bereits niedrigen Quecksilber-Reingaskonzentrationen - der derzeit in Deutschland zulässige Halbstundenmittelwert für Quecksilberemissionen aus Abfallverbrennungsanlagen beträgt 30 $\mu g/m^3$ i. N. tr. (i. N. tr.: im Normalzustand trocken) - werden aufgrund großer Volumenströme, beispielsweise aus Großkraftwerken, beachtliche Quecksilberfrachten erzielt, so dass eine weitere Minderung der derzeit zulässigen Grenzwerte angestrebt wird.

[0003] Diverse Verfahren zur Minderung von Quecksilberemissionen aus Kraftwerken, Abfallverbrennungsanlagen oder dgl. sind aus der Literatur bekannt. Welches der Verfahren für eine bestimmte Anwendung zweckmäßig ist, hängt stark von der eingebrachten Fracht und vom Chlorgehalt des Feuerungsgutes ab. Bei hohem Chlorgehalt ist der Anteil an ionischem Quecksilber im Rauchgas hoch. Ionisches Quecksilber lässt sich gut in Wäschern abscheiden. Das quasi-wasserunlösliche metallische Quecksilber kann beispielsweise durch den Zusatz von Oxidationsmitteln, wie Peroxide, Ozon oder Natriumchlorit, im Kesselrohgas vor der Rauchgasreinigung oder im entstaubten Kesselrohgas in ionisches Quecksilber überführt und anschließend in Wäschern abgeschieden werden. Weitere Verfahren zur Abscheidung des Quecksilbers sind: der Zusatz von Reaktionsmitteln, wie Natriumtetrasulfit, zur Bindung des Quecksilbers mittels Schwefel im Kesselrohgas vor Rauchgasreinigung oder im teilgereinigten Reingas; die verbesserte Auswaschung von ionischem Quecksilber durch pH- bzw. pCl-Absenkung in der sauren Wäsche oder durch Beaufschlagung mit 1,3,5-Triazin-2,4,6-trithiol (Trimercapto-S-triazin, TMT) in der schwach sauren oder schwach alkalischen Wäsche; die sorptive Abscheidung von ionischem und metallischem Quecksilber unter Zusatz von pulvrigen Sorbentien oder zerstäubten Suspensionen.

[0004] Bisherige Techniken zur Minderung sind nicht ausreichend effektiv und sind aufgrund ihrer z.T. hohen Zusatzinvestitionen und dem zusätzlichen Betriebsmittelverbrauch relativ teuer.

[0005] Aufgabe der Erfindung ist es, ein Verfahren zur Abscheidung von Quecksilber, insbesondere zur weitgehend vollständigen Abscheidung von Quecksilber (Hg), aus Rauchgasen von Hochtemperaturprozessen bereitzustellen. Das Verfahren soll breitestmögliche Anwendung finden, wie im Falle von im Wesentlichen konstanten niedrigen Hg-Konzentrationen, z.B. in Kohlekraftwerken, aber auch im Falle von relativ hohen Hg-Konzentrationen, z.B. in der Klärschlammverbrennung, oder sehr hohen Hg-Konzentrationen z.B. in der Hausmüll- oder Sondermüllverbrennung. Des Weiteren sollte das Verfahren keiner umfangreichen Nachrüstung der Hochtemperaturanlagen bedürfen sowie möglichst geringer zusätzlicher Betriebsmittel, so dass das Verfahren kostengünstig implementiert und betrieben werden kann.

[0006] Gegenstand der Erfindung ist ein Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen, welches darin besteht, dass der, gegebenenfalls mehrstufigen, Feuerung und/oder dem Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil Brom und/oder eine bromhaltige Verbindung und/oder eine Mischung verschiedener bromhaltiger Verbindungen zugeführt wird, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt, die Verbrennung in Gegenwart einer schwefelhaltigen Verbindung, insbesondere Schwefeldioxid, gegebenenfalls unter Zusatz von Schwefel und/oder einer schwefelhaltigen Verbindung und/oder einer Mischung verschiedener schwefelhaltiger Verbindungen erfolgt und anschließend das Rauchgas einer, gegebenenfalls mehrstufigen, Reinigung zur Abtrennung von Quecksilber aus dem Rauchgas unterzogen wird, welche eine Nasswäsche und/oder eine Trockenreinigung umfasst.

[0007] Die Abscheidung von Quecksilber aus Rauchgasen in einer der Verbrennung oder einem ähnlichen Hochtemperaturprozess nachgeschalteten Rauchgasreinigung hängt entscheidend davon ab, in welcher Speziesform das Quecksilber vor Eintritt in die Rauchgasreinigung vorliegt. Ein möglichst hoher Anteil an ionischem Quecksilber ist von Vorteil, da das ionische Quecksilber gut wasserlöslich, also auswaschbar, sowie an diversen Adsorbentien gut adsorbierbar ist. Der Zusatz von Brom bzw. bromhaltigen Verbindungen zur Feuerung bewirkt unter den gegebenen Bedingungen eines Hochtemperaturprozesses oder dgl. in Gegenwart einer schwefelhaltigen Verbindung, insbesondere in Gegenwart von Schwefeldioxid, eine weitgehende, im Wesentlichen vollständige, Oxidation des Quecksilbers und erlaubt daher eine starke Abscheidung des Quecksilbers aus Rauchgasen.

[0008] Unter Hochtemperaturanlagen werden im Sinne der vorliegenden Erfindung insbesondere Abfallverbrennungsanlagen, beispielsweise Hausmüll-, Sondermüll- und Klärschlammverbrennungsanlagen, sowie Kraftwerke, beispielsweise Steinkohleoder Braunkohlekraftwerke, aber auch sonstige Anlagen für Prozesse hoher Temperatur, wie z.B. das Zementbrennen, sowie Abfall mitverbrennende Hochtemperaturanlagen oder kombinierte (mehrstufige) Hochtemperaturanlagen, wie z.B. Kraftwerke oder Zementdrehrohröfen mit vorgeschalteter Abfallpyrolyse oder Abfallvergasung, verstanden. Die Dimension der Hochtemperaturanlage spielt für das erfindungsgemäße Verfahren keine Rolle.

PAC ET AL. EXHIBIT 1019
Page 1973

Vorteilhaft an dem erfindungsgemäßen Verfahren ist gerade, dass es auf unterschiedliche Typen von Hochtemperaturanlagen und auf Hochtemperaturanlagen von unterschiedlicher Größenordnung anwendbar ist. Dies schließt Anlagen mit einem Rauchgasvolumenstrom von nur $15 \cdot 10^3$ m³ i. N. tr./h, beispielsweise zur Klärschlammverbrennung, oder von $50 \cdot 10^3$ m³ i. N. tr./h, z.B. in Sondermüllverbrennungsanlagen, oder von $150 \cdot 10^3$ m³ i. N. tr./h, z.B. in der Hausmüllverbrennung, ebenso ein wie Großkraftwerke mit z.B. $2\text{-}3 \cdot 10^6$ m³ i. N. tr./h.

[0009] Für das erfindungsgemäße Verfahren ist es unerheblich, in welcher Form das zugeführte Brom vorliegt. Es ist möglich, freies oder organisch gebundenes oder anorganisch gebundenes Brom einzusetzen. Das Brom oder die bromhaltigen Verbindungen können einzeln oder im Gemisch zugeführt werden. Besonders bevorzugt wird eine wässrige Lösung von Bromwasserstoff oder ein Alkalibromid, insbesondere Natriumbromid, oder eine wässrige Lösung des Alkalibromids verwendet. Durch diese Ausführungsform ist das Verfahren wirtschaftlich besonders interessant, da die Kosten für zusätzliche Betriebsmittel niedrig gehalten werden können. Weiterhin bevorzugt ist eine Ausführungsform, in der die bromhaltige Verbindung bzw. das Gemisch verschiedener bromhaltiger Verbindungen aus bromreichen Abfallstoffen, wie z.B. niedrig- oder hochhalogenierte Flüssigabfälle, bestehen, welche Teil des Verbrennungsguts sind oder dem Verbrennungsgut, beispielsweise Sondermüll, beigemengt werden.

[0010] Das erfindungsgemäße Verfahren findet in Gegenwart einer schwefelhaltigen Verbindung statt. Die Zugabe einer bromhaltigen Verbindung nach dem erfindungsgemäßen Verfahren führt zu einer Gasphasenreaktion zwischen Quecksilber und Brom in Gegenwart von Schwefeldioxid. Da bei den im Sinne dieser Erfindung üblichen Verbrennungs- und sonstigen Hochtemperaturprozessen in der Regel Schwefeldioxid entsteht, ist für das erfindungsgemäße Verfahren in der Regel ein ausreichendes Angebot einer schwefelhaltigen Verbindung vorhanden. Ein ausreichendes Angebot im Sinne dieser Erfindung liegt vor, wenn unter Zugabe einer bromhaltigen Verbindung zu der Feuerung der Gehalt an Schwefeldioxid im Rauchgas vor der Rauchgasreinigung deutlich größer als Null ist. Wird bei einem Verbrennungsprozess jedoch kein oder nicht ausreichend Schwefeldioxid gebildet, muss dem Prozess eine schwefelhaltige Verbindung zugeführt werden. Dies kann in Form von freiem oder gebundenem Schwefel, beispielsweise Schwefelgranulat, Abfallschwefelsäure oder andere schwefelreiche Abfallstoffe, erfolgen. Darüber hinaus kann insbesondere auch zur Minderung eines zu hohen Gehalts an freien Halogenen im Rauchgas eine schwefelhaltige Verbindung zugesetzt werden, wenn z.B. mehr bromhaltige Verbindung zugeführt worden ist, als zur Oxidation des vorliegenden Quecksilbers notwendig ist. Die Zudosierung einer schwefelhaltigen Verbindung kann z.B. nach dem in der bisher unveröffentlichten Patentanmeldung DE 10131464 beschriebenen Verfahren zur korrosions- und emissionsarmen Mitverbrennung hochhalogenierter Abfälle in Abfallverbrennungsanlagen erfolgen. Nach diesem Verfahren wird in den primären und/oder sekundären Feuerraum Schwefel oder ein entsprechender Schwefelträger geregelt zudosiert. Die Regelung der Schwefelmenge erfolgt im Wesentlichen proportional zur mit den Abfällen eingetragenen aktuellen Halogengesamtfracht im Kesselrauchgas. Der zudosierte Schwefel verbrennt im Feuerraum zu Schwefeldioxid, was kesselintern zu einer weitgehenden Unterdrückung zwischenzeitlich gebildeter freier Halogene im Kesselrauchgas sowie nachfolgend zur stabilen Halogeneinbindung in der alkalischen Wäsche führt. Die Zudosierung von Schwefel wird so geregelt, dass der Soll-Schwefeldioxidgehalt im Rauchgas am Kesseleingang oder der Soll-Schwefeldioxidrestgehalt am Kesselende, d.h. im Kesselrohgas vor einer beispielsweise nassen Rauchgasreinigung, im stationären Betriebszustand über einen einfachen primären Regelkreis eingehalten werden.

[0011] Wird speziell Natriumbromid der Feuerung zugesetzt, so ist ein Mehrverbrauch an Schwefeldioxid zu beobachten, welcher auf die Sulfatierung des Natriumbromids im Hochtemperaturbereich zurückzuführen ist.

[0012] Andererseits stellt ein relativ hoher Gehalt einer schwefelhaltigen Verbindung, insbesondere an Schwefeldioxid, im Rauchgas keinen Nachteil für das erfindungsgemäße Verfahren dar. Ein hoher Gehalt an Schwefeldioxid kann beispielsweise bei der Verbrennung von Steinkohlen auftreten, welche üblicherweise zwischen 0,5 und 1 Gew.-% Schwefel enthalten, oder bei einer geregelten Zudosierung einer schwefelhaltigen Verbindung, welche zur Unterdrükkung zwischenzeitlich gebildeter freier Halogene (s.o.) zugesetzt wird. Unter den gegebenen Bedingungen eines Hochtemperaturprozesses findet auch in Gegenwart von überschüssigem Schwefeldioxid die Oxidation des Quecksilbers statt, welche nach dem erfindungsgemäßen Verfahren durch den Zusatz einer oder mehrerer bromhaltiger Verbindungen erzielt wird. Darin liegt ein besonderer Vorteil des vorliegenden Verfahrens, denn die Oxidation des Quecksilbers durch den Zusatz von bromhaltigen Verbindungen zeigt sich - anders als durch den Zusatz von chlorhaltigen Verbindungen - weitgehend unempfindlich gegenüber einem Überschuss an Schwefeldioxid.

[0013] Die Zugabe einer bromhaltigen Verbindung sowie gegebenenfalls einer schwefelhaltigen Verbindung erfolgt erfindungsgemäß zur Feuerung und/oder zum Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt. Die bromhaltige Verbindung, z.B. Natriumbromid, kann entweder in fester, z.B. als Salz, oder flüssiger Form, z.B. als wässrige Lösung, dem zu verfeuernden Abfallgemisch, der Kohle oder dgl. vor der Feuerung beigemengt werden. Die Zugabe kann auch in einen der Feuerung vorgeschalteten Anlagenteil erfolgen, beispielsweise einer Pyrolysetrommel, welche z.B. dem thermischen Aufschluss mitverbrannter Abfallstoffe dient, oder einer Kohlemühle. Die Verbindung kann ebenso während des Verbrennungsprozesses zugeführt werden. Umfasst die Feuerung mehrere Stufen, z.B. eine primäre und eine sekundäre Feuerung, kann die bromhaltige Verbindung in eine oder

PAC ET AL. EXHIBIT 1019
Page 1974

beide Brennkammern, beispielsweise in den Drehrohrofen und/oder die Nachbrennkammer, ebenfalls in fester oder flüssiger Form eingeführt werden. Vorzugsweise wird eine wässrige Lösung der Verbindung in einer der Brennkammern eingedüst. Ferner kann die Zugabe auch nach der Verbrennung, z.B. in einem nachgeschalteten Abhitzekessel, erfolgen, sofern die Temperatur des Rauchgases ausreichend hoch ist, d.h. mindestens 500°C, insbesondere mindestens 800°C, beträgt. In anderen Hochtemperaturprozessen, wie z.B. dem Zementbrennen, wird beispielsweise der heiße Ofenkopf des Zementdrehrohrofens und/oder die befeuerte Entsäuerungsstufe des nachgeschalteten Zementrohmehlvorwärmers mit der bromhaltigen Verbindung bestückt.

[0014] In einer weiteren Ausführungsform des erfindungsgemäßen Verfahrens ist es auch möglich, die bromhaltige Verbindung, beispielsweise eine wässrige Lösung von Bromwasserstoff oder von Natriumbromid, fein dispergiert der Verbrennungsluft und/oder gegebenenfalls einem rückgeführten Teilstrom, insbesondere rückgeführtem Rauchgas, rückgeführter Asche und rückgeführten Flugstäuben, zuzuführen.

[0015] Um eine möglichst vollständige, insbesondere 100%ige, Oxidation des Quecksilbers durch die Zugabe einer bromhaltigen Verbindung zu erzielen, wird die bromhaltige Verbindung bevorzugt in einem Massenverhältnis von Brom zu Quecksilber im Bereich von 10^2 bis 10^4 zugegeben. Wird die bromhaltige Verbindung in großem Überschuss zugefügt, wirkt sich dies nicht nachteilig auf das erfindungsgemäße Verfahren aus. Ein zu großer Überschuss muss jedoch vermieden werden, nicht zuletzt aus Kostengründen. Gegebenenfalls müssen zwischenzeitlich gebildete freie Halogene, wie z.B. freies Brom, durch die Zugabe einer schwefelhaltigen Verbindung unterdrückt bzw. stabil eingebunden werden (s.o.), da auch Bromemissionen in der Regel gesetzlich festgelegten Grenzwerten unterliegen.

[0016] Die Oxidation von Quecksilber kann prinzipiell auch durch chlorhaltige oder jodhaltige Verbindungen erfolgen. Es zeigt sich jedoch, dass bromhaltige Verbindungen Quecksilber unter den gegebenen Bedingungen von Hochtemperaturprozessen, wie der Temperatur, und insbesondere auch bei einem hohen Gehalt an Schwefeldioxid (s.o.) wirksamer oxidieren als chlorhaltige Verbindungen. Jodhaltige Verbindungen oxidieren im Vergleich zu bromhaltigen Verbindungen Quecksilber wirksamer. Aus wirtschaftlichen Gesichtspunkten werden in dem erfindungsgemäßen Verfahren allerdings bromhaltige Verbindungen bevorzugt eingesetzt. Gegebenenfalls in den Abfallstoffen, z.B. in Sondermüll, vorliegende chlor- oder jodhaltige Verbindungen tragen demnach zur Oxidation des Quecksilbers bei. In einer bevorzugten Ausführungsform erfolgt das erfindungsgemäße Verfahren zusätzlich zu den bromhaltigen Verbindungen in Gegenwart von Chlor und/oder Jod und/oder einer chlorhaltigen Verbindung und/oder einer jodhaltigen Verbindung und/oder einem Gemisch solcher Verbindungen. Die chlorhaltige und/oder jodhaltige Verbindung kann beispielsweise in Form von chlor- oder jodreichen Abfallstoffen in Ergänzung zu oder unter teilweisem Ersatz der zugesetzten bromhaltigen Verbindung zugeführt werden.

[0017] Nach dem erfindungsgemäßen Verfahren folgt nach der Verbrennung oder einem ähnlichen Hochtemperaturprozess unter Zusatz einer bromhaltigen Verbindung eine Reinigung des Rauchgases, wodurch das oxidierte Quecksilber möglichst weitgehend aus dem Rauchgas abgeschieden wird. Verschiedene Rauchgasreinigungsverfahren zur Abscheidung von u.a. ionischem Quecksilber sind aus dem Stand der Technik bekannt. Sie basieren entweder auf einer Nasswäsche oder einer Trockenreinigung oder einer Kombination beider und kann ggf. mehrstufig sein. Die Nasswäsche umfasst z.B. eine saure Wäsche, welche beispielsweise in einer mit Kreislaufwaschwasser bedüsten Quenche, einem Druckdüsen- oder Rotationszerstäuberwäscher oder einem Füllkörperwäscher erfolgt. Eine Wäsche kann aber ggf. auch nur schwachsauer oder alkalisch ausgeführt sein, beispielsweise im Fall niedriger Chlorwasserstofffrachten, aber hoher Schwefeldioxidfrachten.

[0018] In einer bevorzugten Ausführungsform umfasst die Rauchgasreinigung eine mehrstufige nasse Rauchgaswäsche mit mindestens einer stark sauren (pH kleiner 1) und/oder mindestens einer schwach sauren (pH 3-4) und/oder mindestens einer alkalischen Waschstufe.

[0019] Die Rauchgasreinigung kann auch eine auf der Adsorption von ionischen Quecksilberverbindungen basierende Trockenreinigung umfassen. Eine solche Reinigung kann beispielsweise durch quasitrockene Entschwefelung in einem Sprühtrockner durchgeführt werden, welcher mit einer Kalkmilch-Kohle-Suspension beaufschlagt ist, oder mit Hilfe von Festbettadsorbern, z.B. auf Basis von körniger Aktivkohle oder von Herdofenkoks oder von Mischungen derartiger Adsorbentien mit gekörntem Kalk, oder mit Hilfe von Flugstromadsorbern, z.B. elektrostatischen Gasreinigungsfiltern (EGR-Filter), oder mit Hilfe von Gewebefiltern, welche mit einem eingeblasenen feinpulvrigen Kalkhydrat-Aktivkohle- oder Kalkhydrat-Herdofenkoks-Gemisch beaufschlagt sind. Auch Zeolithe eignen sich zur Abscheidung von quecksilberhaltigen Verbindungen. Im Bezug auf die trockene Rauchgasreinigung zeigt sich ein weiterer Vorteil des erfindungsgemäßen Verfahrens. Die Anwendung des Verfahrens ist insbesondere auch für jene Hochtemperaturanlagen interessant, welche über keine nasse Rauchgasreinigung, sondern ausschließlich über eine trockene Reinigung mit einer Quecksilbersorptionsstufe verfügen. Quecksilberbromid $HgBr_2$ adsorbiert stärker an Trockensorbentien als Quecksilberchlorid $HgCl_2$. Beispielsweise verstärkt sich die Adsorption von Quecksilber am Flugstaub von EGR-Filtern.

[0020] In einer bevorzugten Ausführungsform umfasst die Rauchgasreinigung daher mindestens eine trockene oder quasitrockene, auf Adsorption basierende Reinigungsstufe, insbesondere unter Verwendung von elektrostatischen oder filternden Staubabscheidern.

PAC ET AL. EXHIBIT 1019
Page 1975

[0021] Des weiteren werden die mit Quecksilber beladenen Flugstäube aus gegebenenfalls vorhandenen Staubabscheidern zwecks Quecksilberentfrachtung vorzugsweise thermisch nachbehandelt, insbesondere in einer auf Temperaturen von mindestens 200°C beheizten Drehtrommel.

[0022] Bevorzugt wird in dem erfindungsgemäßen Verfahren der Quecksilbergehalt des Rauchgases, insbesondere der Gehalt an metallischem Quecksilber, nach der Rauchgasreinigung kontinuierlich gemessen und anhand des gemessenen Quecksilbergehalts die Menge an zugeführtem Brom und/oder bromhaltigen Verbindungen und/oder der Mischung bromhaltiger Verbindungen sowie gegebenenfalls Schwefel und/oder schwefelhaltigen Substanzen und/oder der Mischung schwefelhaltiger Substanzen geregelt. Ein relativ hoher Gehalt an metallischem Quecksilber im Rauchgas ist ein Indikator dafür, dass die Oxidation des Quecksilbers unvollständig verläuft und damit das Quecksilber in der Rauchgasreinigung unvollständig abgetrennt wird. Um Quecksilber möglichst vollständig zu oxidieren, muss in einem solchen Fall mehr bromhaltige Verbindung zugeführt werden. Zusätzlich kann der Gehalt an ionischem Quecksilber nach der Rauchgasreinigung gemessen werden und daraus der Abscheidegrad des ionischen Quecksilbers in der Rauchgasreinigung bestimmt werden. Der Gehalt an metallischem Quecksilber und ggf. an Quecksilber insgesamt im Kesselrohgas kann nach entsprechender Gasaufbereitung beispielsweise mit Hilfe eines Differenz-Absorptionsphotometers gemessen werden. Die kontinuierliche Messung von metallischem Quecksilber und ggf. auch von Quecksilber insgesamt im Reingas nach der nassen und/oder trockenen Rauchgasreinigung erfolgt vorzugsweise vor einer gegebenenfalls vorhandenen, nachgeschalteten SCR-Entstickungsanlage (SCR: selective catalytic reduction), da der metalloxidreiche Festbettkatalysator erhebliche Mengen an metallischem Quecksilber adsorbiert.

[0023] Nachfolgend wird die Erfindung anhand der Beispiele unter Bezugnahme auf die anliegenden Figuren näher erläutert. Es zeigen:

Figur 1 ein Schema einer Sondermüllverbrennungsanlage

Figur 2 ein Diagramm, welches den Gehalt von metallischem Quecksilber (Hg_{met}) im gewaschenen Kesselrauchgas, d.h. im Reingas, nach der Nasswäsche in µg/m³ i. N. tr. (Kurve 21, linke Ordinate) sowie den Gesamtgehalt von Brom (Br_{ges}) im Kesselrauchgas in mg/m³ i. N. tr. (Kurve 22, rechte Ordinate) in Abhängigkeit von der Zeit darstellt,

Figur 3 ein Diagramm, welches den Gesamtgehalt von Quecksilber (Hg_{ges}) im Kesselrauchgas, d.h. zugleich im Kesselrohgas, vor der Nasswäsche in µg/m³ i. N. tr. (Kurve 31, linke Ordinate) sowie den Gehalt von metallischem Quecksilber (Hg_{met}) im Reingas nach der Nasswäsche in µg/m³ i. N. tr. (Kurve 32, rechte Ordinate) in Abhängigkeit von der Zeit darstellt,

Figur 4 ein Diagramm, welches den Gesamtgehalt von Brom (Br_{ges}) im Kesselrauchgas, d.h. zugleich im Kesselrohgas, vor der Nasswäsche in mg/m³ i. N. tr. (Kurve 41, linke Ordinate) sowie den Gehalt von metallischem Quecksilber (Hg_{met}) im Reingas nach der Nasswäsche in µg/m³ i. N. tr. (Kurve 42, rechte Ordinate) als Funktion der Zeit darstellt,

Figur 5 ein Diagramm, welches das Massenverhältnis von Brom zu Quecksilber im Kesselrauchgas (Kurve 51, linke Ordinate) sowie den erzielten Gesamtabscheidegrad von Quecksilber in der mehrstufigen Nasswäsche in % (Kurve 52, rechte Ordinate) als Funktion der Zeit darstellt,

Figur 6 ein Diagramm, welches das Gewichtsverhältnis von metallischem Quecksilber zur Summe aus metallischem und ionischem Quecksilber (Hg_{met}/Hg_{ges}), d.h. den Hg_{met}-Speziesanteil im Kesselrohgas, in Gew.-% als Funktion des Gesamtgehaltes an Chlor (Kurve 61) bzw. an Brom (Kurve 62) im Kesselrohgas in mg/m³ i. N. tr. darstellt,

Figur 7 ein Diagramm, welches den Gesamtgehalt an Quecksilber (Hg_{ges}) im entstaubten Rohgas nach der elektrostatischen Gasreinigung (Kurve 71, linke Ordinate) bzw. den Gehalt an metallischem Quecksilber (Hg_{met}) nach der elektrostatischen Gasreinigung (Kurve 72, linke Ordinate) sowie die durch Quecksilberzudosierung herbeigeführte Anhebung des Gesamtgehalts an Quecksilber (Hg_{ges}) im Kesselrauchgas (Kurve 73, rechte Ordinate) als Funktion der Zeit darstellt,

Figur 8 ein Diagramm, welches das Gewichtsverhältnis von metallischem Quecksilber (Hg_{met}) zu der Summe aus metallischem und ionischem Quecksilber (Hg_{ges}), d.h. den Hg_{met}-Speziesanteil (Hg_{met}/Hg_{ges}), im entstaubten Kesselrohgas nach der elektrostatischen Gasreinigung in Gew.-% (Kurve 82) sowie den Gesamtgehalt an Brom (Br_{ges}) im Kesselrauchgas in mg/m³ i. N. tr. (Kurve 81) als Funktion der Zeit darstellt.

PAC ET AL. EXHIBIT 1019
Page 1976

Figur 9 ein Schema eines Industriekraftwerks mit zwei Schmelzkammerkesseln.

Beispiele

[0024] Die Beispiele 1-4 wurden in einer dem Schema in Figur 1 entsprechenden Sondermüllverbrennungsanlage der Bayer AG in Leverkusen durchgeführt. Der Drehrohrofen 3 als primärer Feuerraum wird mit Feststoffabfällen aus dem Bunker 1 über einen Krangreifer 2, mit Flüssigabfällen aus einem Flüssigabfalltank sowie mit Abfallgebinden über eine Gebindeaufgabe befeuert. Auch die Nachbrennkammer 4 als sekundärer Feuerraum wird mit Flüssigabfällen befeuert. Das Rauchgas wird über den Abhitzekessel 5 abgekühlt und anschließend, als sogenanntes Kesselrohgas, der nassen Rauchgasreinigung (mehrstufige Wäsche) zugeführt, welche eine Quenche 6, einen sauren Rotationszerstäuberwäscher 7, einen alkalischen Rotationszerstäuberwäscher 8 und eine elektrostatische Gasreinigung mit Wasserdampf-Teilkondensation 9 (KEGR) umfasst. Über Saugzüge 10 gelangt das gewaschene Rauchgas, als sogenanntes Reingas, in die nachgeschaltete katalytische Entstickungsanlage 11 (selektive katalytische Entstickung des Reingases mittels Ammoniak) und wird von dort über den Kamin 12 emittiert. Der Gehalt an metallischem Quecksilber (Hg_{met}) sowie gegebenenfalls der Gesamtgehalt an Quecksilber (Hg_{ges}) im gewaschenen Reingas nach KEGR wurde - nach entsprechender Aufbereitung - an der Messstelle 16 mit Hilfe eines Differenz-Absorptionsphotometers kontinuierlich bestimmt. Der Gehalt an Quecksilber insgesamt (Hg_{ges}) im emittierten Reingas wurde an der Messstelle 17, d. h. in einer Kaminhöhe von 22 m, quasikontinuierlich bestimmt durch Amalgamierung an einer periodisch ausgeheizten Goldfolie mit nachfolgendem Differenz-Absorptionsphotometer.

[0025] Beispiel 5 beschreibt die Anwendung des erfindungsgemäßen Verfahrens in einem Kohlekraftwerk der Bayer AG in Uerdingen, welches im Wesentlichen einen Schmelzkammerkessel und eine kraftwerkstypische Rauchgasreinigung, bestehend aus einer trockenen elektrostatischen Gasreinigung (EGR), einem schwachsauren, auf Kalkstein basierten Nasswäscher zur Rauchgasentschwefelung sowie einer SCR-Entstickungsanlage (SCR: selective catalytic reduction), umfasst.

Beispiel 1

[0026] Über einen Zeitraum von 116 Minuten wurde dem sekundären Feuerraum (Nachbrennkammer 4) über die Schauluke 15 eine Serie von Proben von metallischem Quecksilber in Kunststoffkapseln zugeführt (in Summe 3400 g, siehe Tabelle 1). Die Zugabe erfolgte in Abständen von ca. 5-10 Minuten mit zunehmender Quecksilbermenge. Das eingeworfene Quecksilber verdampft innerhalb von ca. 2-4 Minuten; demzufolge können die im Kesselrauchgas mit einem Volumenstrom von ca. $45 \cdot 10^3$ m^3 i. N. tr./h aufgetretenen momentanen Spitzenkonzentrationen an Quecksilber abgeschätzt werden. Die Abschätzung liefert zum Versuchsende hin Spitzenkonzentrationen von mehr als $130 \cdot 10^3$ $\mu g/m^3$ i. N. tr.

Tabelle 1:

Zugabe der Hg-Proben			
Uhrzeit	**Hg-Menge [g]**	**Uhrzeit**	**Hg-Menge [g]**
9:24	5	10:32	180
9:32	10	10:37	200
9:38	15	10:43	220
9:49	20	10:48	240
9:54	40	10:53	260
9:59	60	10:58	280
10:04	80	11:03	300
10:09	100	11:08	310
10:15	120	11:13	320
10:20	140	11:20	340
10:26	160		
Versuchsdauer [min]		**Hg-Gesamtmenge [g]**	
116		**3400**	

PAC ET AL. EXHIBIT 1019
Page 1977

[0027] Während des Versuchszeitraums wurde durch Mitverbrennung eines hochbromierten Flüssigabfalls (Zugabe zum Drehrohrofenkopf) im Kesselrauchgas von $45 \cdot 10^3$ m³ i.N. tr./h ein Bromgehalt von ca. $4 \cdot 10^3$ mg/m³ i. N. tr. aufrechterhalten, wie die Kurve 22 (rechte Ordinate) in Figur 2 zeigt (Bestimmung anhand des Durchsatzes und Bromgehaltes des hochbromierten Flüssigabfalls). Der Rest-SO_2-Gehalt im Kesselrohgas vor der Quenche war dabei mittels Zudosierung von Schwefelgranulat zum Drehrohrofenkopf auf $5{,}5 \cdot 10^3$ mg/Nm³ i. N. tr. ungewöhnlich hoch eingestellt (direkte SO_2-Messung im Kesselrohgas vor der Quenche). Damit war sichergestellt, dass für das erfindungsgemäße Verfahren ein ausreichendes Angebot an Schwefeldioxid vorhanden war. Das sonstige Verbrennungsgut bestand aus Festabfällen und schwachchlorierten Lösemitteln. Vor, während und nach der Quecksilberzugabe wurde an der Messstelle 16, d.h. nach der Rauchgasreinigung, der Gehalt an Quecksilber im Rauchgas gemessen. Wie die Kurve 21 (linke Ordinate) in Figur 2 zeigt, steigt trotz der Zugabe von erheblichen Quecksilbermengen der Gehalt an metallischem Quecksilber, welches durch die Wäsche durchschlägt, praktisch nicht an.

[0028] Darüber hinaus sind in Tabelle 2 die momentanen Austragungsströme von Quecksilber um 11:30 Uhr, d.h. kurz nach der Zugabe der letzten Quecksilberprobe und damit zum Zeitpunkt der höchsten Quecksilberkonzentration, aufgeführt, welche mit den Wäscherabwässern der nassen Rauchgasreinigung ausgetragen wurden. Umfangreiche abwasserseitige Messungen belegen, dass ca. 99,93 % des insgesamt ausgetragenen Quecksilbers als ionisches Quecksilber mit dem Abwasser der stark sauren Quenche (pH-Wert kleiner 1) und ca. 0,066 % mit dem Abwasser des alkalischen Rotationszerstäuberwäschers (pH-Wert ca. 7,5) ausgetragen wurden. Der geringe, nicht ausgewaschene Rest von nur 0,004 % des insgesamt ausgetragenen Quecksilbers wurde mit dem gewaschenen Reingas als metallisches Quecksilber ausgetragen. Nachweislich war im gewaschenen Reingas praktisch kein Hg_{ion} zu finden (Hg_{ion} = Null, d.h. vollständige Auswaschung des ionischen Quecksilbers und somit $Hg_{ges} = Hg_{met}$).

Tabelle 2:

Momentane Quecksilber-Austragungsströme [g/h] um 11:30 Uhr	
Quenche (einschließlich dem sauren Rotationszerstäuberwäscher)	1931
(Saurer Rotationszerstäuberwäscher, dessen Abwasser zur Quenche rückgeführt wird)	(468)
Alkalischer Rotationszerstäuberwäscher	1,32
Gewaschenes Reingas nach KEGR	0,069

Beispiel 2

[0029] Über einen Zeitraum von 130 Minuten wurde dem sekundären Feuerraum (Nachbrennkammer 4) über eine Düse in der Nachbrennkammerdecke kontinuierlich eine wässrige $HgCl_2$-Lösung zugeführt. Dabei wurde die zudosierte Menge in Zeitschritten von etwa 5 Minuten angehoben. Figur 3 zeigt den so herbeigeführten Anstieg der Konzentration von Quecksilber im Kesselrauchgas in der Zeit zwischen ca. 10:45 und 13:00 Uhr. Das eindosierte Quecksilber wird in der Nachbrennkammer unverzüglich als metallisches Quecksilber Hg_{met} freigesetzt. Die Gesamtkonzentration von Quecksilber im Kesselrauchgas stieg auf diese Weise bis auf Werte von $18 \cdot 10^3$ µg/m³ i. N. tr. an (Kurve 31 und linke Ordinate). Die Hg-Konzentration im Kesselrauchgas wurde aus dem zugegebenen Quecksilbermengenstrom und dem betrieblich gemessenen Rauchgasvolumenstrom berechnet. Während des Versuchszeitraums wurde durch Mitverbrennung eines hochbromierten Flüssigabfalls (Zugabe über einen Brenner am Drehrohrofenkopf) im Kesselrauchgas von $45 \cdot 10^3$ m³ i.N. tr./h ein Bromgehalt von ca. $9 \cdot 10^3$ mg/m³ i. N. tr. aufrechterhalten (Bestimmung anhand des Durchsatzes und Bromgehalt des mitverbrannten hochbromierten Flüssigabfalls). Der Rest-SO_2-Gehalt im Kesselrohgas vor Quenche war dabei mittels Zudosierung von Schwefelgranulat zum Drehrohrofenkopf auf ca. $4 \cdot 10^3$ mg/Nm³ i. N. tr. eingestellt (direkte SO_2-Messung im Kesselrohgas vor der Quenche).

[0030] Im Zeitraum zwischen ca. 11:00 und 13:00 Uhr wurde im gewaschenen Reingas nach der KEGR eine Konzentration von metallischem Quecksilber von weniger als 10 µg/m³ i. N. tr. beobachtet. Nachweislich war im gewaschenen Reingas auch hier praktisch kein Hg_{ion} zu finden (Hg_{ion} = Null, d.h. vollständige Auswaschung des ionischen Quecksilbers und somit $Hg_{ges} = Hg_{met}$). Bei einem kurzzeitigen Ausfall der Bromzugabe gegen 13:05 Uhr stieg die Konzentration von Hg_{met} sprunghaft auf ca. 800 µg/m³ i. N. tr. an und kehrte aber unverzüglich auf ihren niedrigen Ausgangswert von weniger als 10 µg/m³ i. N. tr. zurück, als die Bromzugabe wieder einsetzte (Kurve 32 und rechte Ordinate).

Beispiel 3

[0031] In der Zeit zwischen ca. 8:30 und 14:45 Uhr, d.h. über einen Zeitraum von 675 Minuten, wurde dem sekundären Feuerraum (Nachbrennkammer 4) über eine Düse in der Nachbrennkammerdecke kontinuierlich eine wässrige

PAC ET AL. EXHIBIT 1019
Page 1978

$HgCl_2$-Lösung zugeführt. Dabei wurde nunmehr aber der zudosierte Hg-Mengenstrom konstant gehalten, entsprechend einer Konzentration von Quecksilber im Kesselrauchgas von ca. $9{,}6 \cdot 10^3$ µg/m³ i. N. tr.

[0032] In diesem Versuchszeitraum (vgl. Fig. 4 bzw. Fig. 5) wurde Brom in Form eines hochbromierten Flüssigabfalls über einen Brenner am Drehrohrofenkopf zugegeben, jedoch wurde die zugegebene Brommenge schrittweise verringert, womit der Bromgehalt im Kesselrauchgas stufenweise von ca. $9 \cdot 10^3$ auf ca. $3 \cdot 10^3$ mg/m³ i. N. tr. abgesenkt wurde (Kurve 41 in Fig. 4 und linke Ordinate). Der mittels Zudosierung von Schwefelgranulat herbeigeführte Rest-SO_2-Gehalt im Kesselrohgas war mit ca. $4{,}3 \cdot 10^3$ mg/m³ i. N. tr in diesem Versuchszeitraum wiederum sehr hoch gewählt worden. Neben dem hochbromierten Flüssigabfall wurde auch ein chlorierter Flüssigabfall mitverbrannt.

[0033] Wie Figur 4 bzw. Figur 5 zu entnehmen ist, war der Gehalt an metallischem Quecksilber im gewaschenen Reingas nach KEGR deutlich kleiner als 2 µg/m³ i. N. tr. (Kurve 42 in Fig. 4 und rechte Ordinate). Nachweislich war im gewaschenen Reingas auch hier praktisch kein Hg_{ion} zu finden (Hg_{ion} = Null, d.h. vollständige Auswaschung des ionischen Quecksilbers und somit $Hg_{ges} = Hg_{met}$). Entsprechend war der Abscheidegrad von Quecksilber in der Nasswäsche deutlich größer als 99,98 % (Kurve 52 in Fig. 5 und rechte Ordinate), solange der Bromgehalt größer als $3 \cdot 10^3$ mg/m³ i. N. tr. (Kurve 41 und linke Ordinate) bzw. das Brom-Quecksilber-Massenverhältnis größer als 500 µg Brom/µg Quecksilber betrug (Kurve 51 in Fig.5 und linke Ordinate). Gegen 13:30 Uhr sinkt der Bromgehalt im Rauchgas auf $3 \cdot 10^3$ mg/m³ i. N. tr. bzw. das Brom-Quecksilber-Massenverhältnis auf ca. 335 µg Brom/µg Quecksilber. Dabei steigt die Konzentration von metallischem Quecksilber nach der Nasswäsche auf bis zu 20 µg/m³ i. N. tr. (Kurve 42 in Fig. 4 und linke Ordinate) bzw. nimmt der Hg-Abscheidegrad auf 99,8 % ab (Kurve 52 in Fig. 5 und rechte Ordinate). Darüber hinaus führt eine kurzzeitige Unterbrechung der Chlor-Zugabe kurz nach 14:30 Uhr zu einer Spitzenkonzentration von metallischem Quecksilber nach der Wäsche von ca. 117 µg/m³ i. N. tr. (Kurve 42 in Fig. 4 und linke Ordinate) bzw. zu einem kurzzeitigen Abfall des Abscheidegrades auf ca. 98,4 % (Kurve 51 in Fig. 5 und rechte Ordinate). Hieran wird die gegenüber Brom vergleichsweise geringe Wirkung von Chlor deutlich.

Beispiel 4

[0034] Figur 6 illustriert einen Versuch zum Vergleich der Wirkung von Brom und Chlor auf die Oxidation von Quecksilber im Kesselrauchgas der oben beschriebenen Sondermüllverbrennungsanlage. Dabei lagen ein durch Zudosierung von $HgCl_2$ eingestellter Hg_{ges}-Gehalt von 130 µg/m³ i. N. tr. bei einem durch Mitverbrennung chlorarmer Lösemittel eingestellten Chlorgehalt (Cl_{ges}) im Kesselrauchgas von $1{,}35 \cdot 10^3$ mg/m³ i. N. tr. sowie einem durch Zudosierung von Schwefelgranulat eingestellten Restgehalt an Schwefeldioxid im Kesselrohgas von $1{,}5 \cdot 10^3$ mg/m³ i. N. tr. vor. Der Messpunkt 63 zeigt den zunächst ohne Bromzusatz, d.h. allein durch Chlor, erzielten Hg_{met}-Speziesanteil von ca. 63 Gew.-% im Kesselrohgas vor der Nasswäsche. Die anlagenspezifische Kurve 61, welche auf ca. 20 Betriebsversuchen an einer Sondermüllverbrennungsanlage mit Verbrennung hochchlorierter Flüssigabfälle basiert, zeigt, wie der Hg_{met}-Speziesanteil (Hg_{met}/Hg_{ges}) mit wachsendem Chlorgehalt Cl_{ges} im Kesselrauchgas zurückgeht.

[0035] Ausgehend von einem Hg_{met}-Speziesanteil von ca. 63 Gew.-% im Kesselrohgas vor der Nasswäsche (Messpunkt 63 mit Cl_{ges}-Gehalt als Abszisse bzw. Messpunkt 63' mit Br_{ges}-Gehalt als Abszisse) wurde dann in drei Schritten eine zunehmende Menge einer bromhaltigen Verbindung zudosiert (vgl. Pfeil 64, der den Übergang von der Darstellung des Hg_{met}-Speziesanteil in Abhängigkeit von dem Cl_{ges}-Gehalt zu der Darstellung in Abhängigkeit von dem Br_{ges}-Gehalt markiert). Dabei wurde der Bromgehalt im Kesselrauchgas von zunächst 0 mg/m³ i. N. tr. (Messpunkt 63' mit Brges-Gehalt als Abszisse) durch Zudosierung von wässriger Bromwasserstofflösung bzw. von wässriger Natriumbromidlösung (Eindüsung an der Nachbrennkammerdecke 14, Fig. 1) in drei Schritten auf 50, 100 und 120 mg/m³ i. N. tr. (Messpunkte 62 mit Brg_{es}-Gehalt als Abszisse) angehoben. Dabei ging der Hg_{met}-Speziesanteil (Hg_{met}/Hg_{ges}) im Kesselrohgas vor der Nasswäsche - ausgehend von ca. 63 Gew.-%-bis auf 30 Gew.-% zurück.

[0036] Der Vergleich weist die deutlich effektivere Oxidation des Quecksilbers durch bromhaltige Verbindungen im Vergleich zu chlorhaltigen Verbindungen am Beispiel einer Sondermüllverbrennungsanlage nach. Um allein mittels Chlor einen Hgmet-Speziesanteil von nur 30 Gew.-% zu erreichen, müsste man den Cl_{ges}-Gehalt gemäß der Chlorierungskurve 61 auf $4 \cdot 10^3$ mg/m³ i. N. tr. erhöhen. Statt dessen erreicht man dies mit nur 120 mg/m³ i. N. tr. an Brom. Brom erscheint daher etwa 25-fach wirksamer als Chlor. Die Hg-Bromierungskurve 65 (Br_{ges}-Gehalt als Abszisse) entspricht unter Berücksichtigung dieses Faktors der vollständig vermessenen Hg-Chlorierungskurve 61 (Cl_{ges}-Gehalt als Abszisse). Gleiches gilt für im Fall von Kraftwerksrauchgasen, wo allerdings die anlagenspezifische Hg-Chlorierungskurve und die entsprechende Hg-Bromierungskurve 65 zu wesentlich niedrigeren Halogengehalten hin verschoben sind.

Beispiel 5

[0037] Figur 7 und Figur 8 illustrieren Versuche zum Nachweis der Wirkung von Brom auf die Quecksilberabscheidung in einem Kohlekraftwerk der Bayer AG in Uerdingen (vgl. Fig. 9). In dem Kohlekraftwerk erfolgte ein Versuch mit Zudosierung von wässriger $HgCl_2$-Lösung und von wässriger NaBr-Lösung in den Feuerraum zum Nachweis der Wir-

PAC ET AL. EXHIBIT 1019
Page 1979

kung von Brom auf die Hg-Oxidation. Das Kraftwerk umfasst zwei parallele Schmelzkammerkessel 91, 91' mit Temperaturen im Feuerraum um 1450°C. Die Schmelzkammerkesssel 91, 91' werden mit Kohle 92, 92' bestückt. Über die jeweiligen Luftvorwärmer 93, 93' wird den Schmelzkammerkesseln 91, 91' Frischluft 94, 94' zugeführt. Das Kesselrohgas 95, 95' wird über elektrostatische Gasreiniger (EGR) 96, 96' dem gemeinsamen schwachsauren (pH = 5,3) Nasswäscher als Rauchgasentschwefelungsanlage (REA-Wäscher) 97 zugeführt. Das gewaschene Kesselrauchgas (Reingas) wird anschließend in zwei parallele katalytisch wirkende Entstickungsanlagen (SCR-Entstickungsanlage) 98, 98' überführt, bevor es über Kamine 100, 100' emittiert wird. Der in den EGR abgeschiedene Flugstaub 99, 99' wird zu 100 % in die Feuerung des jeweiligen Schmelzkammerkessels zurückgeführt. An der Messstelle 101 nach der EGR 96 wurden die Gehalte an Hg_{met} und Hg_{ges} im entstaubten Kesselrohgas kontinuierlich erfasst.

[0038] Es wurde kein Schwefel zudosiert. Der Gehalt an Schwefeldioxid im Kesselrauchgas von $1{,}3 \cdot 10^3$ i. N. tr. resultierte ausschließlich aus dem verbrannten Kohleschwefel selbst. Der Gesamtquecksilbergehalt im entstaubten Rohgas nach der EGR, d.h. vor der Nasswäsche, betrug zu Beginn bei reiner Kohleverbrennung (polnische Steinkohle) im Mittel nur 22,5 $\mu g/m^3$ i. N. tr., vgl. Fig. 7, Kurve 71 (Gesamtgehalt an Quecksilber Hg_{ges}) um 8:30 Uhr, der Gehalt an metallischem Quecksilber im Mittel nur 8,8 $\mu g/m^3$ i. N. tr., vgl. Fig. 7, Kurve 72 (Gehalt an metallischem Quecksilber Hg_{met}) um 8:30 Uhr. Die Zahnung beider Kurven 71, 72 im 10-Minuten-Takt beruht auf der regelmäßigen Abklopfung der EGR; wodurch unmittelbar nach Abreinigung der Staubschichten im entstaubten Kesselrohgas hinter der EGR höhere Gehalte auftreten. Um 9.15 Uhr wurde mit der Zudosierung von Quecksilber (als wässrige $HgCl_2$-Lösung) und um 10:30 dann auch mit der Zudosierung von Brom (als wässrige NaBr-Lösung) in den Feuerraum begonnen. Die Kurve 73 (Figur 7, rechte Ordinate) stellt die durch Zudosierung von Quecksilber herbeigeführte Erhöhung des Hg_{ges}-Gehalts im Kesselrauchgas dar. Zwischen ca. 9:30 und 13:00 Uhr betrug die mittels $HgCl_2$-Zudosierung herbeigeführte Anhebung des Gesamtgehalts an Quecksilber im Rauchgas vor der EGR mindestens ca. 220 $\mu g/m^3$ i. N. tr. (Kurve 73, rechte Ordinate). Die Kurve 81 in Fig. 8 stellt die durch Zudosierung von wässriger NaBr-Lösung herbeigeführte Erhöhung des Br-Gehalts im Kesselrauchgas dar. Um 10:30 Uhr wurde der Bromgehalt im Rauchgas vor der EGR zunächst um mindestens 75 mg/m^3 i. N. tr. angehoben und schrittweise wieder abgesenkt. Um 16:10 Uhr erfolgte eine neuerliche Anhebung des Bromgehalts um ca. 43 mg/m^3 i. N. tr. Wegen der Rückführung der Flugasche in die Schmelzkammerfeuerung und somit auch der Rückführung von an der Flugasche sorbiertem Quecksilber bzw. Brom handelt es sich hierbei um Mindestanhebungen, wie sie sich aus den zudosierten Mengenströmen und dem Rauchgasvolumenstrom (ca. $110 \cdot 10^3$ m^3 i. N. tr./h) ergeben. Die tatsächlichen Hg- und Br-Gehalte im Rohgas vor der EGR liegen demzufolge (Kreislauf zwischen Schmelzkammerfeuerung und EGR) etwas höher.

[0039] Die Kurven 71 bzw. 72 (linke Ordinate) in Figur 7 zeigen, wie mit dem Zusatz der bromhaltigen Verbindung der Gehalt an Quecksilber im Rauchgas deutlich zurückgeht. Dies gilt einerseits für das ionische Quecksilber (Differenz zwischen Hg_{ges} und Hg_{met}), welches in Anwesenheit der bromhaltigen Verbindung vermehrt gebildet und offensichtlich am rückgeführten Flugstaub adsorbiert wird, und gilt andererseits aber stärker noch für das metallische Quecksilber, dessen Gehalt im entstaubten Rohgas nach EGR trotz des Zusatzes von Quecksilber annähernd auf den Ausgangsgehalt vor der Quecksilberzugabe zurückkehrt. Von 10:30 Uhr bis 13:00 Uhr (Ende der Br-Zudosierung) und weit darüber hinaus betrug der Gehalt an Hg_{met} weniger als 10 $\mu g/m^3$ i. N. tr. Erst mit dem Ende der neuerlichen Zugabe der Natriumbromidlösung gegen 19:00 Uhr steigt der Gehalt von Hg_{ges} deutlich an. Weiterhin zeigt die Kurve 82 in Figur 8 den zunächst schlagartigen Rückgang des Speziesanteils an metallischem Quecksilber mit der Zugabe von Brom (Absenkung von ca. 40 Gew.-% auf ca. 10 Gew.-% gegen 10:30 Uhr). Entsprechendes zeigt sich nach ca. 17:00 Uhr bei der neuerlichen Quecksilber- und Bromzugabe an dem allmählichen Rückgang des Hg_{met}-Speziesanteils bis auf nur ca. 5 Gew.-% gegen 20:45 Uhr. Infolge der Hg-Zudosierung und der verstärkten Hg-Adsorption stieg der Hg-Gehalt im zur Schmelzkammer rückgeführten EGR-Flugstaub von anfänglich ca. 2-5 mg/kg im Laufe des Versuchs auf 55 mg/kg an.

Patentansprüche

1. Verfahren zur Abscheidung von Quecksilber aus Rauchgasen von Hochtemperaturanlagen, insbesondere von Kraftwerken und Abfallverbrennungsanlagen, **dadurch gekennzeichnet, dass**

   - der, gegebenenfalls mehrstufigen, Feuerung und/oder dem Rauchgas in einem der Feuerung nachgeschalteten Anlagenteil Brom und/oder eine bromhaltige Verbindung und/oder eine Mischung verschiedener bromhaltiger Verbindungen zugeführt wird, wobei die Temperatur beim Kontakt der bromhaltigen Verbindung mit dem Rauchgas mindestens 500°C, vorzugsweise mindestens 800°C, beträgt,

   - die Verbrennung in Gegenwart einer schwefelhaltigen Verbindung, insbesondere Schwefeldioxid, gegebenenfalls unter Zusatz von Schwefel und/oder einer schwefelhaltigen Verbindung und/oder einer Mischung verschiedener schwefelhaltiger Verbindungen erfolgt

PAC ET AL. EXHIBIT 1019
Page 1980

- und anschließend das Rauchgas einer, gegebenenfalls mehrstufigen, Reinigung zur Abtrennung von Quecksilber aus dem Rauchgas unterzogen wird, welche eine Nasswäsche und/oder eine Trockenreinigung umfasst.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die bromhaltige Verbindung eine wässrige Lösung von Bromwasserstoff und/oder ein Alkalibromid, insbesondere Natriumbromid, und/oder eine wässrige Lösung von Alkalibromid ist.

3. Verfahren nach einem der Ansprüche 1 bis 2, **dadurch gekennzeichnet, dass** die bromhaltige Verbindung und/oder die Mischung bromhaltiger Verbindungen flüssige und/oder feste bromreiche Abfallstoffe sind.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** das Brom und/oder die bromhaltige Verbindung und/oder die Mischung bromhaltiger Verbindungen der Verbrennungsluft und/oder gegebenenfalls einem rückgeführten Teilstrom, insbesondere dem rückgeführtem Rauchgas und den rückgeführten Flugstäuben, zugesetzt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** das Massenverhältnis von Brom zu Quecksilber im Bereich von 10^2 bis 10^4 liegt.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** die Verbrennung zusätzlich in Gegenwart von Chlor und/oder einer chlorhaltigen Verbindung und/oder einer Mischung verschiedener chlorhaltiger Verbindungen und/oder Jod und/oder einer jodhaltigen Verbindung und/oder einer Mischung verschiedener jodhaltiger Verbindungen durchgeführt wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, dass** die Rauchgasreinigung eine mehrstufige nasse Rauchgaswäsche mit mindestens einer stark sauren und/oder mindestens einer schwach sauren und/oder alkalischen Waschstufe umfasst.

8. Verfahren nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, dass** die Rauchgasreinigung mindestens eine trockene oder quasitrockene, auf Adsorption basierende Reinigungsstufe umfasst, insbesondere unter Verwendung von elektrostatischen oder filternden Staubabscheidern.

9. Verfahren nach Anspruch 8, **dadurch gekennzeichnet, dass** die mit Quecksilber beladenen Flugstäube aus gegebenenfalls vorhandenen Staubabscheidern zwecks Quecksilberentfrachtung thermisch nachbehandelt wird, insbesondere in einer auf Temperaturen von mindestens 200°C beheizten Drehtrommel.

10. Verfahren nach einem der Ansprüche 1 bis 9, **dadurch gekennzeichnet, dass** der Quecksilbergehalt des Rauchgases, insbesondere der Gehalt an metallischem Quecksilber, nach der Rauchgasreinigung kontinuierlich gemessen wird und anhand des gemessenen Quecksilbergehalts die Menge an zugeführtem Brom und/oder bromhaltigen Verbindungen sowie gegebenenfalls Schwefel und/oder schwefelhaltigen Verbindungen geregelt wird.

PAC ET AL. EXHIBIT 1019
Page 1981

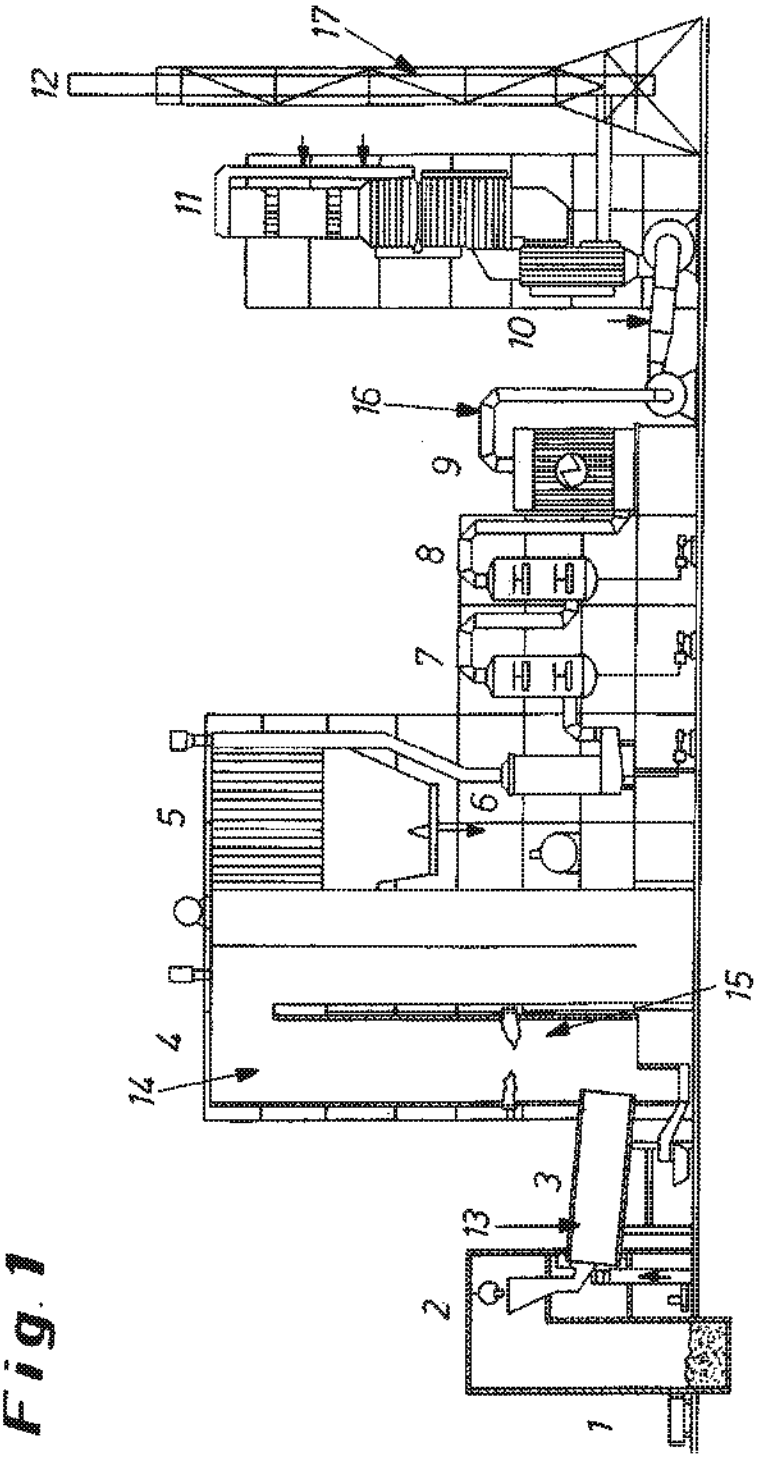


Fig. 1

PAC ET AL. EXHIBIT 1019
Page 1982

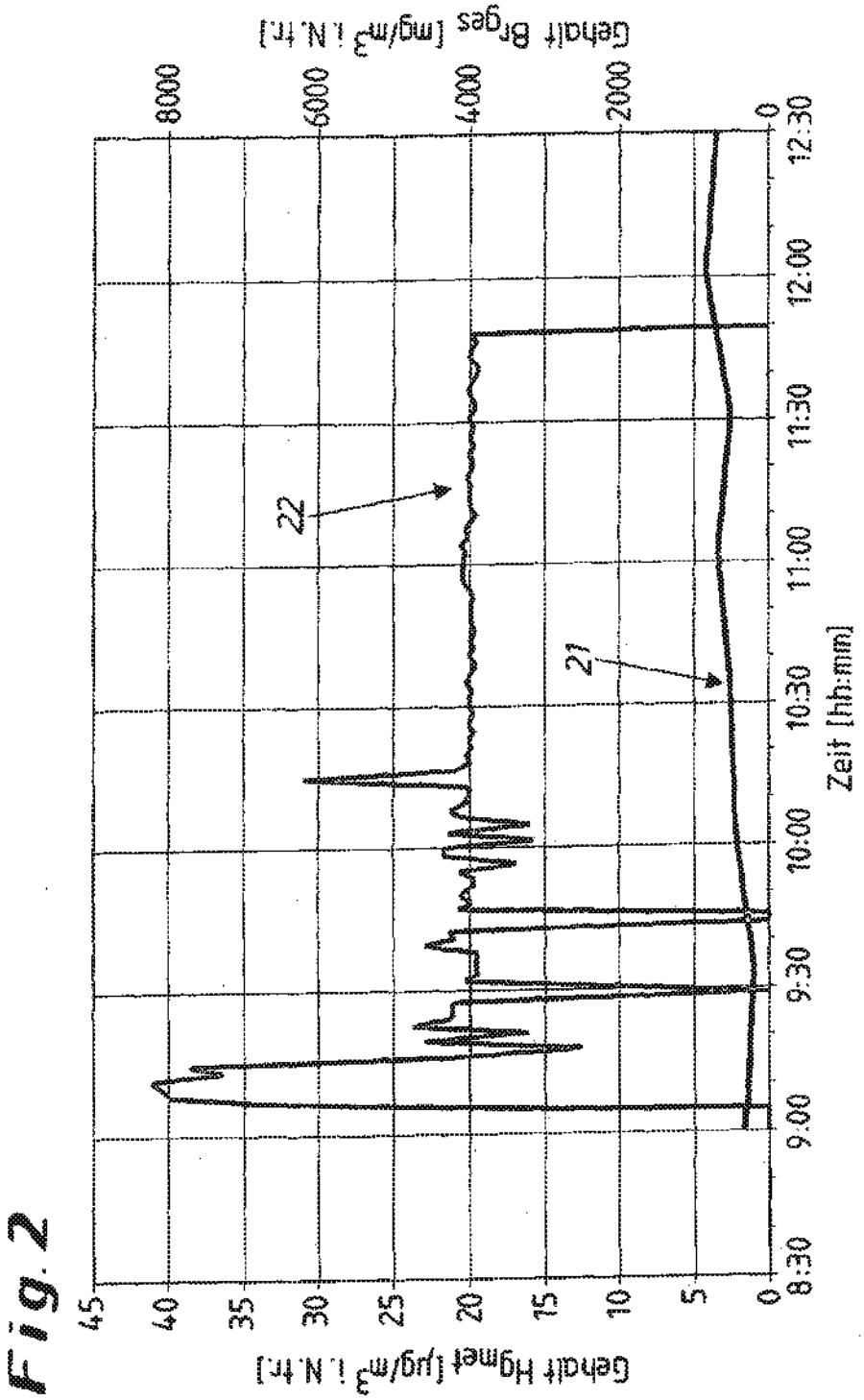


Fig. 2

PAC ET AL. EXHIBIT 1019
Page 1983

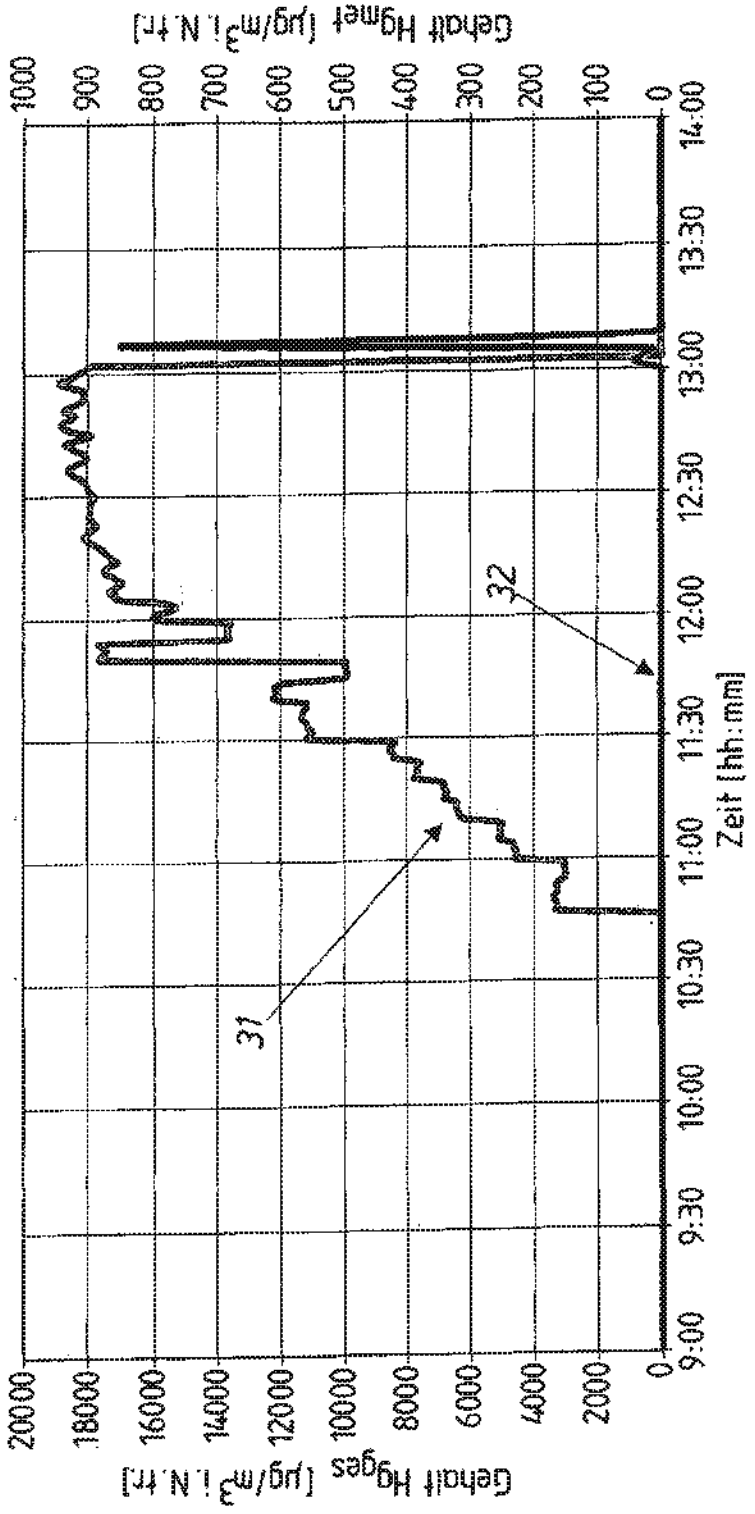
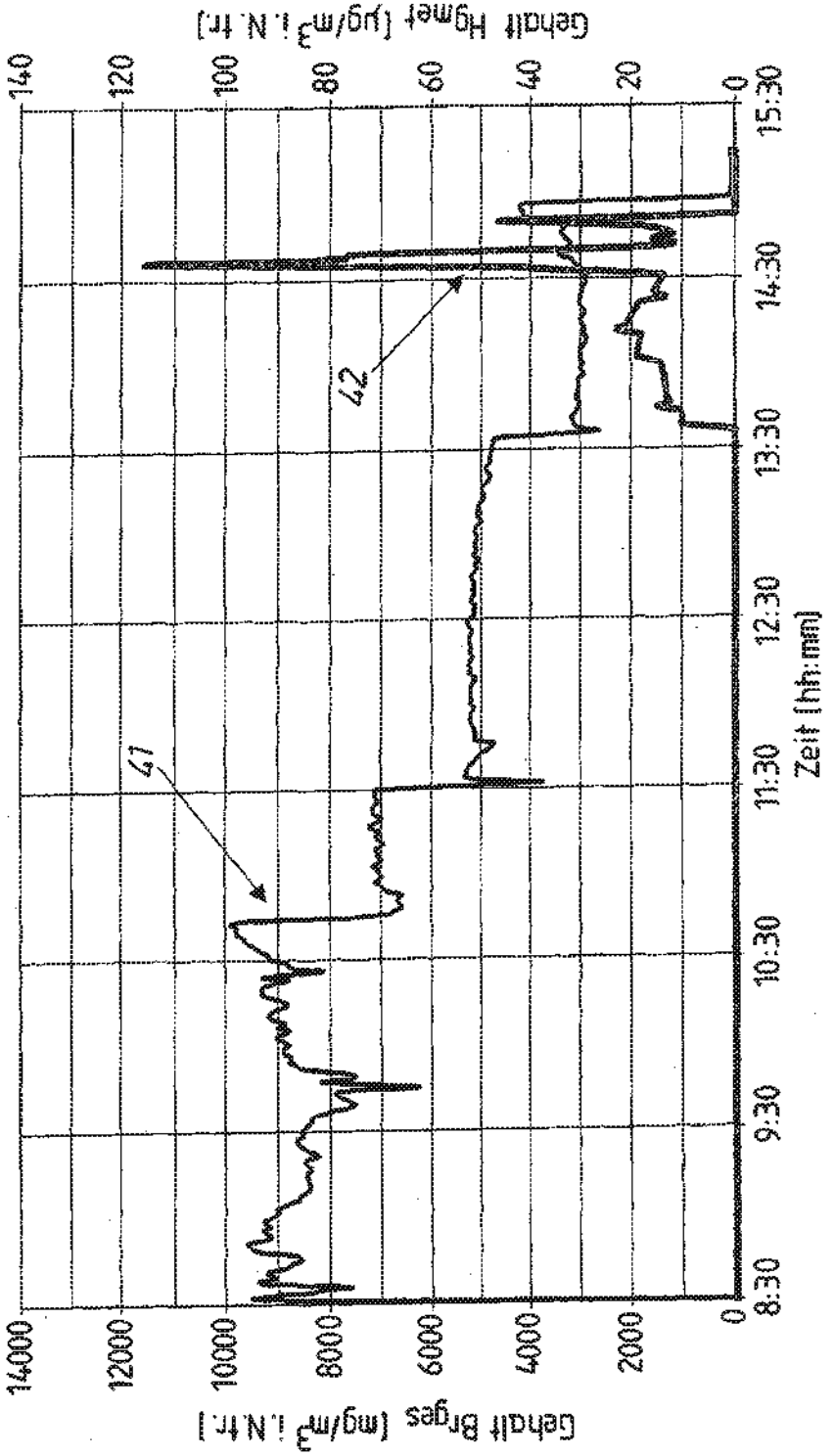


Fig. 3

PAC ET AL. EXHIBIT 1019
Page 1984

Fig. 4



PAC ET AL. EXHIBIT 1019
Page 1985

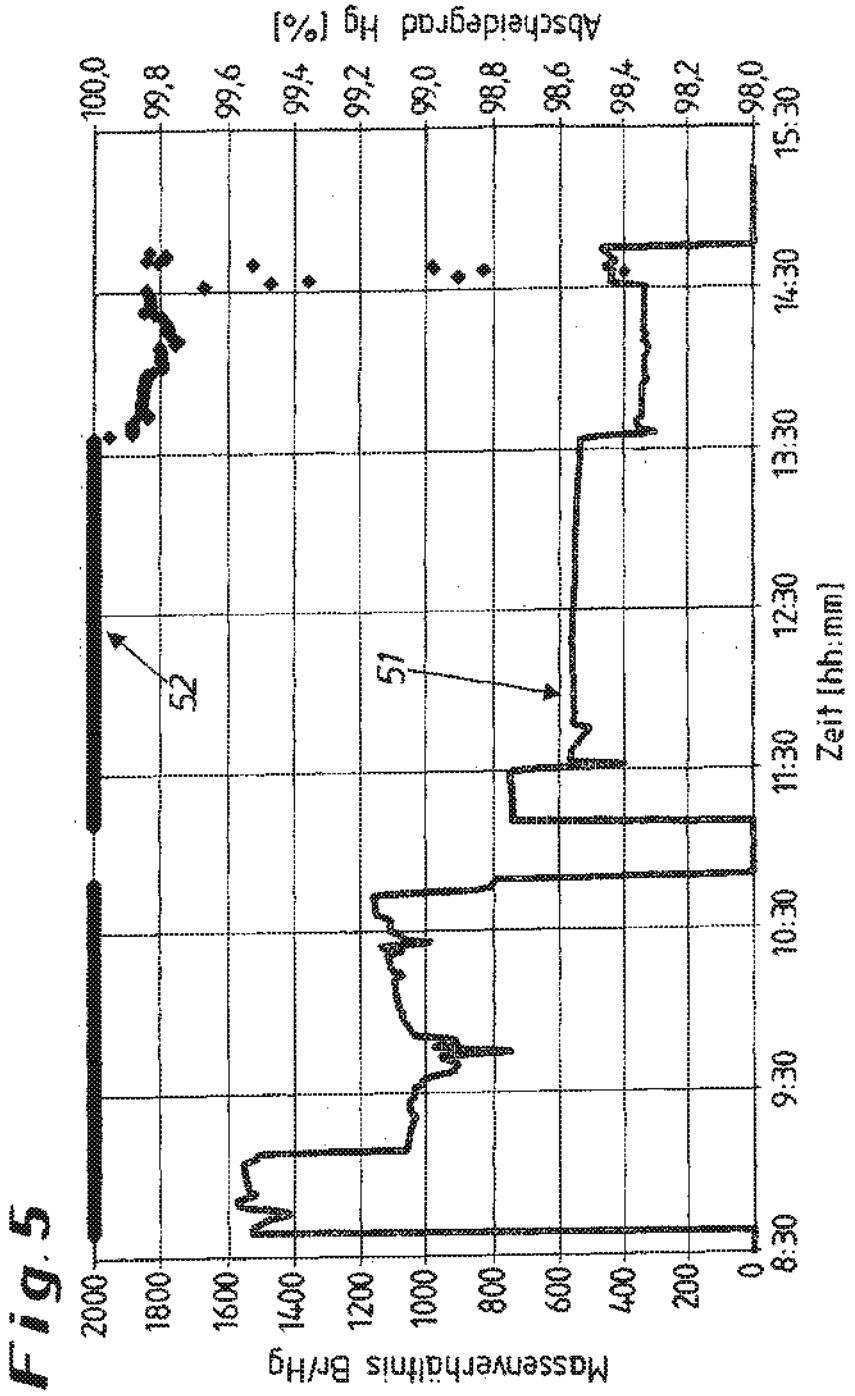


Fig. 5

PAC ET AL. EXHIBIT 1019
Page 1986

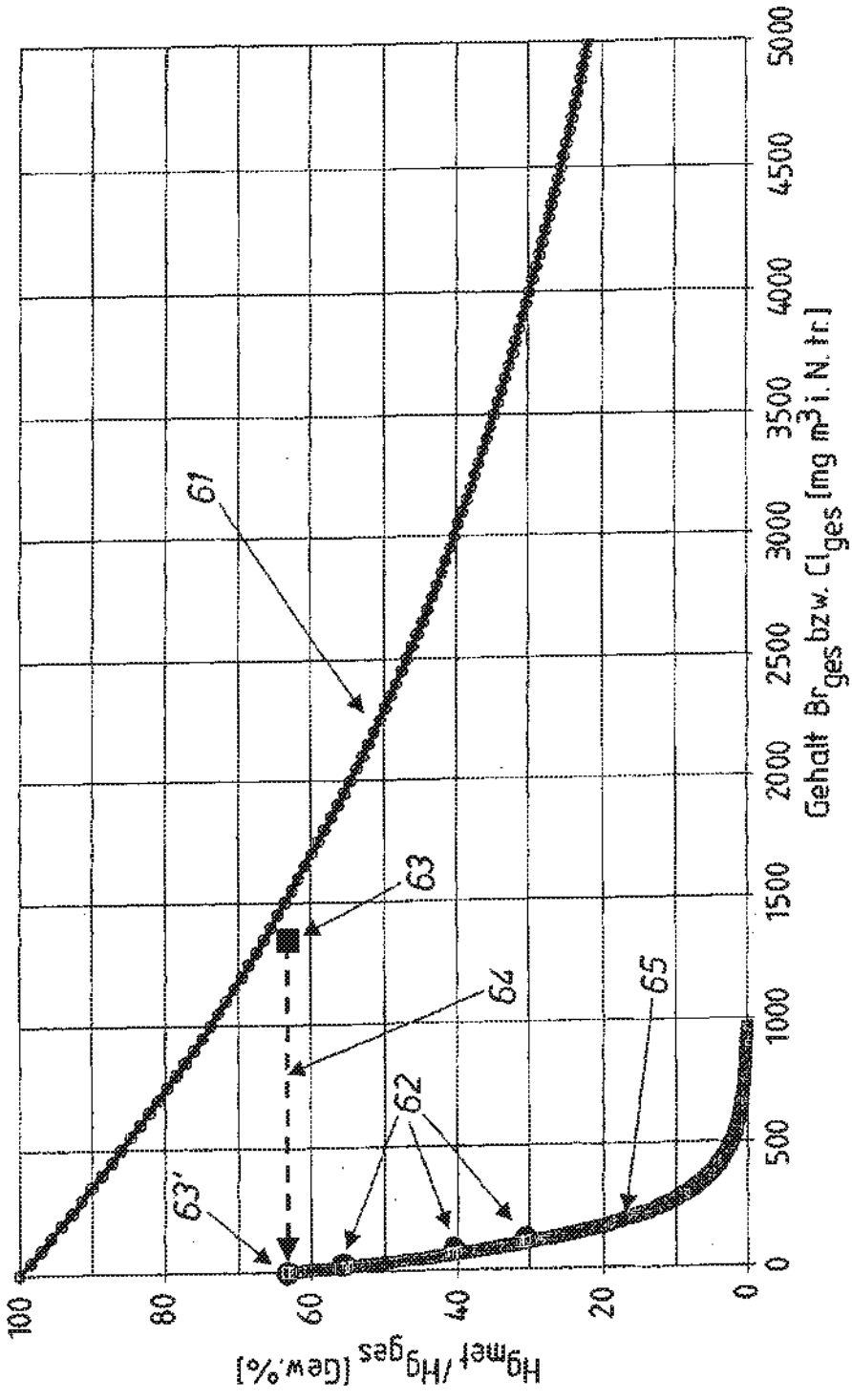


Fig. 6

PAC ET AL. EXHIBIT 1019
Page 1987

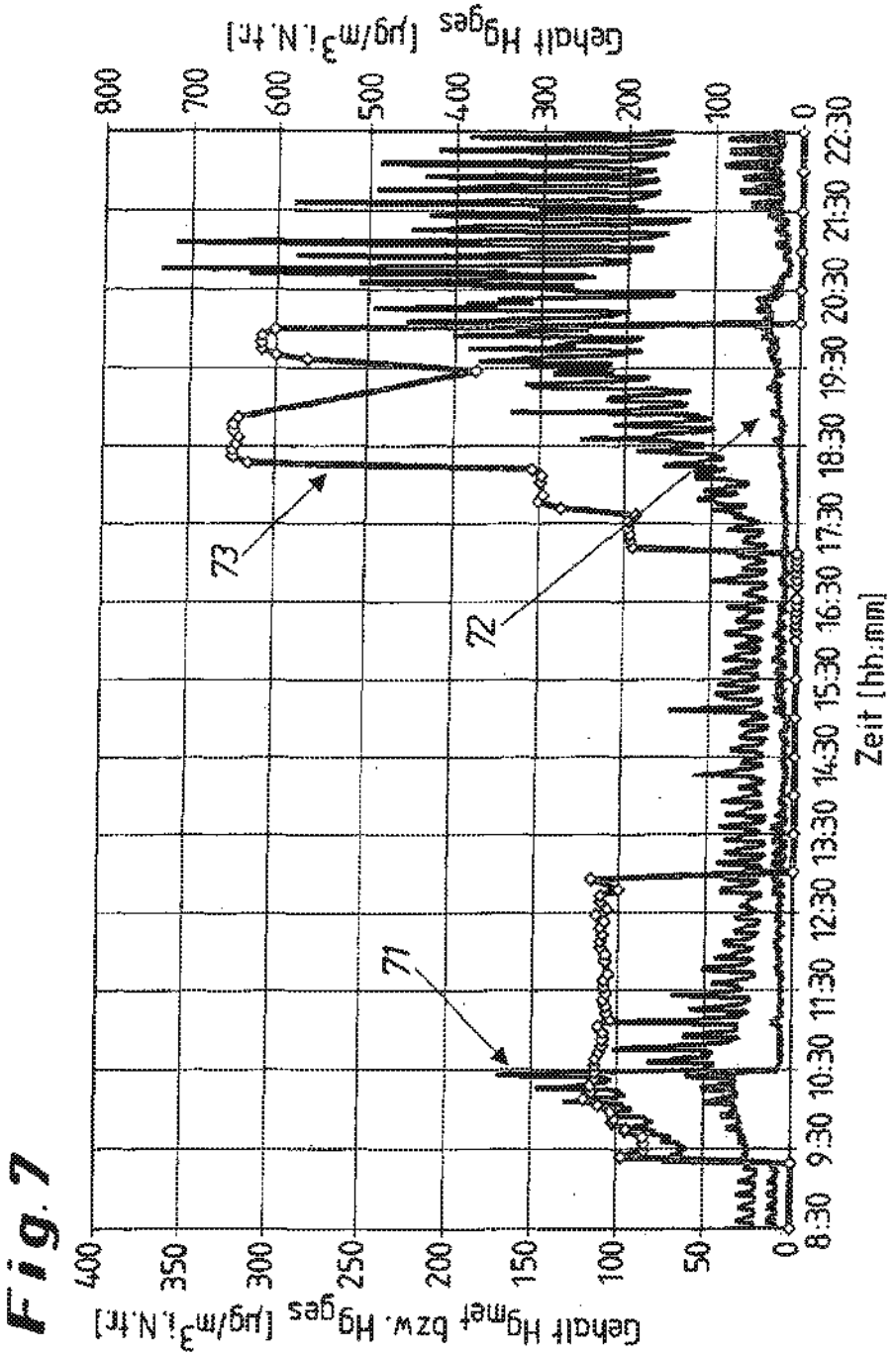


Fig. 7

PAC ET AL. EXHIBIT 1019
Page 1988

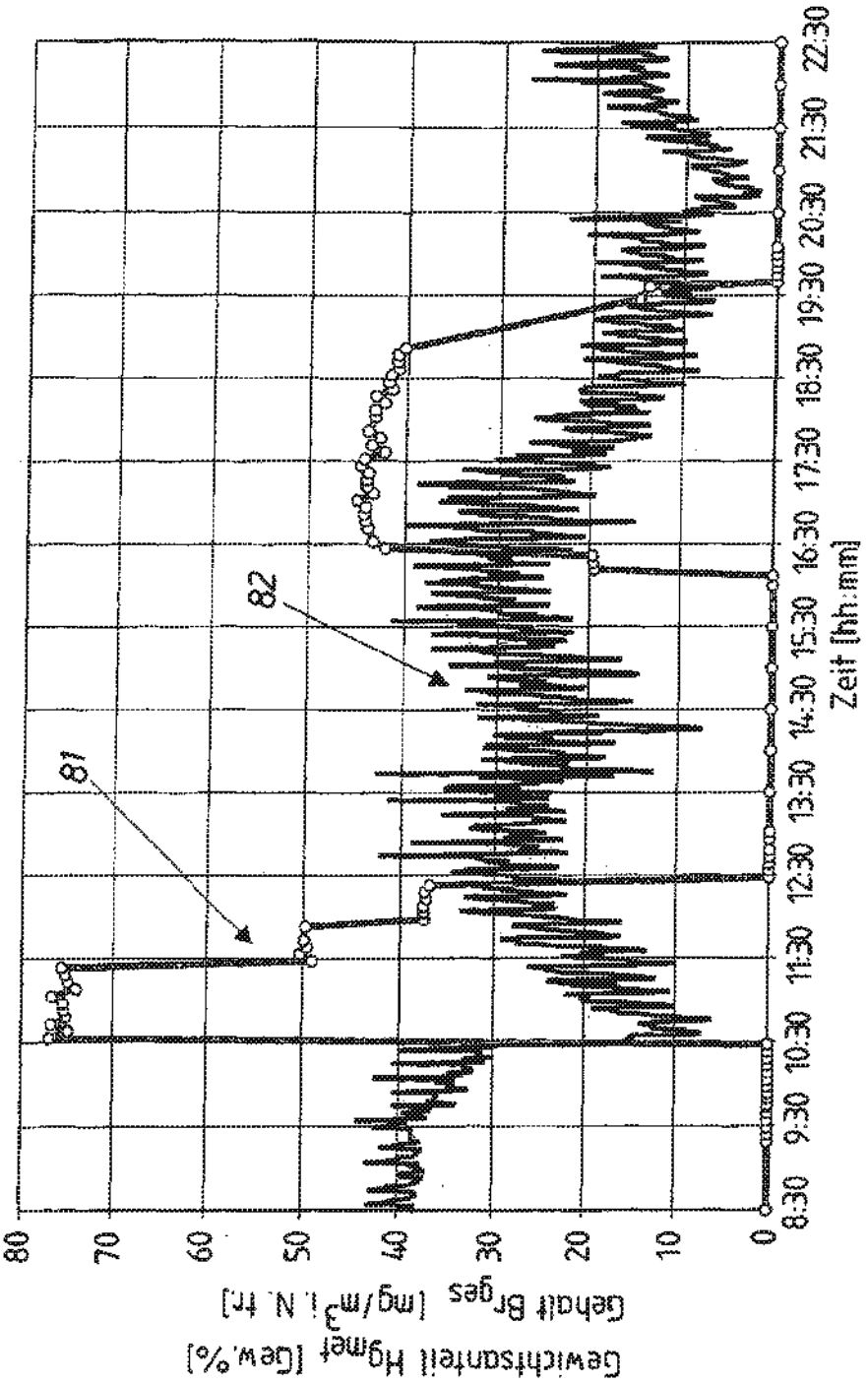


Fig. 8

PAC ET AL. EXHIBIT 1019
Page 1989

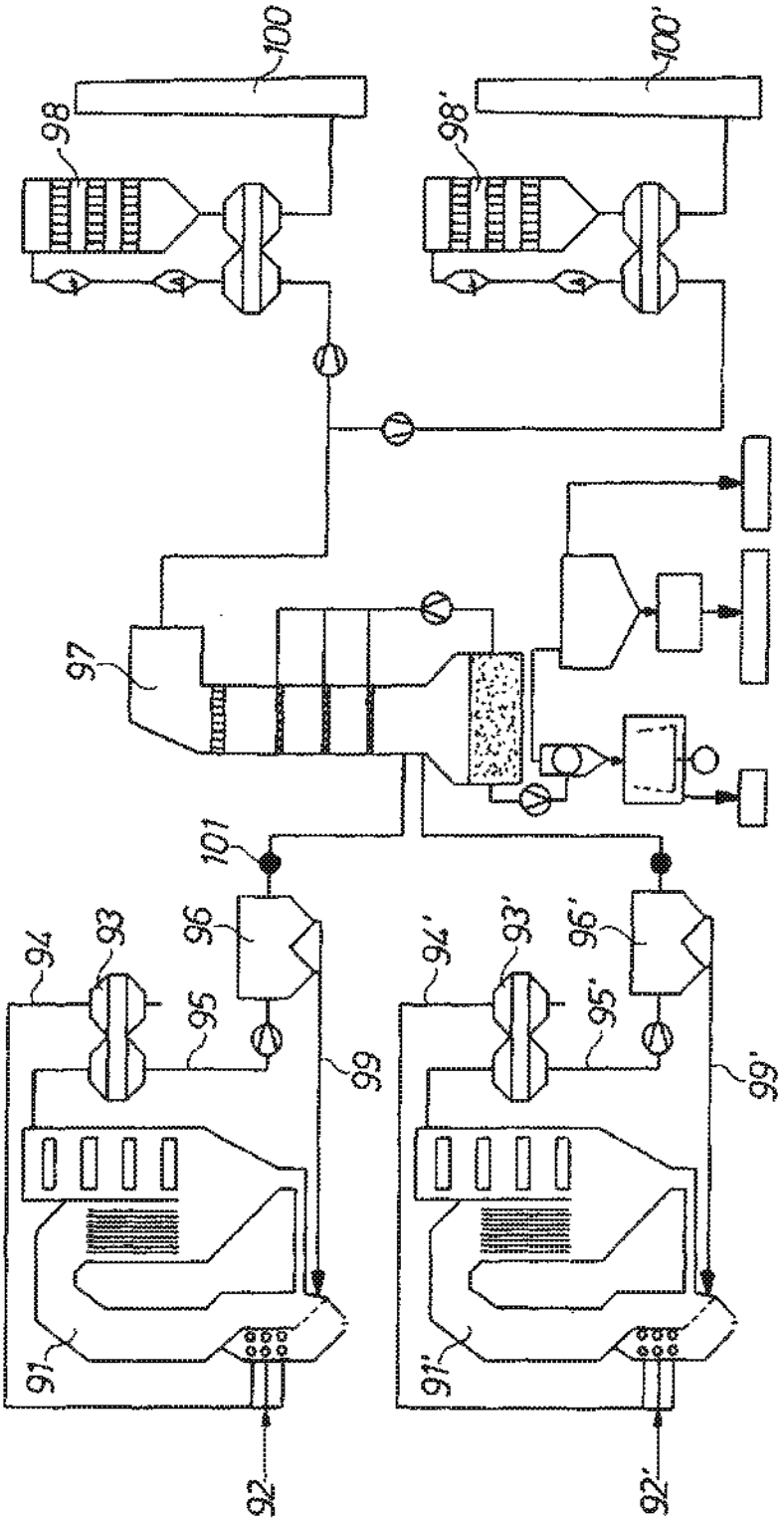


Fig.9

PAC ET AL. EXHIBIT 1019
Page 1990

Europäisches Patentamt

EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung
EP 03 01 6026

EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int.Cl.7)
A	DE 198 58 054 A (KARLSRUHE FORSCHZENT) 4. Mai 2000 (2000-05-04) * Seite 1, Zeile 46 - Zeile 47; Ansprüche 1,2; Beispiel 1 * ---	1	B01D53/64
A	US 5 900 042 A (MENDELSOHN MARSHALL H ET AL) 4. Mai 1999 (1999-05-04) * Anspruch 1 * ---	1	
A	DE 44 22 661 A (PATRA PATENT TREUHAND) 4. Januar 1996 (1996-01-04) * Seite 1, Zeile 55 - Zeile 66 * ---	1	
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 10, 17. November 2000 (2000-11-17) & JP 2000 197811 A (KAWASAKI HEAVY IND LTD), 18. Juli 2000 (2000-07-18) * Zusammenfassung * -----	1	

RECHERCHIERTE SACHGEBIETE (Int.Cl.7)

B01D

Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt

Recherchenort	Abschlußdatum der Recherche	Prüfer
BERLIN	4. November 2003	Clement, J-P

KATEGORIE DER GENANNTEN DOKUMENTE

X : von besonderer Bedeutung allein betrachtet
Y : von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie
A : technologischer Hintergrund
O : nichtschriftliche Offenbarung
P : Zwischenliteratur

T : der Erfindung zugrunde liegende Theorien oder Grundsätze
E : älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist
D : in der Anmeldung angeführtes Dokument
L : aus anderen Gründen angeführtes Dokument

& : Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument

EPO FORM 1503 03.82 (P04C03)

PAC ET AL. EXHIBIT 1019
Page 1991

ANHANG ZUM EUROPÄISCHEN RECHERCHENBERICHT ÜBER DIE EUROPÄISCHE PATENTANMELDUNG NR. EP 03 01 6026

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten europäischen Recherchenbericht angeführten Patentdokumente angegeben.
Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

04-11-2003

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
DE 19850054 A	04-05-2000	DE 19850054 A1	04-05-2000
US 5900042 A	04-05-1999	KEINE	
DE 4422661 A	04-01-1996	DE 4422661 A1	04-01-1996
		CA 2150529 A1	29-12-1995
JP 2000197811 A	18-07-2000	JP 3023102 B2	21-03-2000

EPO FORM P0461

Für nähere Einzelheiten zu diesem Anhang : siehe Amtsblatt des Europäischen Patentamts, Nr.12/82

PAC ET AL. EXHIBIT 1019
Page 1992

Espacenet

Description: EP1458474 (A1) — 2004-09-22

PRETREATMENT AND REGENERATION OF OXIDES OF MANGANESE

Description not available for EP1458474 (A1)
Description of corresponding document: WO03072241 (A1)

A high quality text as facsimile in your desired language may be available amongst the following family members:

CN1620334 (A) MXPA04005896 (A) US2003219368 (A1) WO03072241 (A1)

The EPO does not accept any responsibility for the accuracy of data and information originating from other authorities than the EPO; in particular, the EPO does not guarantee that they are complete, up-to-date or fit for specific purposes.

PRETREATMENT AND REGENERATION
OF OXIDES OF MANGANESE Related Applications
This application claims priority to US Provisional Application No. 60/342, 587 filed December 21,2001, which is incorporated herein by reference.

Field of the Invention
The invention relates to systems and processes for treating oxides of manganese that may be utilized as a sorbent for capture and removal of target pollutants from industrial and other gas streams. Further, the invention relates to pollution removal systems incorporating such methods and apparatus and to oxides of manganese, oxides of manganese sorbent particles, and oxides of manganese filter cake formed by the processes of the invention.

Background of the Invention
The element manganese (Mn) may exist in six different valence (oxidation) states. Of particular interest and usefulness in the PahlmanTM systems and processes are those oxides of manganese having valence states of +2, +3, and +4, which correspond to the oxides MnO, Mon203, and Mn02. The oxide Mn04 is probably a solid-solution of both the +2 and +3 states.

A characteristic of most oxides of manganese species is non-stoichiometry; that is, most oxides of manganese molecules or Mn02 species typically contain on average less than the theoretical number of 2 oxygen atoms, with numbers more typically ranging between 1.5 to 2.0. The non-stoichiometry characteristic is thought to result from solid-solution mixtures of two or more oxide species, and exists in all but the beta (ss), or pyrolusite, form of manganese dioxide. Oxides of manganese having the formula MnOX where X is about 1.5 to about 2.0 are particularly suitable for dry

removal of target pollutants from gas streams.

However, the most active types of oxides of manganese for use as a sorbent for target pollutant removal usually have the formula MnOl. 7 to 1. 95, which translates into manganese valence states of +3. 4 to +3.9, as opposed to the theoretical +4.0 state. It is unusual for average valence states above about 3.9 to exist in most forms of oxides of manganese. The

formula Mn02, as used herein, symbolically represents all varieties of manganese dioxide including those with valence states ranging from +3 to +4, or MnOl. s 2. o.

Oxides of manganese are known to exhibit several identifiable crystal structures, which result from different assembly combinations of their basic molecular structural units.

These basic structural"building block"units are Mn06 octahedra, which consist of one manganese atom at the geometric center, and one oxygen atom at each of the six apex positions of an octahedral geometrical shape. The octahedra may be joined together along their edges and/or corners, to form"chain"patterns, with void spaces ("tunnels"). Regular (and sometimes irregular) three-dimensional patterns consist of layers of such"chains"and "tunnels"of joined octahedra. These crystalline geometries are identified by characteristic x- ray diffraction (XRD) patterns. Most oxides of manganese are classifiable into one or more of the six fundamental crystal structures, which are called alpha (a), beta ( ), gamma (y), delta (8), epsilon (s), and ramsdellite. Certain older literature also included rho (p) and lambda (X) structures, which are now thought obsolete, due partly to improvements in XRD technique. Some (amorphous) forms of MnO2 exhibit no crystalline structure.

Certain characteristics of oxides of manganese probably arise from the size and shape of voids within these crystalline patterns and from certain elements, and compounds, which may occupy the voids and appear to help prevent collapse of certain structures. Applicants believe that these characteristics in addition to the oxidation state may have and affect upon the loading capacity of oxides of manganese sorbent. Further, many oxides of manganese are hydrous, and include structurally bound water. This bound water may also contribute to chemical reactivity and possibly catalytic behavior of the species.

Some oxides of manganese have the ability to absorb oxygen from gas. Manganous oxide (MnO) will oxidize to MnO2 in the presence of air, for example. Additionally, the dioxides are themselves oxidizers, they readily exchange oxygen in chemical reactions, and they are known to have catalytic properties. This oxygen exchange ability may be related to proton mobility and lattice defects common within most MnO2 crystal structures. The oxidizing potential of Mn02 is advantageously utilized in target pollutant removal in the PahlmanTM and other systems and processes. Target pollutants, such as NOx and SO2 gases, mercury (Hg) and other pollutants, require oxidation of the species prior to reaction with MnO2 sorbent to form reaction products, such as manganese sulfates and nitrates, mercury compounds, and other corresponding reaction products, in order for them to be captured and removed from gas stream.

Manganese compounds are soluble in water in the +2 valence state, but not in the +4 state. Therefore Mn+2 compounds, including MnO are readily soluble in aqueous solutions, as opposed to MnO2. During the formation of reaction products such as manganese nitrates and sulfates, the manganese is reduced from about the +4 state to the +2 state. This property allows the reaction products formed on the surface of oxides of manganese sorbent particles to be readily dissolved and removed from the sorbent

particles in aqueous solutions by disassociation into sulfate, nitrate, and Mn+2 ions.

Manganese dioxides are divided into three origin-based categories, which are: 1) natural (mineral) manganese dioxide (NMD), 2) chemical manganese dioxide (CMD), and 3) electrolytic manganese dioxide (EMD). As implied, NMD occurs naturally as various minerals, which may be purified by mechanical or chemical means. The most common form of NMD is pyrolusite (ss-MnO2), which is inexpensive, but has rather low chemical activity and therefore low pollutant loading capacity. CMD and EMD varieties are synthetic. EMD is produced primarily for the battery industry, which requires relatively high bulk density (which often results from relatively large, compact particles), relatively high purity, and good electrochemical activity. Though useful as a sorbent, characteristics such as low surface area and large compact particle size make EMD somewhat inferior to CMD for gas removal applications, despite its good electrochemical activity. Chemically synthesized oxides of manganese of all kinds falls into the CMD category and includes chemically treated oxides of manganese. In chemical synthesis, a great deal of control is possible over characteristics such as particle size and shape, porosity, composition, surface area, and bulk density in addition to electrochemical or oxidation potential. It is believed that these characteristic contribute the loading capacity of some oxides of manganese.

EnviroScrub Technologies Corporation has developed pollutant removal systems and processes utilizing dry and wet removal techniques and combinations thereof, incorporating the use of oxides of manganese as a sorbent. These systems and processes, commonly known as PahlmanTM systems and processes are the subject of co-pending U. S. Patent Application Numbers 09/919,600, 09/951,697, 10/044,089 and 10/025,270, the disclosures of which are incorporated herein. High target pollutant removal efficiencies have been obtained utilizing the Pahlmanrm systems and processes with oxides of manganese as the sorbent. Due to pollutant loading during the removal process, the Pahlman system or some of its system components must be periodically taken off-line so that sorbent may be removed for regeneration and recovery of useful by-products. The frequency of such disruptions and

related downtime could be decreased if it were possible to increase the loading capacity of the sorbent. It would therefore be desirable to enhance the loading capacities of the oxides of manganese in order to extend the period of sorbent use and its loading capacity. Applicants have developed methods of treating virgin oxides of manganese and of recycle processing of loaded oxides of manganese with oxidants or oxidizers that result in treated oxides of manganese having enhanced or increased loading capacity.

Brief Description of the Drawings
Figure 1 is a block flow diagram depicting an embodiment of a treatment system and method of the invention.

Figure 2 is a block flow diagram depicting an embodiment of a treatment system and method of the invention.

Figure 3 is a sorbent loading graph.

Figure 4 is a sorbent loading graph.

Figure 5 is a sorbent loading graph.

Figure 6 is a sorbent loading graph.

Figure 7 is a block flow diagram of a treatment system and method of the invention incorporating a controller.

Figure 8 is a block flow diagram of a embodiment of a treatment system and method of the invention incorporating a controller.

Figure 9 is a Pourbaix diagram for an aqueous solution of 1 mole/liter manganese ion concentration.

Figure 10 is a Pourbaix diagram for an aqueous solution of 10-6 mole/liter manganese ion concentration.

Summary of the Invention

The invention relates to systems and processes for treatment of oxides of manganese that may be utilized as a sorbent for removal of target pollutants from a gas stream.

An embodiment of a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprises the steps of washing virgin oxides of manganese in wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the Mn02 stability area; and filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of

manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

Another embodiment of a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprises the steps of washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO2 stability area; monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO2 stability area; and filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese. The monitoring and adjusting step may be carried out by a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the Mn02 stability area.

An embodiment of a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprises the steps of washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the MnO2 stability area; and removing the pretreated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese.

An embodiment of a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream comprises the steps of washing loaded oxides of manganese in a rapid

filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; and removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed.

An embodiment of a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system comprises the steps of rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the Mn02 stability area; and removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed.

The above processes may further comprise the steps of drying the filter cake ; and comminuting and sizing the dried filter cake to provide oxides of manganese particles. The may alternative further comprise the steps of drying the filter cake ; and comminuting and sizing the dried filter cake to provide oxides of manganese particles for introduction into a feeder or reaction chamber of a dry pollution removal system. In a further alternative, they processes may further comprise the steps of drying the filter cake; comminuting and sizing the dried filter cake to provide oxides of manganese particles for introduction into a feeder or reaction chamber of a dry pollution removal system; and introducing the comminuted and sized oxides of manganese particles into the feeder or reaction chamber. In yet a further alternative, the above described processes may further comprise the step of conveying the filter cake to a dryer configured to inject the a wet filter cake or a slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system. In yet another further alternative, the above-described processes may further comprise the steps of conveying the filter cake to a dryer configured to inject the a wet filter cake or a slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system; and injecting the wet filter cake or the slurry into the reaction chamber.

In the above-described processes the aqueous oxidizing solution contains an oxidizer.

The oxidizer may be selected from the group consisting of hypochlorites, perchlolates, permanganates, oxygen (ou), air, ozone, peroxides, persulfates, and combinations thereof.

13 An embodiment of a system for pretreatment of virgin oxides of manganese comprising a wash unit configured to hold and agitate a slurry of virgin oxides of manganese in an aqueous oxidizing solution, the solution have Eh and pH values within the Mn02 stability area, the wash unit being optionally equipped with a pH probe, an Eh probe, and a temperature probe, the wash unit being further configured to receive the slurry of virgin oxides of manganese or to individually receive virgin oxides of manganese and the aqueous oxidizing solution; a filtration unit configured to receive the slurry from the wash unit and to filter the slurry to form a filtrate and a pretreated

oxides of manganese filter cake; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the Mn02 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being optionally equipped with an Eh probe; an oxides of manganese vessel containing a supply of virgin oxides of manganese, the vessel having a feeder configured to feed oxides of manganese directly to the wash unit or, in conjunction with the aqueous oxidizing solution feeder to feed a slurry of virgin oxides of manganese to the wash unit; and a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the wash unit. The system of this embodiment may further comprise a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the Mn02 stability area.

This embodiment of a system for treatment of virgin or loaded oxides of manganese may further comprise a dryer for drying the filter cake ; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the wash unit.

14 Another embodiment of a system for treatment of virgin or loaded oxides of manganese comprising a rapid filtration wash unit, the wash unit being configured to individually receive oxides of manganese and an aqueous oxidizing solution having a Eh and

pH values within the Mn02 stability area, the wash unit being further configured to rapidly remove the aqueous oxidizing solution from contact with the oxides of manganese forming a filtrate and a treated oxides of manganese filter cake; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the Mn02 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being optionally equipped with a probe selected from the group consisting of an Eh probe, a pH probe, a temperature probe, or any combination thereof; an oxides of manganese vessel containing a supply of virgin of loaded oxides of manganese, the vessel having a feeder configured to feed oxides of manganese to the wash unit ; optionally, a oxidizer vessel containing a supply of oxidizer, the oxidizer vessel having feeder configured to feed oxidizer to the aqueous oxidizing solution vessel; and optionally, a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the aqueous oxidizing solution vessel. The system of this embodiment may further comprise a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of the temperature, Eh values, and pH values within the aqueous oxidizing solution vessel in order to maintain conditions of the aqueous oxidizing solution within the mon02 stability area.

This embodiment of a system for treatment of virgin or loaded oxides of manganese may further comprise a dryer for drying the filter cake; a device for comminuting and

sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the aqueous oxidizing solution vessel.

Another embodiment of a system for pretreatment of virgin oxides of manganese comprises a wash unit configured to hold and agitate a slurry of virgin oxides of manganese in an aqueous oxidizing solution, the solution have Eh and pH values within the Mn02 stability area, the wash unit being equipped with a pH probe, an Eh probe, and a temperature probe, the wash unit being further configured to receive the slurry of virgin oxides of manganese or to individually receive virgin oxides of manganese and the aqueous oxidizing

solution; a filtration unit configured to receive the slurry from the wash unit and to filter the slurry to form a filtrate and a pretreated oxides of manganese filter cake ; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the Mn02 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being equipped with an Eh probe; an oxides of manganese vessel containing a supply of virgin oxides of manganese, the vessel having a feeder configured to feed oxides of manganese directly to the wash unit or, in conjunction with the aqueous oxidizing solution feeder to feed a slurry of virgin oxides of manganese to the wash unit; a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the wash unit; and a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control within the wash unit of the temperature, Eh values, and pH values in order to maintain conditions of the aqueous oxidizing solution within the MnOz stability area, the controller being electronic communication with the probes and feeders of the system.

This embodiment of a for pretreatment of virgin oxides of manganese may further comprise a dryer for drying the filter cake; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the wash unit.

18 Another embodiment of a system for treatment of virgin or loaded oxides of manganese comprises a rapid filtration wash unit, the wash unit being configured to individually receive oxides of manganese and an aqueous oxidizing solution having a Eh and pH values within the MnO2 stability area, the wash unit being further configured to rapidly remove the aqueous oxidizing solution from contact with the oxides of manganese forming a filtrate and a treated oxides of manganese filter cake ; an aqueous oxidizing solution vessel containing a supply of aqueous oxidizing solution, the solution having Eh and pH values within the Mn02 stability area, the vessel having a feeder configured to feed aqueous oxidizing solution to the wash unit and being

equipped with a probe selected from the group

consisting of an Eh probe, a pH probe, a temperature probe, or any combination thereof; an oxides of manganese vessel containing a supply of virgin of loaded oxides of manganese, the vessel having a feeder configured to feed oxides of manganese to the wash unit; a oxidizer vessel containing a supply of oxidizer, the oxidizer vessel having feeder configured to feed oxidizer to the aqueous oxidizing solution vessel; a pH adjust vessel having a supply of acid or base or separate supplies of acid and base, the pH adjust vessel having a feeder configured to feed acid and/or base to the aqueous oxidizing solution vessel; and a controller capable of individually or simultaneously monitoring and adjusting system operational parameters, the controller providing integrated control of the temperature, Eh values, and pH values within the aqueous oxidizing solution vessel in order to maintain conditions of the aqueous oxidizing solution within the Mn02 stability area, the controller being in electronic communication with the probes and feeders of the system.

This embodiment of a system for treatment of virgin or loaded oxides of manganese may further comprise a dryer for drying the filter cake ; a device for comminuting and sizing the dried filter cake to form oxides of manganese particles; and a reaction chamber of a pollutant removal system into which the oxides of manganese particles are introduced to capture target pollutants from a gas, the reaction chamber being equipped with at least one target pollutant concentration reader for measuring target pollutant concentration of the gas as it exits the reaction chamber, the reader being in electronic communication with the controller for checking the loading performance of the oxides of manganese particles and signaling need for adjustment of operational parameters within the aqueous oxidizing solution vessel.

In the above-described systems the aqueous oxidizing solution contains an oxidizer.

The oxidizer may be selected from the group consisting of hypochlorites, perchlolates, permanganates, oxygen (O2), air, ozone, peroxides, persulfates, and combinations thereof.

The invention also relates to oxides of manganese, oxides of manganese particles, and oxides of manganese filter cakes formed by the above-described processes.

Oxides of manganese particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprising the steps of washing virgin oxides of manganese in wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the Mn02 stability area; filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese; drying

the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO2 stability area; monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO2

stability area; filtering the washed oxides of manganese to form a filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese; drying the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream comprising the steps of washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the Mn02 stability area; removing the pretreated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese; drying the filter cake ; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese particles may formed by a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream comprising the steps of washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values within the MnO2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed; drying the filter cake; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese sorbent particles may formed by a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface

thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system, comprising the steps of rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the Mn02 stability area; removing the regenerated oxides of manganese filter cake from the rapid filtration unit, the oxides of manganese of the filter cake having a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed; drying the filter cake ; and comminuting and sizing the dried filter cake to form oxides of manganese particles.

Oxides of manganese filter cakes particles may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the steps of washing virgin oxides of manganese in a wash unit with an aqueous oxidizing solution, the solution having Eh and pH values within the MnO2 stability area; monitoring and adjusting the pH and/or the Eh values of the solution so as to maintain the Eh and pH values of the solution within the MnO2 stability area; and filtering the washed oxides of manganese to form a

filtrate and a pretreated oxides of manganese filter cake, the oxides of manganese of the filter cake having a pollutant loading capacity greater than the pollutant loading capacity of the virgin oxides of manganese.

Oxides of manganese filter cake may be formed by a process for pretreatment of virgin oxides of manganese for use as a sorbent to remove target pollutants from a gas stream, comprising the step of washing virgin oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution to form a filtrate and a pretreated oxides of manganese filter cake, the solution having Eh and pH values within the Mn02 stability area; wherein the oxides of manganese of the pretreated oxides of manganese filter cake have a pollutant loading capacity greater that the pollutant loading capacity of the virgin oxides of manganese.

Oxides of manganese filter cake formed by a process for regeneration of loaded oxides of manganese formed through reaction between unreacted oxides of a manganese and target pollutants in a gas stream comprising the step of washing loaded oxides of manganese in a rapid filtration wash unit with an aqueous oxidizing solution having Eh and pH values

within the MnO2 stability area to form a filtrate and a regenerated oxides of manganese filter cake; wherein the oxides of manganese of the regenerated oxides of manganese filter cake have a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese from which the loaded oxides of manganese are formed.

Oxides of manganese filter cake may be formed by a process for regeneration of loaded oxides of manganese sorbent particles bearing a reaction product layer of the surface thereof formed during reaction between unreacted oxides of manganese sorbent particles and target pollutants in a gas stream in a pollution removal system comprising the step of rapidly washing and filtering the loaded oxides of manganese sorbent particles in a rapid filtration wash unit with an aqueous oxidizing solution to dissolve the reaction product layer from the surface of the loaded oxides of manganese sorbent particles into the solution to form a filtrate and a regenerated oxides of manganese filter cake, the solution having Eh and pH values within the Mn02 stability area; wherein the oxides of manganese in the regenerated oxides of manganese filter cake have a pollutant loading capacity equal to or greater than the pollutant loading capacity of the unreacted oxides of manganese sorbent particles from which the loaded oxides of manganese sorbent particles are formed.

In the processes for formation of the above-described oxides of manganese particles and oxides of manganese filter cakes, the aqueous oxidizing solution contains an oxidizer.

The oxidizer may be selected from the group consisting of hypochlorites, perchlolates, permanganates, oxygen (02), air, ozone, peroxides, persulfates, and combinations thereof.

Detailed Description of Preferred Embodiments

The following definitions will be useful in understanding the invention disclosed herein: "Reacted"or"loaded,"as used interchangeably herein, refers in conjunction with "oxides of manganese"and/or"sorbent"to oxides of manganese or sorbent that has interacted with one or more target pollutants in a gas whether by chemical reaction, adsorption or absorption. The term does not mean that all reactive or active sites of the sorbent have been utilized as all such sites may not actually be utilized.

"Unreacted"or"virgin, "as used interchangeably herein, refers in conjunction with "oxides of manganese"and/or"sorbent"to oxides of manganese or sorbent that has not interacted with target pollutants in a gas or gas stream.

"Nitrates of manganese, "as used herein, refers to and includes the various forms of manganese nitrate, regardless of chemical formula, that may be formed through the chemical reaction between NOx and the sorbent and includes hydrated forms as well.

"Sulfates of manganese, "as used herein, refers to and includes the various forms of manganese sulfate, regardless of chemical formula that may be formed through the chemical reaction between SOx and the sorbent and includes hydrated forms as well.

"Target pollutant, "as used herein, refers to the pollutant or pollutants that are or are to be captured and removed from a gas stream.

"Mn02 stability area, "as used herein, refers to the region of thermodynamic stability for manganese dioxide delineated by Eh and pH values for aqueous solutions. More specifically, it refers to the region of thermodynamic stability for manganese dioxide delineated by Eh and pH values for aqueous solutions in an electrochemical stability diagram, such as presented by Pourbaix diagrams.

Oxides of manganese may be utilized for various applications. one such application is in the use as a sorbent for removal of target pollutants in gas streams. Examples of target pollutants that may be removed with an oxide of manganese sorbent, include but are not limited to, NOx, SOx,, mercury (Hg) and some mercury compounds, H2S and other totally reduced sulfides (TRS), and oxides of carbon. As previously noted above, certain target pollutant removal systems and processes methods utilizing oxide of manganese sorbents and referred to as Pahlman systems and Pahlman processes are described and disclosed in co-pending U. S. patent application numbers 09/919,600, 09/951,697, 10/044,089 and 10/025,270, all assigned to EnviroScrub Technologies Corporation, the assignee of this application. The disclosures of these four patent applications are incorporated herein by reference.

Oxides of manganese sorbents are introduced into these and other pollution removal systems and interact with the target pollutants in gas streams routed through the systems as a catalyst, a reactant, an absorbent or an adsorbent.

During such interaction in the process of pollutant removal, the oxidation (or valence) state of the oxides of manganese sorbent is reduced from its original state during reaction with the target pollutants. For example, where the target pollutants are NOx or SOx, possibly through overall reactions such as the following:

SO2+MnO2 9 MnSO4 Reaction (1) 2NO + 02+Mn02 Mn (N03) 2 Reaction (2) In both of the reactions above, manganese (Mn) is reduced from the +4 valence state to +2 valence state during formation of the reaction products shown. It should be noted that the actual reactions may include other steps not shown, and that indicating Reactions 1 and 2 is not in any way intended to limit the scope of the invention, but is used only to illustrate the process.

Additionally, it is believed that reaction products, such as the salts of Reaction (1) and Reaction (2) above, form on the surfaces of the sorbent particles of oxides of manganese.

These reactions may extend to some depth inside the sorbent particles. Applicants believe that formation of such reactions products occurs on the surfaces of the oxides of manganese particles, resulting in a layer or coating, which effectively isolates the covered portion of the particle surface and thereby prevents continued rapid reaction with additional target pollutants. Further, the oxidation state and thus the loading capacity of the oxides of manganese below the surface of the reaction product coating may be reduced during the pollutant removal, thus diminishing the loading capacity of sorbent even after the reaction product have been removed or disassociated into an aqueous solution.

Following reaction with the target pollutants, it is desirable for economic reasons to re-use the unreacted portions of the sorbent for subsequent cycles of pollutant gas removal.

These unreacted portions may exhibit decreased loading capacity. In order to render reacted oxides of manganese effective for subsequent re-use as a gas sorbent with high removal efficiency, it is necessary to: (1) remove reaction products, such as salts from the sorbent particle surfaces and (2) restore or increase the target pollutant loading capacity of the oxides of manganese sorbent. Applicants have found that washing the loaded oxides of manganese in an aqueous oxidizing solution that has been adjusted to within the Mn02 stability area can accomplish these requirements. Further, Applicants have found that loading capacity of virgin or unreacted sorbent can be increased by washing with aqueous oxidizing solutions.

Without being bound by theory, Applicants believe that the processing of oxides of manganese according to the invention in aqueous oxidizing solution systems maintained with the Mn02 stability window may beneficially affect a number of sorbent characteristics. Such characteristics may include particle size and shape, crystalline structure or morphology,

porosity, composition, surface area, bulk density, electrochemical or oxidation potential or manganese valence states.

Regardless, the increased loading capacity is achieved with aqueous oxidizing solutions. Hypochlorites, such as sodium hypochlorite (NaOCl), have been found to be a suitable oxidizers for use in the aqueous oxidizing solutions, although many other oxidizers may also be suitable for this purpose. Other suitable oxidizers include, but are not limited to chlorates, such as sodium chlorate (NaCl03), perchlorates such as sodium perchlorate (Na2C104), permanganates, such as potassium permanganate (KMn04), oxygen (02) or air, ozone (03), peroxides, such as H202, and persulfates, such as sodium peroxidisulfate (Na2S208). The electrochemical potential of the aqueous oxidizing solution, and therefore the effectiveness of the treatment methods of the invention, depends, in part, upon the strength of the oxidizer and/or the concentration of the oxidizer in the solution.

In the treatment methods and systems disclosed herein, the oxidizer used to prepare the aqueous oxidizing solution, must be able to provide the required electrochemical (oxidizing) potential (Eh), within the specified pH range, to provide an Eh-pH combination to achieve stable solution equilibrium, as defined by the Mn02 stability area as delineated in a Pourbaix diagram, such as those depicted in Figures 9 and 10. In a Pourbaix diagram, the Mn02 stability area is defined by the thermodynamically stable ranges or boundaries of pH- Eh combinations that promote the existence and formation Mn02 (having valence state of +4) as the most thermodynamically stable form of manganese in an aqueous solution system.

The domain of Mn02 stability for an aqueous solution varies based upon the various components of the system. For example, changes in dissolved manganese ion concentration, solution temperature, and competing dissolved ions will affect the boundaries of stability for Mn02. The effects of such changes upon the boundaries of the Mn02 stability area on a Pourbaix Eh-pH diagram can be determined either by empirical data derived from experimentation or with computer software programs known to those skilled in the art, such as HSC Chemistry distributed by Outokumpu Oy of Finland. Software may also be written to determine the Mn02 stability area as defined by other diagrams, such as the Latimer Diagram or the Frost Diagram.

In Figure 9, ranges of pH and Eh values for thermodynamically stable aqueous solutions of various manganese compounds are illustrated in graph form for aqueous solution systems at 25 C and a Imole/liter manganese ion concentration. Figure 10 similarly illustrates ranges of pH and Eh values for aqueous solution systems at 25 C but with a 1.0 x

10-6 mole/liter manganese ion concentration. The Pourbaix Window diagrams depicted in Figures 9 and 10 were derived from the diagram presented in Atlas Of Electrochemical Equilibria in Aqueous Solutions,"Marcel Pourbaix, pages 286-293, National Association of Corrosion Engineers, Houston, Texas.

The Eh and pH values as plotted on the graphs delineate the boundaries of the Mn02 stability area for each of the two aqueous solution systems, emphasized with shading in Figures 9 and 10. A comparison of the boundaries of the two shaded areas on Figures 9 and 10 is illustrative of the different stability areas that exist under different system conditions.

Regardless of the specific system conditions, under the thermodynamically stable conditions for Mn02 at a given pH and corresponding Eh range within the MnO2 stability area or the given system conditions, the desired manganese valence state (theoretically +4) will exist. Thus, there is no propensity for Mn compounds in the +4 valence state to degrade to +3 or +2 valence states. Applicants have found that oxides of manganese treated in oxidizing solutions maintained within the MnO2 stability area will exhibit a Mn valence state of close to +4, resulting in a Mn02 with target pollutant loading capacities equal to and/or greater than (increased) the loading capacities of virgin or loaded oxides of manganese.

From the graph presented in Figure 9 or 10, the thermodynamically stable ranges or boundaries of pH-Eh combinations for the particular aqueous system that will promote the existence and formation of MnO2 can be identified. Through their understanding of the relationships between these system parameters of the MnO2 stability area of a Pourbaix Window diagram and application thereof to conditions of a given aqueous system, Applicants are able to treat both virgin and loaded oxides of manganese sorbents so as to yield a treated sorbent, both pretreated and recycled, having equal or increased loading capacity when compared to the untreated sorbent.

Oxidizing solutions having the desired pH-Eh combination can be prepared, maintained or adjusted by increasing or decreasing oxidizer, acid, or base concentrations and/or temperature adjustment, as appropriate, so that the conditions are adjusted to remain within the MnO2 stability area. With monitoring of Eh and pH data, an operator can make necessary adjustments in order to maintain or return the oxidizing solution to conditions within the MnO2 stability area. Monitoring and adjusting can also be automated utilizing electronic sensors and controllers.

Virgin (unreacted) oxides of manganese sorbent particles may be treated or pretreated to increase the oxidation state and/or target pollution loading capacity. This can be

accomplished by washing virgin (unreacted) sorbent with a wash solution of volume-to-sample weight ratio (liquid-to-solids ratio) of 2: 1 or greater. However, effective treatment can also be accomplished with both lower and higher liquid-to-solids ratios as well. The sorbent powder is added to an aqueous oxidizing solution, for example a hypochlorite solution, stirred or agitated for a time sufficient to achieve an increased oxidation state and/or target pollution loading capacity. The then treated sorbent is separated by filtering, and the wet particles dried, which prepares the sorbent for target pollutant removal.

This method of virgin sorbent treatment may be better understood with reference to Figure 1. Turning to Figure 1 a virgin sorbent pretreatment system 10 is illustrated. The pretreatment system includes a washing unit 12, optionally equipped with pH probe 14 and Eh probe 16. As explained later in the specification, these probes may be utilized to provide information on aqueous solution conditions that may be utilized to provided manual or electronically controlled adjustments to relative to providing and maintaining the desire pH- Eh combination and other operating conditions. For example, temperature probe (not shown) may also optionally be provided. Virgin sorbent from virgin sorbent storage 18 is introduced into wash unit 12 along with an aqueous oxidizing solution prepared to have the desired pH- Eh combination within the Mn02 stability area. Optionally, adjustments to the slurry pH and Eh can be made using appropriate oxidants for Eh adjustment and mineral acids and bases for pH adjustments.

The solid-liquid mixture or slurry is agitated or stirred and maintained at the desire operating conditions so as to increase the loading capacity and/or the Mn oxidation state.

Optionally, adjustments to the slurry pH and Eh can be made using appropriate oxidants for Eh adjustment and mineral acids or bases for pH adjustment, so that the pH/Eh combination of the slurry is maintained within the window of Mn02 stability for the specific system.

A filtration unit 22 configured for solid-liquid separation is next provided. Suitable filtration units known and readily identified by those skilled in the art may be utilized for filtration unit 22. The slurry from wash unit 12 is conveyed to filtration unit 22 where the treated sorbent is separated from the solution, with the wash solution or filtrate being routed for re-use, other processing or disposal. Since the filtrate may yet contain useful residual oxidizer, it may not be economic or desirable to dispose of the solution after a single use.

However, after multiple uses, the solution may contain an accumulation of undesired constituents, such as contaminants and debris, that may be present in a load of virgin sorbent.

Such undesired constituents may impact the efficiency or continued usefulness of the filtrate

for subsequent sorbent pretreatment. At that juncture the filtrate may be disposed of or otherwise processed to recover useful values.

In any event, the treated sorbent that has been separated from the slurry is in the form of a wet sorbent cake and may be dried prior to use in a pollutant removal system such as the Pahlman system if the sorbent is to be fed dry into the removal system. In some removal systems the sorbent may be fed as a slurry or even as a wet sorbent cake and for such removal systems a drying step would not be required. However, where drying is required or desired prior to introduction into a pollution removal system, the wet sorbent cake is routed to a dryer 24. A variety of dryers known to those skilled in the art may be utilized for this purpose, such as a rotary kiln, heat exchanger, oven, or other suitable dryers. After drying the treated sorbent may require comminution and possible sieving to reduce the sorbent particles to the desired size. Further, the sorbent dryer 24 may be a standard cake or slurry drying system known to those skilled in the art of drying, which could include a fluidized bed dryer or a spray dryer, configured or designed to inject the wet cake or slurry of oxides of manganese sorbent into the flow of a gas stream prior to introduction into a reaction chamber of a pollutant removal system. Whether dried and comminuted or routed to a cake or slurry drying system, the resulting sorbent having increased loading capacity is ready for use in a pollution removal system

Loaded (reacted) sorbent requires a different treatment in order to prepare it for reuse for target pollutant removal. Specifically, applicants have found it advantageous to rapidly remove the aqueous oxidizing solution from contact with the loaded sorbent being treated during washing once dissolved reaction products, such as soluble salts, have disassociated into solution. Applicants believe that such rapid removal of soluble salts is necessary in order to prevent possible re-deposition of a reaction product coating or layer, through precipitation of reaction products, e. g. , sulfate and nitrate compounds or their derivatives, upon the washed oxides of manganese sorbent particles. Such coatings are believed to be detrimental to target pollutant removal efficiency of the sorbent. In order to prevent re-deposition of such coatings or layer, the washing or rinsing equipment is configured to prevent buildup of high dissolved salt concentrations and avoids prolonged sorbent contact with the wash solutions used.

Prolonged sorbent-solution contact should be avoided for another reason. As the reaction products are dissolved into solution, the acidity of the wash solution has been observed to increase, perhaps having a pH as low as 2.0-4. 0, as a result of sulfate and nitrate salts, for example, combining with wash solution to form weak acids. Such pH shifts during

washing can and oxidizing of loaded sorbent can take the oxidizing solution outside of the MnO_2 stability area At the lower pH ranges, as illustrated in the Pourbaix Window diagram of Figure 9, an upward, sometimes significant, Eh adjustment would be required to remain within the MnO_2 stability area. Base could also be added to accomplish the desired adjustment; however, this will be ineffective if the oxidizer has been depleted, requiring oxidizer addition. As some oxidizers or oxidants are inexpensive, such Eh adjustment can be uneconomic. However, if not otherwise made, a treated sorbent with a lower valance state and/or loading capacity would result. Through avoidance of prolonged contact potentially, costly Eh adjustments and pH adjustments can be avoided or minimized and a treated sorbent with increased loading capacity can be obtained.

Rapid filtration can be accomplished by various methods such as vacuum or pressure filtration. On the laboratory scale, rapid filtration can be accomplished by placing the loaded oxides of manganese sorbent to be washed on a filter media, using an apparatus such as a Beuchner funnel, and maintaining a vacuum to the filter while applying the wash solution onto the loaded oxides of manganese sorbent. This results in rapid filtration of wash solutions through the sorbent, accompanied by rapid transport

of dissolved salts away from the washed sorbent.

Loaded oxides of manganese sorbent samples are washed with an oxidizing wash solution of volume-to-sample weight ratio (liquid-to-solids ratio) of between 2: 1 and 50: 1 or greater, preferably 25: 1 to 35: 1. Within these liquid-to-solid ratios and with rapid filtration, effective dissolution and rapid removal of reaction products can be achieved, resulting in a treated or recycle processed (sometimes referred to as regenerated) sorbent having an increased oxidation state and/or target pollution loading capacity.

The system and method of recycle processing of loaded sorbent can be understood with reference to Figure 2. Turning to Figure 2 a loaded sorbent treatment or recycle processing system 30 is illustrated. The system 30 includes a combination rapid filtration wash unit 32. The wash unit 32 is configured to receive loaded sorbent from loaded sorbent storage 34 and to aqueous oxidizing solution. The wash unit 32 is further configured and operated so as to avoid and pooling of oxidizing solution or creation of a liquefied slurry or other conditions that would lead to prolonged solid-liquid contact such that the solution no longer remains within the Mn02 stability area. Devices such as moving belt filters presses, filter presses, and filter drum presses or pressurized or vacuum filters or other such devices

known to those skilled in the art for rapid filtration washing can be used for rapid filtration wash unit 32.

Loaded sorbent is introduced into rapid-wash filtration unit 32 from loaded sorbent storage 34. An aqueous oxidizing solution prepared to have the desired pH-Eh combination within the Mn02 stability area is then passed over and through the loaded sorbent with rapid filtration. The aqueous oxidizing solution may be monitored and adjusted prior to application to the loaded sorbent and the Eh and pH of the filtrate may be monitored. However, monitoring is not really required as long as there is no pooling so as to cause undesirable prolonged solid-liquid contact. Once the load sorbent had been washed for a time sufficient to restore or increase the loading capacity and/or Mn oxidation state, solution is no longer applied and the wet sorbent cake is routed to dryer 36. The same types and variety of dryers suitable as dryer 24 in the virgin sorbent pretreatment system 10 are suitable for use as dryer 36 in the loaded sorbent treatment system 30. And similarly, the selection will depend upon whether the recycle processed sorbent is to be introduced into a pollutant removal system dry or as a wet sorbent cake. If to be introduced dry, with comminution and possibly sieving, as necessary, the treated or recycle processed loaded sorbent is ready for re-introduction into a pollutant removal system.

It should be noted that the embodiment of the system of the invention in Figure 2 may be utilized for treatment of virgin oxides of manganese as well, even though prolonged liquid-solid contact need not be avoided for pretreatment. Thus, virgin sorbent may be treated in the system depicted in either Figure 1 or Figure 2 and by the same method as loaded sorbent.

Respectively, Figures 7 and 8 illustrate embodiments of the invention incorporating electronic controller to provide integrated simultaneous monitoring and adjustment of operational parameters for treatment of oxides of manganese with option feed back loop for checking the loading capacity of the treated sorbent.

With reference to Figure 7, the pretreatment system 40, illustrated in block flow, has a wash unit 42, a filtration unit 44, and a dryer 46. Wash unit 42 is equipped with temperature probe 47A, pH probe 47B and Eh probe 47C which are in electronic

communication with a controller 50. A vessel 52 containing oxidizing solution is configured to feed oxidizing solution to wash unit 42. Virgin sorbent vessel 53 containing virgin sorbent is configured to feed virgin sorbent to wash unit 42. Acid and/or base vessel 54 is configured to feed acid and or base to wash unit 42. The feeders (not shown) of vessels 52,53 and 54 are in electronic

communication with the controller 50. The controller is also in electronic communication with the Eh probe 55 with which the oxidizing solution vessel 53 is equipped. As illustrated treated sorbent from dryer 46 is routed to reaction chamber 56. Alternatively, sorbent from dryer 46 may be routed for storage or to a sorbent feeder prior to introduction to the reaction chamber 56. Reaction chamber 56 represents a pollution removal system or a reaction zone of a pollution removal system such as a Pahlman dry removal system described in co- pending U. S. patent application numbers 09/919, 600,09/951, 697,10/044, 089 and 10/025, 270 or any other pollution control system that utilizes oxides of manganese as a sorbent for removal of target pollutants from gas streams. Reaction chamber 56 is equipped with optional target pollutant concentration readers or continuous emission monitors (CEMS) for NOx and SOx readers 57A and 57B in electronic communication with controller 50.

The controller 50 interfaces with probes 47A-47C, readers 57A, 57B and the feeders of the vessels 52-54 for measurement and adjustment of operational parameters with in the pretreatment system. These parameters are important in determining the proper Eh of the aqueous oxidizing solution prior to addition to the washing unit 42 and the conditions in the washing unit 42 when the virgin sorbent is added. Eh probe 55 is in communication with controller 50 to adjust the Eh of oxidizing solution vessel 52. The controller 50 adds oxidant to vessel 52 until the desired Eh reading is abtained prior to addition to the wash unit 42. The temperature, pH, and Eh of the washing unit are monitored and adjusted so as to maintain conditions within the Mn02 stability area.

The controller 50 contains a programmable logic controller (PLC) and other hardware components necessary for the operation of the controller such as a power supply, input and output nodules that would communicate with the probes 47A-47C and/or readers 57A, 57B, and the feeders of the vessels 52-54. The controller 50 receives inputs from the various probes and readers and converts them into ladder logic language that would be used by an internal proportional integral derivative (PID) loop to individually and simultaneously monitor system operational parameters and to reconcile the inputs with predetermined or computer generated calculated set points for the operational parameters, such as temperature, and Eh and pH levels. As determined by computer logic, the controller 50 will send an output as necessary to any of the feeders of vessels 52-53 signaling a feeder to cycle on or to change feeder rate so as to maintain or adjust system operational parameters to within the Mn02 stability area. The controller 50 may also contain an Ethernet card or other component that allows onsite or offsite remote display and operator interface and control as needed.

The controller 50 would be given a start command and direct the feeders of vessels 52 and 53 to inject, respectively, a predetermined amounts of virgin sorbent and oxidizing solution into the washing unit 42. The controller would signal the feed of a predetermined amount of oxidant into the aqueous oxidizing solution vessel checking and or adjusting the Eh and/or pH of the solution prior to feeding into the washing unit. The Eh of the oxidizing solution in vessel 52 may be adjusted by addition of an oxidizer in sufficient quantity as to raise the Eh to the desired level from an oxidizer vessel, not shown in Figure 7, containing a supply of oxidizer. As determined by programmed controller logic, the controller 50 would also check, based on inputs received from the probes 47A-47C and/or adjust the conditions of the washing unit by adjusting the

temperature utilizing a heater or heat exchanger (not shown in Figure 7) to increase or decrease solution temperature; the pH, if needed, by increasing or decreasing the rate of base or acid feed; and the Eh, if needed, by increasing or decreasing the oxidizer concentration of the aqueous oxidizing solution. An optional, final quality control loop may be provided utilizing the readers 57A, 57B checking the loading performance of the treated sorbent by sending, for example, SOx and NOx readings back to the controller 50. As determined by controller logic, the controller 50 would then adjust the washing unit parameters, if needed, to provide treated oxides of manganese having increased loading capacity as compared to the untreated virgin sorbent contained in vessel 53. The same controller may also be used to control the entire operation of both the reaction chamber 56 and the pretreatment system 40, or separate controllers may be provided.

With reference to Figure 8, a recycle processing or regeneration system 60, for treating loaded sorbent is illustrated as a block flow diagram. The regeneration system 60 has a rapid filtration wash unit 62 from which treated sorbent is routed to dryer 64. The filtrate from wash unit 62 is directed for disposal or for other processing to recover useful values therein. Loaded sorbent vessel 66 is configured to feed loaded sorbent to wash unit 62. An oxidizing solution vessel 68 containing oxidizing solution is configured to feed oxidizing solution to wash unit 62. The feeders (not shown) of vessels 66,68 are in electronic communication with the controller 70. Vessel 68 is equipped with an Eh probe 72A and pH probe 72B which are also in electronic communication with the controller 70. As illustrated, treated sorbent from the dryer 64 is routed to a reaction chamber 56. It being understood that, as in pretreatment system of Figure 7, the treated sorbent may be routed to a sorbent feeder or to a sorbent storage bin. Similarly, optional readers 57A, 57B are in electronic

communication with controller 70, providing a optional control loop to check loading performance of treated sorbent.

The controller 70 interfaces with the Eh probe 72A, pH probe 72B, temperature probe 72C, the readers 57A, 57B, and the feeders of the vessels 66,68 to monitor and adjust the operational parameters of pH, Eh and temperature within the regeneration system 60.

Additionally, the controller 70 interfaces with a vessel (not shown in Figure 8) and the feeder thereof to provide acid or base as necessary to the aqueous oxidizing solution. It is important to determine and adjust, as necessary, the operational parameters prior to introducing the oxidizing solution into wash unit 62 in order to assure that conditions of the oxidizing solution are within the Mn02 stability area.

The controller 70 contains a programmable logic controller (PLC) and other components that would be necessary for the operation of the controller such as a power supply, input and output modules that would communicate with the probes 72A, 72B, 72C, the readers 57A, 57B and the feeders that supply the loaded sorbent, the aqueous oxidizing solution, and acid or base. The controller 70 receives inputs from the various probes and readers and convert them into ladder logic language that would be used by the internal proportional integral derivative (PID) loop to individually or simultaneously monitor system operational parameters and to reconcile the inputs with predetermined or computer generated calculated set points for the operational parameters. The controller 70 may also contain an Etc-remet card or other component that allows onsite or offsite remote display and operator interface and control as needed. Such integrated control of the regeneration system allows a practical alternative to manual adjustments by an operator and lends itself to automation of the

regeneration system even from remote locations.

The controller 70 would be given a start command and signal the feeders of the vessels 66,68, simultaneously or in desired sequence, to inject a predetermined amount of loaded sorbent and oxidizing solution into rapid filtration wash unit 62. In order to maintain conditions of the solution within the MnOa stability area, the controller 70 would, as necessary, signal feed of a predetermined amount of oxidizer, acid or base into the aqueous oxidizing solution in vessel 68, regularly monitoring and/or adjusting the Eh and/or pH of the solution prior to being fed into the washing unit. As determined by the controller logic, the controller 70 would also check, based on inputs received from the probes 72A, 72B, 72C, and/or adjust the conditions of the aqueous oxidizing solution in vessel 68 by adjusting the temperature utilizing a heater or heat exchanger (not shown in Figure 8) to increase or

decrease solution temperature; the pH, if needed, by increasing or decreasing the rate of base or acid feed; and the Eh, if needed, by increasing or decreasing the oxidizer concentration of the aqueous oxidizing solution.

As in the pretreatment system, an optional, final quality control loop may be provided utilizing the readers 57A, 57B, checking the loading performance of the treated sorbent by sending, for example, SOx and NOx readings back to the controller 70. As determined by controller logic, the controller 70 would then adjust oxidizing solution parameters, if needed, to provide treated oxides of manganese having increased loading capacity as compared to the untreated loaded sorbent contained in vessel 66. The same controller may also be used to control the entire operation of both the reaction chamber 56 and the treatment system 40, or separate controllers may be provided.

Applicants conducted a series of lab-scale tests utilizing a live slipstream of an actual exhaust gas from a coal-fired combustion source in order to demonstrate the increased loaded capacity achieved with the invention. A glass reactor designed to mimic the gas-solid interactions known to be present in the reaction zones of a Pahlman dry target pollutant removal system was utilized for the tests. The glass reactor was a vertically positioned Pyrex glass cylinder having an internal diameter of 2 inches and a length of approximately 18 inches. For each test run, 50.0 grams of oxides of manganese were suspended in the reactor using a permeable fritted glass filter positioned approximately 4 inches from the bottom of the reactor, allowing for flow of the gas stream through the reactor while keeping the oxides of manganese suspended. The test reactor was insulated and configured with thermocouples for temperature readings and heating elements for temperature control to maintain a temperature set point, which in the purposes of the conducted testes was 250 F.

A NOx and SOx laden gas stream was pumped into the bottom of the test reactor at a flow rate which provided adequate fluidization of the bed of sorbent to promote optimal gas/solids contact. The reactor was heated during the testing to 250 F and the gas flow rate was metered at a constant 6.5 liters per minute (lpm). The slipstream of actual exhaust gas was from a 570 MW tangentially-fired coal-burning boiler operating on Powder River Basin (PRB) western coal.

The composition of the exhaust gas was measured both on the inlet and outlet of the test reactor with appropriate gas analyzers, as one skilled in the art would employ and for the test run examples presented found to be within the following ranges: Oxygen (02) 6-7%, carbon dioxide (CO2) 10-12%, oxides of nitrogen (NOx) 190-250ppm, sulfur dioxide (S02)

400-500ppm. The composition of the inlet gas to the test reactor varied slightly from test to test, therefore the data was normalized and presented as pounds (lbs) of NOx or SO2 into and out of the test reactor. The extent of NOx and S02 loading was then calculated to determine the effectiveness of the aqueous oxidizing rinse. The slipstream was passed through the fluidized bed of oxides of manganese, where the flow carried a portion of the sorbent up onto the filter, thus creating a filter cake, which mimics a bag house reaction chamber of a Pahlman dry target pollutant removal system.

S02 and NOx concentrations were measured continuously alternating from the reactor inlet and outlet utilizing a continuous emissions monitoring system (CEMS). S02 concentrations were measured utilizing a Bovar Western Research model 921NMP spectrophotometric instrument and NOx concentrations were measured utilizing a Thermo Electron model 42H chemiluminescent instrument. In order to obtain accurate and reliable emission concentrations, sampling and reporting was conducted in accordance with US EPA Reference CFR 40, Part 60, Appendix A, Method 6C. Inlet gas temperature was 250 F, with a differential pressure across the permeable fritted glass filter was 2. 00" of WC. Figures 3 and 4 show the results of comparative test runs conducted utilizing 50g of each of virgin EMD type oxides of manganese sorbent, to provide a baseline, and treated virgin EMD type oxides of manganese sorbent prepared according to the invention. The treated virgin EMD type oxides of manganese sorbent sample was prepared by first treating with an aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl). The measured pH and Eh values of the starting aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl) were 8.5 and 900mV respectively, which provided a solution within the Mn02 stability area. A quantity of virgin EMD type oxides of manganese sorbent (75. 3g) was then added to a mixing beaker of 151g of the aqueous oxidizing solution of 0. 01% sodium hypochlorite (NaOCl). The slurry was then continually stirred for a period of 15 minutes while recording data on the changing pH and Eh of the solution. The starting pH of 8.5 quickly dropped to 6.2 within the first minute of mixing and after 15 minutes had dropped to 6.1. The Eh which started at 900mV rose to 1040mV within the first minute of mixing then started slowly dropping in about even increments to a finial value of 885mV after 15 minutes. The slurry was then placed in a paper filter to separate the solids from the filtrate. The now treated EMD type oxides of manganese sorbent was then placed in a drying oven and dried for 5 hrs at 185 F (85 C). The dried sorbent was then gently deagglomerated and 50g were then placed in the laboratory test reactor for subsequent target pollutant loading, the measured data points

are plotted and identified in Figures 3 and 4 as"Virgin Sorbent Following Treatment".

Along with the treated virgin EMD type sorbent loading rates, data points from untreated virgin EMD type oxides of manganese sorbent are alos plotted in Figure 3 and 4 as"Virgin Sorbent Baseline"to provide a baseline for loading capacity comparison.

Figure 3 shows the NOx loading curves. Looking at the virgin sorbent baseline, the virgin EMD type sorbent was at least achieving 90% NOx removal on a ppm basis for 24 minutes, during which time an accumulative total of 158 x 10-6 pounds of NOx entered into the laboratory test reactor with only 5. 6 x 10-6 pounds of NOx exiting the reactor, for a total of 152.4 x 10'"pounds of NOx being captured by the virgin EMD type oxides of manganese sorbent. The treated virgin EMD type sorbent is shown to exhibit substantially improved loading rates. NOx removal time at a NOx removal rate of at least 90% was increased to 47 minutes. For comparison, an accumulative total of 331 x

10'"pounds of NOx entered the laboratory test reactor with only 6.1 x 10-6 pounds of NOx exiting the reactor for a total of 324.9 x 10-6 pounds of NOx being captured by the treated virgin EMD type oxides of manganese sorbent
Figure 4 shows the SO2 loading curves. Looking at the virgin sorbent baseline, the virgin EMD type sorbent was at least achieving 99% S02 removal on a ppm basis for 24 minutes, during which time an accumulative total of 548 x 10-6 pounds of SO2 entered into the laboratory test reactor with only 1.9 x 10-6 pounds of SO2 exiting the reactor, for a total of 546. 1 x 10-6 pounds of S02 being captured by the virgin EMD type oxides of manganese sorbent. The treated virgin EMD type sorbent is shown to exhibit substantially improved loading rates. SO2 removal time a a removal rate of at least 99% was increased to 61 minutes. For comparison, an accumulative total of 1266 x 10-6 pounds of S02 entered the laboratory test reactor with only 0.9 x 10'"pounds of S02 exiting the reactor, for a total of 1265.1 x 10-6 pounds of S02 being captured by the treated virgin EMD type oxides of manganese sorbent.

Figures 5 and 6 show the results of comparative test runs conducted utilizing 50g of each of virgin EMD type oxides of manganese sorbent, to provide a baseline, and treated loaded EMD type oxides of manganese sorbent prepared according to the invention. The treated loaded EMD type sorbent sample was first treated with an aqueous oxidizing solution of 0. 01% sodium hypochlorite (NaOCl). The measured pH and Eh values of the starting aqueous oxidizing solution of 0. 01% sodium hypochlorite (NaOCl) were 8.9 and 900mV respectively, which provided a solution within the Mn02 stability area. A quantity of loaded

EMD type oxides of manganese sorbent (98.8g) was evenly distributed on moistened filter paper, which was placed in a Beuchner funnel. After applying vacuum, a first quantity of 1650 ml of aqueous oxidizing solution of 0.01% sodium hypochlorite (NaOCl) was evenly applied to the loaded EMD type sorbent surface at a rate such that no solution pooling was allowed to take place. The filtrate was then collected and the pH and Eh was measured to be 2.8 and 1070mV respectively. A second quantity of 1650 ml of an aqueous oxidizing solution of 0. 01% sodium hypochlorite (NaOCl) was again evenly applied to the loaded sorbent surface at a rate such that no solution pooling was allowed to take place. The second filtrate was then found to have a pH of 2.8 and an Eh of 1100mV. The now treated EMD type oxides of manganese sorbent was then placed in a drying oven and dried for 2 hrs at 185 F (85 C). The dried sorbent was then gently deagglomerated and 50g were then placed in the laboratory test reactor for subsequent target pollutant loading, the measured data points are plotted and identified in Figures 5 and 6 as"Loaded Sorbent Following Treatment."The data points from untreated virgin EMD type oxides of manganese sorbent are plotted in Figure 5 and 6 as"Virgin Sorbent Baseline"to provide a baseline for loading capacity comparison.

Figure 5 shows the NOx loading curves. Looking at the virgin sorbent baseline, the EMD type sorbent was at least achieving 90% NOx removal on a ppm basis for 24 minutes, during which time an accumulative total of 158 x 10-6 pounds of NOx entered into the laboratory test reactor with only 5.6 x 10-6 pounds of NOx exiting the reactor, for a total of 152.4 x 10-6 pounds of NOx being captured by the virgin EMD type oxides of manganese sorbent. The loaded EMD type sorbent following treatment is shown to exhibit substantially improved loading rates. NOx removal time at a removal rate of at least 90% was increased to 32 minutes. For comparison, an accumulative total of 222 x 10-6 pounds of NOx entered the laboratory test reactor with 8.4 x 10-6 pounds of NOx exiting the reactor, for a total of 213.6 x 10-6 pounds of NOx being captured by the treated loaded EMD type oxides of manganese sorbent.

Figure 6 shows the S02 loading curves. Looking at the virgin sorbent baseline, the EMD type sorbent was at least achieving 99% SO2 removal on a ppm basis for 24 minutes, during which time an accumulative total of 548 x 10-6 pounds of S02 entered into the laboratory test reactor with only 1.9 x 10-6 pounds of SO2 exiting the reactor, for a total of 546.1 x 10-6 pounds of S02 being captured by the virgin EMD type oxides of manganese sorbent. The treated loaded EMD type sorbent is shown to exhibit substantially improved

loading rates. S02 removal time at a rate of at least 99% was increased to 47 minutes. For comparison, an accumulative total of 901 x 10~6pounds of SO2 entered the laboratory test reactor with only 3.2 x 10-6 pounds of SO2 exiting the reactor, for a total of 897.8 x 10-6 pounds of SO2 being captured by the treated loaded EMD type oxides of manganese sorbent.

The data from the lab-scale tests presented in Figure 3-6 illustrate the increased loading capacity that is achievable with the invention.

While exemplary embodiments of this invention and methods of practicing the same have been illustrated and described, it should be understood that various changes, adaptations, and modifications might be made therein without departing from the spirit of the invention and the scope of the appended claims.

⑲ 日本国特許庁

公開特許公報

⑪特開昭 50－145324
㊸公開日 昭50.(1975)11.21
㉑特願昭 49－53593
㉒出願日 昭49.(1974)5.14
審査請求 未請求 (全4頁)

庁内整理番号
6769 39
7225 39

㊷日本分類
11 B091
11 C1

㊶Int.Cl²
B22D 11/10
B22D 39/00
B22D 41/08

(正)

(1)
(2)
(3)

特 許 願

昭和49年5月14日

特許庁長官殿

1. 発明の名称 連続鋳造における鋳型内介在物浮上法

2. 発明者
住所(居所) 山口県光市光井3204番地の2
氏名 池 富 勝 允 (ほか2名)

3. 特許出願人
住所(居所) 東京都千代田区大手町2丁目6番3号
氏名(名称) (665) 新日本製鉄株式会社
代表者 斗 井 富三郎
国籍 日本

4. 代理人
住所 東京都中央区日本橋茅場町2丁目10番地 共同ビル 電話(666)6563
氏名 (7792) 弁理士 秋 沢 政 光

5. 添付書類の目録
(1) 明細書 1通
(2) 図面 1通
(3) 委任状 1通
(4) 願書副本 1通
(5)
(6)
(7)
(8)

特許庁

明 細 書

1. 発明の名称

連続鋳造における鋳型内介在物浮上法

2. 特許請求の範囲

底面上向きの吐出口をもつ浸漬ノズルを用いて連続鋳造を行うに際し浸漬ノズル吐出口からの吐出流速を下記範囲で鋳造することを特徴とする連続鋳造における鋳型内介在物浮上法。

$100V \cdot S + 150 \geq Y \geq 100V \cdot S + 20$

V＝鋳片の引抜速度（m／min）

S＝鋳型断面積（m^2）

Y＝吐出流速（m／min）

3. 発明の詳細な説明

本発明は連続鋳造において鋳型内で鋳造中の介在物を浮上させる方法に関するものである。

従来連続鋳造においては鋳造用ノズルを鋳型内溶鋼に浸漬させて、且つ溶鋼の吐出口を水平面の如く角度をだけ斜下向きに設けて溶鋼をできる丈け静かに鋳造していた。この場合溶鋼は浸漬ノズル1の吐出口2から矢印イの方向へ吐出され鋳型3の下端部のシェル4に衝突して強い下向きの流れ（矢印ハ）と極めて強い速度を持つ上昇流（矢印ニ）とに分かれる。このため鋳型中の介在物はシェル4に捕捉されシェルに凝固され又シェルに衝突の衝撃の上昇流は極めて強いため介在物は浮上せず、加えて鋳型上部の溶鋼は停滞しているため殆んど除去される。これは湯面が低いための粉体が巻く介在物の分離浮上をさまたげていた。

本発明は連続鋳造におけるこのような鋳型内の溶鋼の流れを改善し、最終的に溶鋼とパウダーを強攪せしめ溶鋼中の介在物をパウダー中へ捕捉させんとする鋳型内介在物浮上法でその特徴は従来と同様の吐出口をもつ浸漬ノズルを用いて連続鋳造を行うに際し浸漬ノズル吐出口からの溶鋼吐出速度を特定範囲で鋳造することにある。

本発明によれば、第2図に示す如く溶鋼の吐出孔は角度だけ上向きとされ且つ浸漬ノズルからの溶鋼の吐出速度は従来の概念を破つて速くされる。

以下、本発明を図面によつて詳細に説明する。

第2図において溶鋼は吐出口3から矢印ヘの方

PAC ET AL. EXHIBIT 1019
Page 2015

内へ吐出されベウダー層の下面に衝突する。このため循環中の介在物は底部ベウダーに吸収してベウダー中へ捕捉される。しかも鋳型上部は常に流速が早い高温の溶鋼が流れてゆき高い温度が保たれているため介在物の浮上促進に寄与して効果がある。

ところで従来鋳型上部の溶鋼流速がある程度大きいと溶鋼にベウダーが巻込まれるという考え方があり、従つて溶鋼流がベウダを巻込まない最適流速をみさえるよう吐出口の断面積、角度及び浸漬深さ等を調整していた。

本発明はこのような従来の考え方を根本的にくつ返し、吐出速度を速くすることによりベウダーと溶鋼の界面の乱れが活発となつて溶鋼中の介在物がベウダー中へ移行するのを促進し介在物の浮上効果に著しい好結果をもたらすとの知見を得、種々実験によつて最適の溶鋼流速度を見出しその条件を規定したものである。

即ち、吐出口の溶鋼流速を鋳片の引抜速度と鋳型断面積との関係において下記式の通りとするものである。

$$100V \cdot S + 150 \geqq v \geqq 100V \cdot S + 20 \quad \cdots (1)$$

ここでV＝鋳片の引抜速度（m/min）

S＝鋳型断面積（m^2）

v＝吐出流速（m/min）

なお、吐出流速vの下限は介在物の浮上促進に効果が出始める点であり、上限は流速が速いことにより鋳片の乱れ等の欠陥が発生する限界点である。

本発明の実施に当つてはまず浸漬ノズルの吐出口の断面積を決定する必要があるが断面積は吐出口における溶鋼の流速と溶鋼の鋳込量との関係において次式によつて求まる。

即ち、

$$\delta = \frac{W \times 10^3}{\rho V_p} \quad \cdots (2)$$

W＝溶鋼の鋳込量（Kg/min）

V_p＝〃の吐出速度（m/min）

ρ＝〃の比重　（g/cm^3）

δ＝吐出口断面積（mm^2）

なお、δは吐出口の全断面積であるから、例えば吐出口が2個の場合は1個当りの吐出口断面積は $\delta/2$ となる。

次に吐出口断面積の巾と幅の寸法を決める。吐出流はベウダー層にできるだけ多く溶鋼を接触させるためできるだけ偏平にすることが望ましい。

従つて吐出口の幅は浸漬ノズルの内径の許す範囲内に於て最大とすべきである。即ち、内径Dの浸漬ノズルを用いたとすると2個の吐出口の全巾の長さδは次式によつて求まる。

$$D\delta = \frac{\delta}{2}$$

$$\therefore \delta = \frac{\delta}{2D}$$

$$\therefore \delta = \frac{W \times 10^3}{2D \rho V_p} \quad \cdots (3)$$

D＝浸漬ノズル内径（mm）

δ＝吐出口の巾の長さ（mm）

ここで例えば溶鋼の鋳込量（W）＝1000 Kg/min

〃　比　重（ρ）＝7.6

吐出口速度　（V_p）＝70m/min

浸漬ノズル内径（D）＝80mm

とするとδ＝19mmとなる。よつて2個の各吐出口の断面寸法は巾19mm、幅80mmとなる。

本発明を実施するには浸漬ノズルの横穴吐出口を上向きとなし、鋳片の引抜速度と鋳型断面積の関係式(1)から横穴吐出孔からの溶鋼流速を求め、求めた溶鋼流速と鋳込量との関係式(2)から浸漬ノズルの横穴吐出孔の断面積を求め、更に吐出孔の断面積と浸漬ノズル内径の関係式(3)から吐出孔の巾の長さを求め吐出孔の寸法を決定すればよい。

なお、溶鋼吐出孔の上向き角度及び浸漬深さは鋳型内全面の溶鋼が均等に移動するように適宜決定する。

第3図はSUS 321 の連続鋳造において S＝0.14 m^2, V＝1.0 m/min, θ＝15°（上向）の場合の実施例に於ける本法の効果を示すグラフであり、斜線で示した範囲が本発明により設定した最適吐出流速である。なお、鋳片介在物評点は鋳片表面下2mmにおける面積100 mm^2中、巾0.2 mm以上の介在物個数であり、各評点の介在物個数は評点5の場合3～4個、評点10の場合6～8

PAC ET AL. EXHIBIT 1019
Page 2016

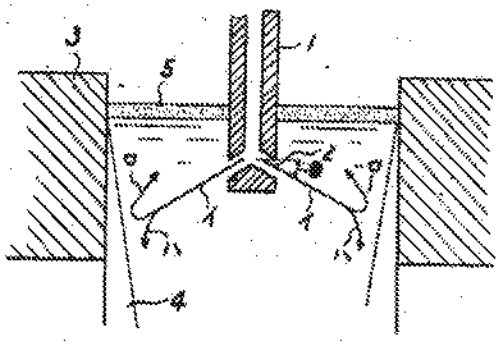
組、評点１５の場合９～１２である。

図から明らかなように転の欠陥が生じなければ速度は早い方が好ましい。

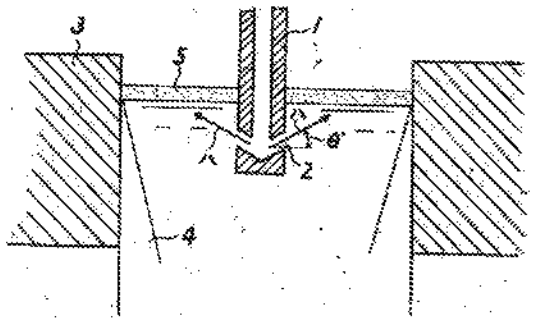
本発明はAl,Ti 等窒化物及び酸化物等の介在物を作りやすい元素を含む鋼種において従来の鋳造法では介在物が製品の表面は表われ表面性状を著しく悪くしていたが、本発明は特にこのような鋼種において極めて顕著な効果を発揮するものである。

4.図面の簡単な説明

第１図は従来法による例を示す略線的断面図，第２図は本発明方法による例を示す略線的断面図，第３図は本発明方法の効果を示すグラフである。図中、１は浸漬ノズル，２は溶鋼吐出口，３は鋳型，４はシエル，５はパウダー，である。



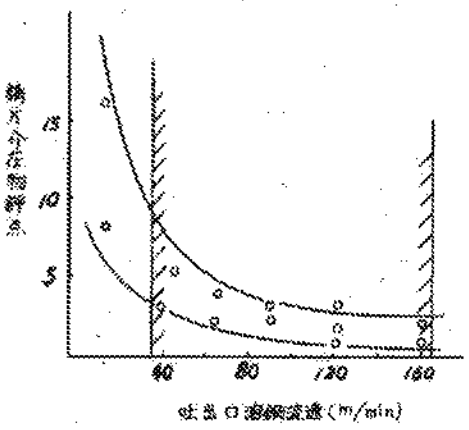
第１図



第２図

代理人弁理士　秋　沢　政　光

外２名



第３図

6. 前記以外の発明者、特許出願人または代理人

（1）発明者・考案者

住所(現住所)山口県光市島田４丁目１０番地

氏名　新藤義昭

住所(現住所)山口県光市大字島田竹字島田５５７０番地の３

氏名　岸井晴巳

住所(現住所)

氏名

住所(現住所)

氏名

（2）特許出願人・実用新案登録出願人

住所(居所)

氏名(名称)

代表者

国籍

住所(居所)

氏名(名称)

代表者

国籍

（3）代理人

住所　東京都中央区日本橋室町３丁目２番地
八重洲ビル　電話（５６６）５５６３

氏名　(6724)佐竹一彦

住所　同上

氏名　(7081)井口定雄

住所　同上

氏名　(　)

PAC ET AL. EXHIBIT 1019
Page 2017

受入印紙

(省略)

手続補正書

昭和49年6月17日

特許庁長官殿

1. 事件の表示
   特願昭49-53893号
2. 発明の名称
   連続鋳造における鋳型内介在物浮上法
3. 補正をする者
   事件との関係 出願人
   住所(居所) 東京都千代田区大手町2丁目6番3号
   氏名(名称) (683) 新日本製鉄株式会社
4. 代理人
   居所 東京都中央区日本橋兜町2丁目38番地 兜町ビル(仮)
   氏名 (5792) 秋元政光
5. 補正命令の日付 昭和 年 月 日(発送)
6. 補正により増加する発明の数
7. 補正の対象 明細書(発明の詳細な説明)
8. 補正の内容 別紙の通り

特許庁 49.6.18

補正の内容

(1) 明細書第2頁第5行「鋳塊止栓」を「鋳塊上栓」とする。

(2) 同第2頁第7行「…冷却される。これは鋳塊が低いため」を「…冷却されて鋳塊が低いため」とする。

(3) 同第7頁第6行「…表面は覆われ…」を「…表面に覆われ…」とする。

PAC ET AL. EXHIBIT 1019
Page 2018

Patent Translate
Powered by EPO and Google

Notice

This translation is machine-generated. It cannot be guaranteed that it is intelligible, accurate, complete, reliable or fit for specific purposes. Critical decisions, such as commercially relevant or financial decisions, should not be based on machine-translation output.

DESCRIPTION JPS50145324

3, patent application 1 person 40 agent - :::; two =! Ki, m @: s: 4 * Bay 0 Open Patent Publication "■ Special - Crystal 50-145324 - Specification 1, Name of Invention

---

３、特許出願１人４０代理人ー：：：：二＝！ ニー、ｍ＠：ｓ：４＊ベー０公開特許公報“■特ー晶５０－１４５３２４ー明細書１、発明の名称

, In-situ inclusion slag method in continuous casting -

、連続鋳造における鋳蓋内介在物滓上法ー

3, Detailed Description of the Invention The present invention relates to a method for floating inclusions in molten steel in a casting mold in continuous casting. Conventionally continuous casting K> - the casting nozzle is immersed in the mold 1111 c so as to be 1. And as casting molten steel, just drop the molten steel in an oblique downward direction by an angle I as shown in Fig. 1 - え. In this case, it is ejected from the molten steel discharge port 2 of the molten steel immersion nozzle 1 in the direction of the arrow A and casts into the cast l 11 O tin go sieve 4 and the lll - downward flow (arrow c) and the extremely lift And flow (arrow calculation). O inclusions in this rolled molten steel II inclusions When in contact with the shell 4 Collide on shell She collides with WaS steel upward flow Ili Extremely fine # - 9 Incident does not float, additionally the molten steel in the stationary part of the equipment stagnates The - rum is constantly cooled. This is because the temperature is low% /% Rounding viscosity is high so that inclusions are not levitated. The present invention is directed to a continuous mold in which continuous flow in the casting lid is adhered and a molten steel and a powder are brought into contact with each other in order to trap inclusions in the powder in the powder Internal inclusions! In the upper method, the% mold is dipped immersed in a diagonally upward molten

PAC ET AL. EXHIBIT 1019
Page 2019

steel discharge port.) When performing continuous casting using a dip, cast the molten steel discharge speed from the immersion nozzle discharge port in a specific range. According to the present invention, as shown in FIG. 2, the discharge hole of the molten steel is directed to the corner gF, and the discharge speed of the molten steel from the single nozzle is increased by breaking the conventional concept. Hereinafter, the present invention will be described in detail with reference to the drawings. Age 211K> SSW is discharged from the discharge port 2 in the arrow direction EndPage: 1 direction discharged powder 4 w or lower m *. The inclusions in the rolled molten steel are directly caught in the powder and trapped in the powder. Moreover, the casting - upper part always has high flow velocity O #! Steel flowing and snow · It is effective to promote the levitation of inclusions because the temperature is kept high. By the way, as far as tSS express delivery in the upper part of the mold is large, it is thought that when the molten steel KA, wadder is rolled in), so that the Sa flow does not blow the powder, Increase the product. angle and immersion depth etc.% fh mourning. The present invention responds to such an idea of

thought root roughly and thoroughly, by accelerating discharge 1 degree - movement of the interface between Ripau · Gou and molten steel becomes active and intervening in molten steel · We got the finding that the thing promotes the transition to powder, into the effect of levitating on the inclusions, and it gets good results, and we have found the optimum molten steel flow charcoal by various examinations It specifies that condition. .

３、発明の詳細な説明本発明は連続鋳造におーで鋳型内で溶鋼中の介在物を浮上させる方法に関する４のであ′る。 従来連続鋳造Ｋ＞一ては鋳造用ノズルを鋳型内°溶１１１１ｃ浸漬させて１． 且つ溶鋼の吐ｔＨｏｒ矛１図の一如く角度Ｉだけ斜下向きに設けて溶鋼をでぎるだけ、ｉかに鋳造して一え。 この場合溶鋼紘浸漬ノズル１の溶鋼吐出口２から矢印イの方向へ吐出され鋳１１１Ｏ下錫ｇｏシエに４に衝央して１１１一下向きの流れ（矢印ハ）と極めて１１一速度を持つ上昇流（矢印算）とに分かれる。 この丸め溶鋼中Ｏ介在物ＩＩｉシェル４に接触時シェルに捕捉さし叉シェルに衝突ＷａＳ鋼の上昇流ＩＩｉ極めて＃一九め介在物は浮上せず、加えて装置止部の溶鋼は停滞して一るえめ絶えず冷却される。 これは温度が低％／％丸めの粘性が高く介在物の公離浮上をさｔ九けていえ。 本発明は連続１造における一このような鋳蓋内の連流れを被着し、＠極的に溶鋼とパウダーを接触せしめ＃１■中の介在物をパウダー中へ捕捉させんとする鋳型内介在物！ 上法でその％徽は斜め上向きの溶鋼吐出口をもつえ浸漬）ズルを用いて連続鋳造を行うに際し浸漬ノズル吐出口からの溶鋼吐出速度を特定範囲で鋳造することＫあ　る。 本発明によれば、矛２図に示す如く溶鋼の吐出孔は角ｇＦにけ′上　向とされ且ら浸１ノズルからの溶鋼の吐出速度は従来の概念を破って速くされる。 以下、本発明を図面によって詳細に説明する。 才２１１Ｋ＞いてＳＳＷは吐出口２から矢印ハＯ方ＥｎｄＰａｇｅ：１向へ吐出されパウダー４ｗや下ｍＫ＊＊す畢。 この丸め溶鋼中の介在物は直接づクダ二に接触してパウダー中へ捕捉される。 しかも鋳一上部は常に流速が早い高温Ｏ＃！ 鋼が流れて・ゆき高一温度ダ保九れてーるため介在物の浮上促進に著して効果かあ・る。 ところで従来鋳型上部のｔＳＳ速達あま）大きいと溶鋼ＫＡ、ウダーが捲込まれるとーう考え方があ）、従ってＳａ流がパウダを捲込、まない程度流速一をおさえるよう吐出口の４断面、積、角度及び浸漬深さ等を加減して％ｆｈ喪。 本発明はこのような従　来の考え方を根~本的にゝぐつ返し、吐出１度を速くすることによーリパウ・グーと溶鋼の界面の動きが活発となって溶鋼中の介在・物がパウダ、一中へ移行するのを促進し介

PAC ET AL. EXHIBIT 1019
Page 2020

在物の浮上効果に著しニ好結果をも九らすとの知見を得、種々裏験によって最適の溶鋼流達炭を見出　しその条件を規定しえものである。。

In other words, the flow velocity of the discharge port 0 # l is O, which is the passage of the f expression in relation to the withdrawing speed of the cast piece and the mold cross sectional area. (M / mis) 8 - Mold cross - sectional area (-) Mass flow rate discharged (- m / min) - Note that discharge The lower limit of the flow velocity mark is the point at which the effect starts to rise and fall of the inclusions, and the upper limit is the limit that the defect such as multiple casting O cracking occurs, so that the castle gate is fast. In order to implement zero explosion, it is necessary to first decide the sectional area of the discharge port of the immersion nozzle, but the cross sectional area is the relationship between the flow velocity of the molten steel at the discharge port and the casting amount of the molten metal, K $ Pvh is obtained by the following equation. W - The casting amount of molten steel (/ man). V, - 1 outgoing velocity (m / min) of #. For example, 'd dual discharge ports are used because the total area of 1 - # of the discharge ports is the area of 1 - specific gravity - (P / -) - no discharge port cross section (-3) -' Is 4 per day for Ilm. Next, the discharge port cross-sectional area OjI and the lateral dimension are determined. It is recommended that the discharge flow be as flat as possible to round the molten steel as much as possible to the powder layer. Therefore, the width of the discharge port is maximum and within the allowable range of the inner diameter of the immersion nozzle. Inside! It is! DO! Using a picking nozzle and setting it to 9, each of the two outlets is vertical. Is obtained by the following equation. D - Immersion nozzle inner diameter (Ilm). (W) of molten steel = 1000 Np / m 1 n 1 specific gravity (#) - 7, discharge flow velocity (V) = 70 m / min Immersion nozzle inner diameter (D) 750 ss, it becomes p - l 11 -. The resolved dimensions of each of the two discharge ports are 19 m in length and 50 cm in width. In order to carry out the present invention, the molten steel discharge port of the immersion nozzle is directed upward, and the molten steel flow velocity from the discharge hole is obtained from the relationship formula of the casting piece O drawing speed and the mold cross-sectional area (i) Sectional area of one ejection hole of the immersion nozzle from the relational expression (2) of the casting amount and the casting amount and further from the relational expression (3) between the cross-sectional area of the ejection hole and the immersion nozzle inner diameter, the longitudinal length Please check the size and determine the size of the discharge hole. Furthermore, #! Steel Steel Volume Upward Upward angular change and immersion depth are appropriately determined so that the molten steel on the entire surface in the mold will move evenly. Age 3 is a graph showing the effect of the nature in the embodiment in the case of continuous casting of 81 JS 321 in the case of 8-0.14 m ", Vsml, Om / min, # 'ml 5 ° (upward), indicated by hatching The optimum discharge flow rate determined according to the present invention is set in the area.

即ち、吐出　口０＃１鋼流速を鋳片の引抜速度と鋳型断面積との関係においてｆ記式の通ヲとするもＯである。・、７－ノ１００Ｖ、８＋１５ｅｊｖｊ１ＯＯＶ、８＋２０・・・Ｉ１１こむでＶ－鋳片の引抜速度（ｍ／ｍｉｓ）８－鋳型断面積（－）　マ－吐出流速（－ｍ／ｍｉｎ）－な

PAC ET AL. EXHIBIT 1019
Page 2021

お、吐出流速マの下限は介在物の浮上一進に効果が出始める点であり、上限は城門が速いことに一よ多鋳片Ｏ割れ等の欠陥・が発生、する限界返である。 零発一明の実施に当うてはまず浸漬ノズルの吐出口の断面積を決定する必要があるが該断面積は吐出口における溶鋼の流速、と溶一の鋳込量との関係、Ｋ＄Ｐｖｈて次式によって求まる。 Ｗ－溶鋼の鋳込量（す／ｍａｎ）。Ｖ、一＃の１出流速（ｍ／ｍｉｎ）。 Ｉ一々の比重一（Ｐ／一）一ノ一吐出口断面積（－３）一’なシ、ノは吐出口の全１＃を面積であるから、例え’ｄ吐出口が２個の場合はＩｌｍ当りの吐出　日新面積はル４と一なる。 次に吐出口断面積Ｏｊ Ｉと横の寸法、を決める。吐出流はパウダ一層にできるだけ多く溶鋼を接触させる丸めできるにけ偏平にすることがＳま・しい。 従って吐出口の幅は浸漬ノズルの内径の許す限度内に於て最大とすべ龍である。 即ち、内！！ ＤＯ！ 漬ノズルを用い九とすると２個の吐出口の各縦。 の長さ１は次式によって求まる。Ｄ－浸漬ノズル内径（Ｉｌｍ）。 １一吐出口の縦の長さくＷ）ここで例えば溶鋼の鋳込量（Ｗ）＝１０００Ｎｐ／ｍｌｎｌ比重（＃）－７，６吐出口流速（Ｖ）＝７０ｍ／ｍｉｎ浸漬ノズル内径（Ｄ）７５０ｓｓとするとｐ－ｌｌｌ－となる。 よりて２個の各吐出口の断固寸法は縦１９ｍ、横５０－となる。 本発明を実施するには浸漬ノズルの溶鋼吐出口を上向きとなし、鋳片Ｏ引抜速度と鋳型断面積の関係式（ｉ塾から該吐出孔からの溶鋼流速を求め、求めルＳ＊流達と鋳込量との関係式（２）から浸漬ノズルの一一吐出孔の断面積゜を求め、更に吐出孔の断一面積と浸漬ノズル内径の関係式（３）から吐出孔の縦の長ざを求め吐出孔の寸法を決定、すれによ一’。 なお、＃！ 鋼鋼量出孔上向き角変及び浸漬深さは鋳型内全面の溶鋼が均等に移動するように適宜決定する。 才３図は８ｌＪＳ３２１の連続鋳造において８－０．１４ｍ”、ＶｓｍｌＯｍ／ｍｉｎ、＃’ｍｌ５°（上向）の場合の実施例に於ける本性の効果を示すグラフであり、斜線で示しえｉ囲が本発明によ１定した最適吐出流速である。

In addition, - the number of inclusions exceeding the number of 20 voices in the area IQQ 1111 'in cast iron inclusion jurisdiction surface y 2 -, the inclusion score of each grade is 3 in the case of rating 5 4, when the score is 10 6 - 8 EndPage: 2, the score 15 of the score 15 9 - "12. As obvious from the figure, unless other defects occur, the flow rate is preferably at most 10, the present invention is 4 J, the steel type which contains one element easy to produce inclusions such as Ti · isoelectric substances and oxides In the conventional casting method, the inclusions showed the compliment of the product and the surface quality was markedly worsened, but the present invention is one which exhibits extremely remarkable effect in i like this kind in 41 .

なお、一鋳片介在物評点轄鋳片表面ｙ２一におけ一る面積ＩＱＱ１１１１’中、号さ２０声以上の介在物個数であり、各評点の介在物個敬は評点５の場合３へ４個、評点１０の場合６～８ＥｎｄＰａｇｅ：２個、評点１５の揚台９一”１２である。 図から明らかなように他の欠陥が生じなければ流速は早一方が好まし一〇、本発明は４Ｊ、Ｔｉ・等電化物及び酸化物等の介在物を作ヲやす一元素を含む鋼種にお一で従来の鋳造法では介在物が製品の褒面は表われ表面性状を一著しく悪くしていたが、本発明は４１にこのような一種におｉで極めて顕著な効果を発揮するものである。

PAC ET AL. EXHIBIT 1019
Page 2022

4, Brief Description of the Drawing FIG. 1 is a schematic sectional view showing an example according to a conventional method, It-1 immersion nozzle in the figure, 2 is a molten steel discharge port, 3 is a mold, 4 is a shell, and 5 is a powder is there. Attorney Attorney Aki Tsuya, Masamitsu 2 juices 1 group 'Mujutsu mouth refinement (to m / mi) Juice 3 groups 6, Other than 1 = Person, Venge □ Niche Applicant or Agent Name, Address Name of applicant / applicant for utility model registration WrC residence Name (name) representative nationality address (residence j 91) name (name) representative nationality (3) representative name (6724) extractability Chief residence □ Same as above ____ 4 Full name (7031) Atsuo Iguchi - residence _____ _____ 0 Name (-) EndPage: 3, 1. Display of the case - Patent application 49 - No. 5: HO No. 2 "Knee, Levitation method of inclusions in foundry in continuous casting 3, Persons who make corrections - Relationship with the case Applicant's name (name) <6 @ S) New Japan Steel Stock Investigation Company 4, Agent <j) Specifications O 2 pages Contradicted to 6 lines "Mold stop" as "Cast - Top". The Q official line off "2 rows ..." It is compressed. This is temperature <3) lie off page, IF 6 line "... show the surface ..." · · · Table 1iiK! I ... ". EndPage: 4

４、図面の簡単な説明矛１図は従来法による例を示す路線的断面図、図中、Ｉｔ－１浸漬ノズル、２は溶鋼吐出口、３は鋳型、４はシェル、５はパウダー、である。 代理人弁理士秋沢、政光外２名汁１団′吐忠口細充途（ｍ／ｍｉへ）汁３団６、前記以外の１＝者、讐□ニジ出願人または代理人氏、名住所（居所）氏名（２）特許出願人・実用新案登録出願人任ＷｒＣ居所）氏名（名称）代表者国籍住所（居ｊ９１）氏名（名称）代表者国籍（３）代理人氏名（６７２４）抜性章居所□同上一一　－４氏名（７０３１）井口定雄一居所同上氏名（一）ＥｎｄＰａｇｅ：３、１．事件の表示一特願昭４９一第５：ＨＯ２号”ニー、連続鋳造における鋳鷹内介在物浮上法３、補正をする者一事件との関係出願人氏名（名称）＜６＠Ｓ）新日本製鉄株式査社４、代理人＜ｊ）明細書オ２頁矛６行「鋳型止部」を「鋳ー上部」とする。　Ｑ）　同オ２頁オフ行「・・・冷却　される。これは温度＜３）ｌｉｅオフ頁、ＩＦ６行「・・・表面は表われ・・・」を「・・・表１ｉｉＫ！！われ・・・」とする。ＥｎｄＰａｇｅ：４

PAC ET AL. EXHIBIT 1019
Page 2023

1 of 1 DOCUMENT

SU732207A1 1980-05-05 **METHOD OF PRODUCING ADSORBENT FOR ADSORBING BLOOD TOXINS** (en)

Standardized Assignees: VSESOYUZNYJ NAUCHNO ISSLEDOVATELSKIJ INSTITUT MEDITSINSKIKH POLIMEROV

Original Assignees: VSESOYUZNYJ NAUCHNO-ISSLEDOVATELSKIJ INSTITUT MEDITSINSKIKH POLIMEROV

Current Assignees: VSESOYUZNYJ NAUCHNO-ISSLEDOVATELSKIJ INSTITUT MEDITSINSKIKH POLIMEROV

Inventors: VALUEVA SVETLANA PAVLOVNA;
ELTSEFON BORIS SEMENOVICH;
DUBROVSKIJ ANATOLIJ KIRILLOVICH;
MOLODENKOV MIKHAIL NIKOLAEVICH;
SOLNYSHKIN VIKTOR IVANOVICH;
ZEZIN ALEKSANDR BORISOVICH;
ROGACHEVA VALENTINA BORISOVNA;
SURINOVA SOFYA IVANOVNA

Application Number: SU2409772

Application/Filing Date: 1976-10-08

Priority Number and Date: SU2409772 1976-10-08

Classifications:
IPC[5]: 5C01B31/16A 5C01B31#16A 5C01B31/16A
IPC[8]: C01B31/00 (2006-01-01; C, F, I, 1980-05-05; B, M, SU)
IPC[8]: C01B31/16 (2006-01-01; A, F, I, 1980-05-05; B, M, SU)

Patent References Cited-Forward:

Publication Number
US5252321A
EP4566326A1
US7311845B2
US5476715A
EP2978896A1
US5151402A

English Description:

Method consists in disggergirovanii activated coal particles in solution, containing polymer (polyacrylamide, by 1ivin1lovyi alcohol, polyvinylpyrrolidone) and a cross-linking agent (methyl-bis-4-phenyi-isocyanate) and in weight ratio of 20:1, using as solvent mixture of 4 parts dimetipformamida and 1 part of pyridine at weight ratio of activated

coal: polymer from 1:1 to 1:2, with subsequent separation of adsorbent and evaporation of solvent. Deficiency of method is the fact, that for its realization it require introduction in solution of polymer cross-linking agent (metnl -bis-phenyl-isocyanate), which is toxic compound and deteriorate biocompatibility adsorbent, intended for contact with krovyb.

Naiboiee close of known to proposed method by technical essence and made result is method of producing adsorbent with coating representing copolymer of hydro filnogo monomer (is selected from class of carboxylic unsaturated kislotakrilovoi , methacrylic, itaconic, and also of acrylamide, vinilpirollidona , dimetilaminoetilakrilata , hydro sietilmetakrilata and dimetilaminoetilmetakrilaga) and hydro fobnogo monomer (is selected from row of: acrylonitrile, metakrloatril , 2nvinil -pyridine, 2-methyl -5" vinylpyridine, styrene, esters of acrylic, u1etakrilovoi , itaconic acids) at ratio of hydro filnyi monomer: hydro fobnyi monomer, equal 15-40:

.85-60 V3J.

Method of producing adsorbent consists and dispersion activated coal particles in solution of copolymer, of forming coating, with used in as solvent dimethylformamide, following separation adsorbent and evaporation of solvent at heating. Polymer coating sostaviyae by weight from 9.5 to 4% of weight of adsobrenta.

Deficiency izBvstnogo method yavlyaete Your iu absorbing capacity of adsorbent due to the use of toxic, highly fluidized, and consequently difficult to evacuate of solvent (dshyutilformamida), the presence of which whom even in small amounts deteriorate compatibility adsorbent with blood.

For invention is diffusion iu absorbing capacity of adsorbent for cleaning blood with polymer gemosovmestimym coating, which stable in blood, contains no impurities toxic solvent, causes no thrombosis and hemolysis of blood, enhanced mechanical strength, coal, predotvrashaya washed coal dust from adsorbent, and together with the not reduce absorbing capacity of initial activated charcoal on absorption of toxins from blood.

Or-, particles of activated coal is treated with alkaline solutions of polyacrylic acids and polyethylenimine, the obtained suspension podkisl5pot to ph 7-9 and heat treatment is carried out at 130250 with, wherein the weight ratio activated carbon: polanion : prlikation is 5:5:1-10:1:1.

The method is carried out as follows.

Particles of activated coal is treated with solution of polyethyleneimine, then alkaline solution of polyacrylic acid in ratio of activated carbon: polyacrylic acid, : polyethyleneimine 5:5:1-1:1:1. Obtained suspension is treated with acid to ph 7-9 and is subjected to heat treatment at 130-25 0° with.

Example 1. South activated coal, preliminarily washed in running water and dried, is stirred for 30 min at 100 ml of 0.1 n. aqueous solution of polyethyleneimine branched and, continuing to mixing is gradually added 10° ml 0.1 n. solution of sodium and the stirring is continued for another 30 min. Weight ratio of activated carbon: polyacrylic acid, : polyethyleneimine 1:1:1. To solution slowly prikapyvayut hydrochloric acid up to appearance of onalestsentsii , still several minutes the stirring is continued. Coal is decanted, washed several times water n podvergayut thermal treatment at 130135 with absorb cus min.

Example 2. Treatment of aktiviro bath of coal is performed, as in example 1, changing order of addition of polyelectrolytes and temperature of heat treatment,.

Example 3. Treatment of activated coal is carried out, as in example 1.

varying weight ratio of activated carbon: popimetakralovaya acid: polyethyleneimine -5:2:1 and temperatypy heat treatment of 230° with.

Example 4. Treatment of aktiv1fovannogo of coal is performed, as in example 1, changing the weight. ratio of aktivirolannyi coal: polyacrylic acid, : polyethyleneimine -5:5:1.

Absorbing capacity adsorbents, obtained according to this method, was by adsorption of creatinine from

aqueous solutions, 0.6 g adsorbent peryumeshivali in 5° ml of solution creatinine with initial concentration of 4O mg %. After certain intervals of vryumekn was reduced concentration of creatinine, in solution and calculated percentage of adso () birovannogo creatinine. Results of experiments on determination of absorbing capacity of adsorbents, obtained-n described in examples 1-4, are brought in the table.

Number of Claims: 12

ENGLISH CLAIMS:

From results of, given in the table is seen, that adsorbent, obtained method, proposed invention in 2 times more rapidly (30 min.) absorbs creatinine, and consequently, more effective, than adsorbent in the prior art.

Polymer coating, as shown experiments on animals, ensures satisfactory compatibility adsorbent with blood, does not cause thrombosis, hemolysis of erythrocytes and antigenic reactions. In the process of hemosorption is not disturbed integrity of granules of adsorbent and does not exhibit isolation of coal dust, adducting usually to embolism.

Claim

1. Method of producing adsorbent for absorption of blood toxins, kiyuchayushchii treatment of activated coal particles solution of polymers, containing polyacrylic acids, n heat treatment of the obtained product, characterized by, that, with the aim of diffusion condensate absorbing capacity of adsorbent, activated carbon is treated with alkaline solutions of polyacrylic acids and polyethylenimine, obtained suspension is treated with acid to ph 7-9 and thermal treatment osushchest1M1yayut at 130-25 0° with.

7 7322078

2. Method of according to Claim 1, about and tea -4, Frons. vmer. Soc. 3nt Ogaopz

wy and and with th the fact, chtrBfecoBde - sootnosha — 17.246 (4974) Selections

lu aktivironnyiugoiyolakrtlvye2. French form № 2148022

acid: nonHaHni j rti (; " (SdiffletTV 01 d 15/00, opubInk. 1973.

5:5:1-10:1: 1V53. French form № 2235722,

Isgochniki information, cells. In 01 1 15/00, opublik. 07.03.75

received into account at examination (prototype).

Союз Советских Социалистических Республик

Государственный комитет СССР по делам изобретений и открытий

ОПИСАНИЕ ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

(11) 732207

(61) Дополнительное к авт. свид-ву –

(22) Заявлено 08.10.76 (21) 2409772/23-26

с присоединением заявки № –

(23) Приоритет –

Опубликовано 05.05.80. Бюллетень № 17

Дата опубликования описания 08.05.80

(51) М. Кл.[2] C 01 B 31/16

(53) УДК 661.183.2 (088.8)

(72) Авторы изобретения: С. П. Валуева, Б. С. Эльцефон, А. К. Дубровский, М. Н. Молоденков, В. И. Солнышкин, С. И. Сурикова, А. Б. Зезин и В. Б. Рогачева

(71) Заявитель: Всесоюзный научно-исследовательский институт медицинских полимеров

(54) СПОСОБ ПОЛУЧЕНИЯ АДСОРБЕНТА ДЛЯ ПОГЛОЩЕНИЯ ТОКСИНОВ КРОВИ

1

Изобретение относится к области получения адсорбентов с полимерным покрытием и может быть использовано в медицинской практике для очистки крови, плазмы и других биологических жидкостей от ядов эндогенного и экзогенного происхождения.

Известны адсорбенты для очистки крови из активированного угля. Такие адсорбенты, обладая эффективностью выведения из крови ряда токсинов, имеют вместе с тем недостаточную механическую прочность в условиях эксплуатации и неудовлетворительную совместимость с кровью. Это приводит к эмболии, образованию тромбов и гемолизу эритроцитов. Применение активированного угля с защитным покрытием из гемосовместимых материалов позволяет устранить эти недостатки. При этом покрытие не должно ухудшать функциональные свойства адсорбента, в частности снижать эффективность адсорбента по поглощению токсинов из крови.

2

Известен способ получения адсорбента с покрытием из синтетического полимера и природного биополимера – альбумина [1].

Способ заключается в обработке активированного угля раствором нитрата целлюлозы в смеси эфира и спирта при весовом соотношении уголь: полимер = 20:1, отделении адсорбента, высушивании растворителя при 60°С и последующей обработке водным раствором альбумина человеческого при температуре не выше 4°С непосредственно в перфузионном устройстве для очистки крови за несколько часов до употребления. Недостатком способа является то, что используемый биополимер (альбумин) не обладает стабильностью свойств при хранении и не выдерживает условий стерилизации (термообработки).

Известен также способ получения адсорбентов с покрытием из синтетических полимеров [2].

PAC ET AL. EXHIBIT 1019
Page 2027

Способ заключается в диспергировании частиц активированного угля в растворе, содержащем полимер (полиакриламид, поливиниловый спирт, поливинилпирролидон) и сшивающий агент (метил-бис-4-фенил-изоцианат)и в весовом соотношении 20:1, с использованием в качестве растворителя смеси 4 частей диметилформамида и 1 части пиридина при весовом соотношении активированный уголь: полимер от 1:1 до 1:2, с последующим отделением адсорбента и выпариванием растворителя. Недостатком способа является то, что для своего осуществления он требует введения в раствор полимера сшивающего агента (метил-бис-фенил-изоцианат), который является токсичным соединением и ухудшает биосовместимость адсорбента, предназначенного для контакта с кровью.

Наиболее близким из известных к предлагаемому способу по технической сущности и достигаемому результату является способ получения адсорбента с покрытием представляющим собой сополимер гидрофильного мономера (выбирается из класса карбоновых ненасыщенных кислот-акриловой, метакриловой, итаконовой, а также акриламида, винилпирролидона, диметиламиноэтилакрилата, гидроксиэтилметакрилата и диметиламиноэтилметакрилата) и гидрофобного мономера (выбирается из ряда: акрилонитрил, метакрилонитрил, 2-винил-пиридин, 2-метил-5-винилпиридин, стирол, эфиры акриловой, метакриловой, итаконовой кислот) при соотношении гидрофильный мономер: гидрофобный мономер, равном 15-40: :85-60 [3].

Способ получения адсорбента заключается в диспергировании частиц активированного угля в растворе сополимера, формирующего покрытие, с использованием в качестве растворителя диметилформамида, последующего отделения адсорбента и выпаривания растворителя при нагревании. Полимерное покрытие составляет по весу от 9,5 до 4% от веса адсорбента.

Недостатком известного способа является снижение поглотительной способности адсорбента за счет использования токсичного, высококипящего, а следовательно трудноудаляемого растворителя (диметилформамида), присутствие которого даже в малых количествах ухудшает совместимость адсорбента с кровью.

Целью изобретения является повышение поглотительной способности адсорбента для очистки крови с полимерным гемосовместимым покрытием, которое устойчиво в крови, не содержит примесей токсичного растворителя, не вызывает тромбообразования и гемолиза крови, повышает механическую прочность угля, предотвращая вымывание угольной пыли из адсорбента, и вместе с тем не снижает поглотительной способности исходного активированного угля по поглощению токсинов из крови.

Поставленная цель достигается тем, что частицы активированного угля обрабатывают щелочными растворами полиакриловых кислот и полиэтиленимина, полученную суспензию подкисляют до pH 7-9 и термообработку ведут при 130-250°С, причем весовое соотношение активированный уголь: полианион: поликатион составляет 5:5:1 - 10:1:1.

Способ осуществляют следующим образом.

Частицы активированного угля обрабатывают раствором полиэтиленимина, затем щелочным раствором полиакриловой кислоты в соотношении активированный уголь: полиакриловая кислота: полиэтиленимин 5:5:1 - 10:1:1. Полученную суспензию обрабатывают кислотой до pH 7-9 и подвергают термообработке при 130-250°С.

Пример 1. 10 г активированного угля, предварительно отмытого в проточной воде и высушенного, перемешивают в течение 30 мин со 100 мл 0,1 н. водного раствора полиэтиленимина разветвленного и, продолжая перемешивание, постепенно добавляют 100 мл 0,1 н. раствора полиакрилата натрия и продолжают перемешивание еще 30 мин. Весовое соотношение активированный уголь: полиакриловая кислота: полиэтиленимин - 10:1:1. К раствору медленно прикапывают соляную кислоту до появления опалесценции, еще несколько минут продолжают перемешивание. Уголь декантируют, отмывают несколько раз водой и подвергают термообработке при 130-135°С в течение 30 мин.

Пример 2. Обработку активированного угля проводят, как в примере 1, изменяя порядок добавления полиэлектролитов и температуру термообработки, 180°С.

Пример 3. Обработку активированного угля проводят, как в примере 1.

PAC ET AL. EXHIBIT 1019
Page 2028

изменяя весовое соотношение активированный уголь: полиметакриловая кислота: полиэтиленимин – 5:2:1 и температуру термообработки 230°С.

Пример 4. Обработку активированного угля проводят, как в примере 1, изменяя весовое соотношение активированный уголь: полиакриловая кислота: полиэтиленимин – 5:5:1.

Поглотительную способность адсорбентов, полученных по данному способу, определяли по адсорбции креатинина из водных растворов, 0,6 г адсорбента перемешивали в 50 мл раствора креатинина с исходной концентрацией 40 мг%. Через определенные промежутки времени определяли уменьшение концентрации креатинина в растворе и рассчитывали процент адсорбированного креатинина. Результаты опытов по определению поглотительной способности адсорбентов, полученных по предложенному способу и описанных в примерах 1–4, приводятся в таблице.

Поглотительная способность адсорбента	Адсорбент с покрытием, полученный по способу, описанному в прототипе		Адсорбент с покрытием, полученным по предложенному способу	
время адсорбции	адсорбированный креатинин	полимер и уголь	уголь: полианион: поликатион	температура термообработки, °С
1 ч	73	0,5	–	–
1 ч	47	1	–	–
1 ч	12	2,5	–	–
30 мин	72	–	10:1:1	130–135
30 мин	63	–	10:1:1	180
30 мин	40	–	5:2:1	230
30 мин	35	–	5:5:1	130

Из результатов, приведенных в таблице видно, что адсорбент, полученный по способу, предложенному в изобретении, в 2 раза быстрее (30 мин.) поглощает креатинин, а следовательно, более эффективен, чем адсорбент по прототипу.

Полимерное покрытие, как показали опыты на животных, обеспечивает удовлетворительную совместимость адсорбента с кровью, не вызывает тромбообразования, гемолиза эритроцитов и антигенных реакций. В процессе гемосорбции не нарушается целостности гранул адсорбента и не наблюдается выделения угольной пыли, приводящей обычно к эмболии.

Формула изобретения

1. Способ получения адсорбента для поглощения токсинов крови, включающий обработку частиц активированного угля раствором полимеров, содержащим полиакриловые кислоты, и термообработку полученного продукта, отличающийся тем, что, с целью повышения поглотительной способности адсорбента, активированный уголь обрабатывают щелочными растворами полиакриловых кислот и полиэтиленимина, полученную суспензию обрабатывают кислотой до pH 7–9 и термообработку осуществляют при 130–250°С.

PAC ET AL. EXHIBIT 1019
Page 2029

2. Способ по п. 1, о т л и ч а ю щ и й с я тем, что весовое соотношение активированный уголь: полиакриловые кислоты: полиэтиленимин составляет 5:5:1 – 10:1:1.

Источники информации, принятые во внимание при экспертизе

1. Trans. Amer. Soc. Artif Int Organs, 17.246(1971)

2. Французская заявка № 2148022, B 01 D 15/00, опублик. 1973.

3. Французская заявка № 2235722, кл. B 01 D 15/00, опублик. 07.03.75 (прототип).

Составитель В. Виноградова
Редактор Л. Курасова Техред О. Андрейко Корректор Ю. Макаренко

Заказ 1641/14 Тираж 565 Подписное
ЦНИИПИ Государственного комитета СССР
по делам изобретений и открытий
113035, Москва, Ж–35, Раушская наб., д. 4/5

Филиал ППП "Патент", г. Ужгород, ул. Проектная, 4

PAC ET AL. EXHIBIT 1019
Page 2030

Союз Советских Социалистических Республик

Государственный комитет СССР по делам изобретений и открытий

ОПИСАНИЕ ИЗОБРЕТЕНИЯ

К АВТОРСКОМУ СВИДЕТЕЛЬСТВУ

(11) 732207

(61) Дополнительное к авт. свид-ву –

(22) Заявлено 08.10.76 (21) 2409772/23-26

с присоединением заявки № –

(23) Приоритет –

Опубликовано 05.05.80. Бюллетень № 17

Дата опубликования описания 08.05.80

(51) М. Кл.[2] C 01 B 31/16

(53) УДК 661.183.2 (088.8)

(72) Авторы изобретения: С. П. Валуева, Б. С. Эльцефон, А. К. Дубровский, М. Н. Молоденков, В. И. Солнышкин, С. И. Сурикова, А. Б. Зезин и В. Б. Рогачева

(71) Заявитель: Всесоюзный научно-исследовательский институт медицинских полимеров

(54) СПОСОБ ПОЛУЧЕНИЯ АДСОРБЕНТА ДЛЯ ПОГЛОЩЕНИЯ ТОКСИНОВ КРОВИ

1

Изобретение относится к области получения адсорбентов с полимерным покрытием и может быть использовано в медицинской практике для очистки крови, плазмы и других биологических жидкостей от ядов эндогенного и экзогенного происхождения.

Известны адсорбенты для очистки крови из активированного угля. Такие адсорбенты, обладая эффективностью выведения из крови ряда токсинов, имеют вместе с тем недостаточную механическую прочность в условиях эксплуатации и неудовлетворительную совместимость с кровью. Это приводит к эмболии, образованию тромбов и гемолизу эритроцитов. Применение активированного угля с защитным покрытием из гемосовместимых материалов позволяет устранить эти недостатки. При этом покрытие не должно ухудшать функциональные свойства адсорбента, в частности снижать эффективность адсорбента по поглощению токсинов из крови.

2

Известен способ получения адсорбента с покрытием из синтетического полимера и природного биополимера – альбумина [1].

Способ заключается в обработке активированного угля раствором нитрата целлюлозы в смеси эфира и спирта при весовом соотношении уголь: полимер = 20:1, отделении адсорбента, высушивании растворителя при 60°С и последующей обработке водным раствором альбумина человеческого при температуре не выше 4°С непосредственно в перфузионном устройстве для очистки крови за несколько часов до употребления. Недостатком способа является то, что используемый биополимер (альбумин) не обладает стабильностью свойств при хранении и не выдерживает условий стерилизации (термообработки).

Известен также способ получения адсорбентов с покрытием из синтетических полимеров [2].

PAC ET AL. EXHIBIT 1019
Page 2031

Способ заключается в диспергировании частиц активированного угля в растворе, содержащем полимер (полиакриламид, поливиниловый спирт, поливинилпирролидон) и сшивающий агент (метил-бис-4-фенил-изоцианат)и в весовом соотношении 20:1, с использованием в качестве растворителя смеси 4 частей диметилформамида и 1 части пиридина при весовом соотношении активированный уголь: полимер от 1:1 до 1:2, с последующим отделением адсорбента и выпариванием растворителя. Недостатком способа является то, что для своего осуществления он требует введения в раствор полимера сшивающего агента (метил-бис-фенил-изоцианат), который является токсичным соединением и ухудшает биосовместимость адсорбента, предназначенного для контакта с кровью.

Наиболее близким из известных к предлагаемому способу по технической сущности и достигаемому результату является способ получения адсорбента с покрытием представляющим собой сополимер гидрофильного мономера (выбирается из класса карбоновых ненасыщенных кислот-акриловой, метакриловой, итаконовой, а также акриламида, винилпирролидона, диметиламиноэтилакрилата, гидроксиэтилметакрилата и диметиламиноэтилметакрилата) и гидрофобного мономера (выбирается из ряда: акрилонитрил, метакрилонитрил, 2-винил-пиридин, 2-метил-5-винилпиридин, стирол, эфиры акриловой, метакриловой, итаконовой кислот) при соотношении гидрофильный мономер: гидрофобный мономер, равном 15-40: :85-60 [3].

Способ получения адсорбента заключается в диспергировании частиц активированного угля в растворе сополимера, формирующего покрытие, с использованием в качестве растворителя диметилформамида, последующего отделения адсорбента и выпаривания растворителя при нагревании. Полимерное покрытие составляет по весу от 9,5 до 4% от веса адсорбента.

Недостатком известного способа является снижение поглотительной способности адсорбента за счет использования токсичного, высококипящего, а следовательно трудноудаляемого растворителя (диметилформамида), присутствие которого даже в малых количествах ухудшает совместимость адсорбента с кровью.

Целью изобретения является повышение поглотительной способности адсорбента для очистки крови с полимерным гемосовместимым покрытием, которое устойчиво в крови, не содержит примесей токсичного растворителя, не вызывает тромбообразования и гемолиза крови, повышает механическую прочность угля, предотвращая вымывание угольной пыли из адсорбента, и вместе с тем не снижает поглотительной способности исходного активированного угля по поглощению токсинов из крови.

Поставленная цель достигается тем, что частицы активированного угля обрабатывают щелочными растворами полиакриловых кислот и полиэтиленимина, полученную суспензию подкисляют до pH 7-9 и термообработку ведут при 130-250°С, причем весовое соотношение активированный уголь: полианион: поликатион составляет 5:5:1 - 10:1:1.

Способ осуществляют следующим образом.

Частицы активированного угля обрабатывают раствором полиэтиленимина, затем щелочным раствором полиакриловой кислоты в соотношении активированный уголь: полиакриловая кислота: полиэтиленимин 5:5:1 - 10:1:1. Полученную суспензию обрабатывают кислотой до pH 7-9 и подвергают термообработке при 130-250°С.

Пример 1. 10 г активированного угля, предварительно отмытого в проточной воде и высушенного, перемешивают в течение 30 мин со 100 мл 0,1 н. водного раствора полиэтиленимина разветвленного и, продолжая перемешивание, постепенно добавляют 100 мл 0,1 н. раствора полиакрилата натрия и продолжают перемешивание еще 30 мин. Весовое соотношение активированный уголь: полиакриловая кислота: полиэтиленимин - 10:1:1. К раствору медленно прикапывают соляную кислоту до появления опалесценции, еще несколько минут продолжают перемешивание. Уголь декантируют, отмывают несколько раз водой и подвергают термообработке при 130-135°С в течение 30 мин.

Пример 2. Обработку активированного угля проводят, как в примере 1, изменяя порядок добавления полиэлектролитов и температуру термообработки, 180°С.

Пример 3. Обработку активированного угля проводят, как в примере 1.

PAC ET AL. EXHIBIT 1019
Page 2032

изменяя весовое соотношение активированный уголь: полиметакриловая кислота: полиэтиленимин – 5:2:1 и температуру термообработки 230°С.

Пример 4. Обработку активированного угля проводят, как в примере 1, изменяя весовое соотношение активированный уголь: полиакриловая кислота: полиэтиленимин – 5:5:1.

Поглотительную способность адсорбентов, полученных по данному способу, определяли по адсорбции креатинина из водных растворов, 0,6 г адсорбента перемешивали в 50 мл раствора креатинина с исходной концентрацией 40 мг%. Через определенные промежутки времени определяли уменьшение концентрации креатинина в растворе и рассчитывали процент адсорбированного креатинина. Результаты опытов по определению поглотительной способности адсорбентов, полученных по предложенному способу и описанных в примерах 1–4, приводятся в таблице.

Поглотительная способность адсорбента	Адсорбент с покрытием, полученный по способу, описанному в прототипе		Адсорбент с покрытием, полученным по предложенному способу	
время адсорбции	адсорбированный креатинин	полимер и уголь	уголь: полианион: поликатион	температура термообработки, °С
1 ч	73	0,5	–	–
1 ч	47	1	–	–
1 ч	12	2,5	–	–
30 мин	72	–	10:1:1	130–135
30 мин	63	–	10:1:1	180
30 мин	40	–	5:2:1	230
30 мин	35	–	5:5:1	130

Из результатов, приведенных в таблице видно, что адсорбент, полученный по способу, предложенному в изобретении, в 2 раза быстрее (30 мин.) поглощает креатинин, а следовательно, более эффективен, чем адсорбент по прототипу.

Полимерное покрытие, как показали опыты на животных, обеспечивает удовлетворительную совместимость адсорбента с кровью, не вызывает тромбообразования, гемолиза эритроцитов и антигенных реакций. В процессе гемосорбции не нарушается целостности гранул адсорбента и не наблюдается выделения угольной пыли, приводящей обычно к эмболии.

Формула изобретения

1. Способ получения адсорбента для поглощения токсинов крови, включающий обработку частиц активированного угля раствором полимеров, содержащим полиакриловые кислоты, и термообработку полученного продукта, отличающийся тем, что, с целью повышения поглотительной способности адсорбента, активированный уголь обрабатывают щелочными растворами полиакриловых кислот и полиэтиленимина, полученную суспензию обрабатывают кислотой до pH 7–9 и термообработку осуществляют при 130–250°С.

PAC ET AL. EXHIBIT 1019
Page 2033

2. Способ по п. 1, о т л и ч а ю щ и й с я тем, что весовое соотношение активированный уголь: полиакриловые кислоты: полиэтиленимин составляет 5:5:1 – 10:1:1.

Источники информации, принятые во внимание при экспертизе

1. Trans. Amer. Soc. Artif Int Organs, 17.246(1971)

2. Французская заявка № 2148022, B 01 D 15/00, опублик. 1973.

3. Французская заявка № 2235722, кл. B 01 D 15/00, опублик. 07.03.75 (прототип).

Составитель В. Виноградова
Редактор Л. Курасова Техред О. Андрейко Корректор Ю. Макаренко

Заказ 1641/14 Тираж 565 Подписное
ЦНИИПИ Государственного комитета СССР
по делам изобретений и открытий
113035, Москва, Ж–35, Раушская наб., д. 4/5

Филиал ППП "Патент", г. Ужгород, ул. Проектная, 4

PAC ET AL. EXHIBIT 1019
Page 2034

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 April 2006 (13.04.2006)

PCT

(10) International Publication Number
WO 2006/039007 A2

(51) International Patent Classification:
B01D 53/02 (2006.01)

(21) International Application Number:
PCT/US2005/030018

(22) International Filing Date: 23 August 2005 (23.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/605,640	30 August 2004 (30.08.2004)	US
11/209,163	22 August 2005 (22.08.2005)	US

(71) Applicant *(for all designated States except US)*: **ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION** [US/US]; P.O. Box 9018, Grand Forks, North Dakota 58202-9018 (US).

(71) Applicants and
(72) Inventors: **OLSON, Edwin, S.** [US/US]; 223 Circle Hills Drive, Grand Forks, North Dakota 58201 (US). **HOLMES, Michael, J.** [US/US]; 614 6th Street, Thompson, ND 58278 (US). **PAVLISH, John, H.** [US/US]; 42204 210th Street Southwest, East Grand Forks, Minnesota 56721 (US).

(74) Agent: **WESTBY, Timothy, S.**; CONLEY ROSE, P.C., P.O. Box 3267, Houston, Texas 77253-3267 (US).

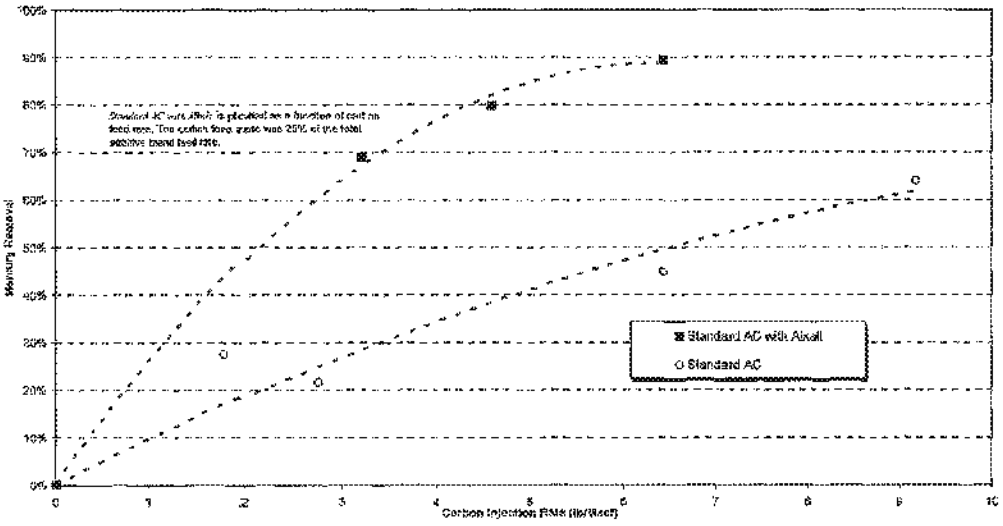
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

[Continued on next page]

(54) Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY



(57) Abstract: A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

WO 2006/039007 A2

(48) **Date of publication of this corrected version:**
27 July 2006

(15) **Information about Correction:**
see PCT Gazette No. 30/2006 of 27 July 2006

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with United States Government support under the U.S. Environmental Protection Agency Grant Nos. R 827649-01 and CR 830929-01. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

Technical Field of the Invention

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic

silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens,

PAC ET AL. EXHIBIT 1019
Page 2038

and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have an mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the

PAC ET AL. EXHIBIT 1019
Page 2039

reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury from a flue gas at lower removal rates with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increased, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

PAC ET AL. EXHIBIT 1019
Page 2040

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-

PAC ET AL. EXHIBIT 1019
Page 2041

containing sorbent particles are regenerated to remove some or substantially all of the mercury. In another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

Figure 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

Figure 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

Figure 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

Figure 4 is a diagram illustrating breakthrough curves for 5 wt/wt% brominated NORIT Darco FGD sorbent (37 mg + 113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

Figure 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg + 113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

Figure 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

PAC ET AL. EXHIBIT 1019
Page 2042

Figure 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

Figure 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

Figure 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

Figure 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a bromide (or other halogen/halide) treatment of the carbon, that capture mercury *via* mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require *in situ* activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to Figure 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas form a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base

PAC ET AL. EXHIBIT 1019
Page 2043

activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

Referring still to Figure 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to Figure 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

PAC ET AL. EXHIBIT 1019
Page 2044

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to Figure 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in Figure 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals

PAC ET AL. EXHIBIT 1019
Page 2045

of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to Figure 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional akali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Optional alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to *both* transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in Figure 3 as compressors or blowers, any source of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points 116 or 119 are shown in Figure 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device (s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at a location upstream and/or downstream of 140 when parallel, sequential, or combinations

PAC ET AL. EXHIBIT 1019
Page 2046

thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142, and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152, and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

An optional Continuous Emission Monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35, to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25, by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury "clean" flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, 209 can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

Referring still to Figure 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base activated carbon from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base activated carbon prior to injection point 116. This option is one form of what is referred to herein as "in-flight" preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121b with base activated carbon prior to entering

PAC ET AL. EXHIBIT 1019
Page 2047

transport line 115. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line 121c into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebullated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and solvent removal (not shown in Figure 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to Figure 1.

Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131b and 131c.

Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions..

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebullated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

PAC ET AL. EXHIBIT 1019
Page 2048

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds. In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the

PAC ET AL. EXHIBIT 1019
Page 2049

mercury on the sorbent and ash is very short – less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. In Addition to halide ions, this phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, the modified cationic carbon has a high chemical potential for oxidation of the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

PAC ET AL. EXHIBIT 1019
Page 2050

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~ an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection

PAC ET AL. EXHIBIT 1019
Page 2051

system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.
- The inventive process uses existing hardware and operation procedures.
- The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.
- The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjection with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or

PAC ET AL. EXHIBIT 1019
Page 2052

optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a *carbocation* that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine- containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1 -Preparation and Testing of Halogenated Carbon (& Comparative Example)

Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, TX (USA), although others are suitable, as will be recognized by those skilled in the

PAC ET AL. EXHIBIT 1019
Page 2053

art), was placed in a rotating plastic barrel with side blades (a 5 ft^3 (0.14 m^3) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°–50°C. The vapor pressure of the bromine was such that a dark red gas is generated a passed out of the generator. The outlet from the gaseous bromine generator is connected via a ¼ inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight to that the excess of nitrogen is released after the bromine is transfer to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2–5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5–17 wt%), but does not require further drying for use. The moisture is driven out at higher temperatures (>150°C), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G.E.; Miller, S.J. Chang, R.; Bergman, P. *Environmental Progress* **1998**, *17*, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (-400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125°C) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O_2 (6%), CO_2 (12%), SO_2 (600 ppm), NO (120 ppm) NO_2 (6 ppm), HCl (1 ppm), Hg^0 (11 $\mu g/m^3$), H_2O (15%), and N_2 (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations

PAC ET AL. EXHIBIT 1019
Page 2054

in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach FL USA), and a $SnCl_2$ cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to Figure 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%–1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30–60 minutes (breakthrough point), depending on the sorbent. Figure 4 illustrates the breakthrough curves for 5 wt/wt% brominated NORIT Darco FGD sorbent (37 mg + 113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a per cent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

Figure 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%–50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2 - Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3 - Liquid Phase (water) Halogenation

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110°C for

PAC ET AL. EXHIBIT 1019
Page 2055

several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4 - Addition of the Optional Second Halide Component.

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5 - Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110°C in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6 - Preparation and Sorption on Larger-Particle Carbon

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 μm) sorbent was developed, prepared, and tested.

Treatment - Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction -170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°–50°C, and the outlet from this gaseous bromine generator was connected via a 1/4 inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had

PAC ET AL. EXHIBIT 1019
Page 2056

combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the "Particulate Test Combustor" (hereinafter "PTC"), is a 550,000-Btu/hr (about 161 kW) pulverized coal ("PC")-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a "fabric filter") or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O_2, CO, CO_2, SO_2, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO_2 was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

PAC ET AL. EXHIBIT 1019
Page 2057

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m^3/min) of flue gas at 300°F (about 150°C), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300°F (150°C). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCMM (normal m^3/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in Figure 6. As can be observed in Figure 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter ("FF"). Note that in Figure 6 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or "MACM").

Referring now to Figure 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square) performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because >60 μm sorbent particles have been successfully demonstrated, superior mercury control can be obtained with >40 μm particles, which may be preferred in some applications, depending

PAC ET AL. EXHIBIT 1019
Page 2058

on the sorbent particle/ash separation system used. Note that in Figure 7 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet.

Example 7 - Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110°C for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8 - Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100°C in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu g/m^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, FL, USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus

PAC ET AL. EXHIBIT 1019
Page 2059

enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9 - Fluidized/Ebullated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10 - Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu g/m^3$. The ash and injected carbon were collected in the baghouse at 350°F to 375°F (about 175-190°C). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 $\mu g/m^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A - Addition of Optional Alkaline Component – Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with

PAC ET AL. EXHIBIT 1019
Page 2060

inert sand is shown in Figure 8, and the breakthrough curve for the mixture with CaO is shown in Figure 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B - Addition of Optional Alkaline Component – Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as "AC") and an alkali material upstream of a fabric filter. Typical results are illustrated in Figure 10. As shown in Figure 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12- Brominated Carbon Sorbent for Gasification Fuel Gas

Preparation of 5%Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol% solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt% brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by

PAC ET AL. EXHIBIT 1019
Page 2061

vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110°C until a stable weight was obtained The moisture was reduced to 15%.

Preparation of 5%Br2D-AC

A brominated sorbent was prepared from Br_2 addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5%PBr3-AC

A phosphohalogenated sorbent was prepared from PBr_3 using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere - Procedure

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/m^3 of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/m^3). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400°C). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no $SnCl_2$ trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5%Br2W-AC and 5%BrD-AC), and the phosphobrominated sorbent

PAC ET AL. EXHIBIT 1019
Page 2062

(5%PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100°C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400°C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400°C.

Table 1

Times for 50% Breakthrough
Maximum Observed Hg Concentrations for Sorbents
(10% Hydrogen Streams)

Sorbent	Temp (°C)	50% breakthrough (min)	Maximum [Hg] ($\mu g/m^3$)	Time (min)
F-400	250	6	20.3	6.5
5%Br2W-AC	250	>150	1.4	150
5%Br2W -AC	300	>180	4.3	180
5%Br2W-AC	350	160	15.1	180
5%Br2W-AC	400	60	13.9	65
5%PBr3-AC	250	>140	0.4	140
5%PBr3-AC	300	>150	0.5	150
5%PBr3-AC	350	>150	1.4	150
5%Br2D-AC	350	>180	2.1	180
5%Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications

PAC ET AL. EXHIBIT 1019
Page 2063

thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

PAC ET AL. EXHIBIT 1019
Page 2064

WE CLAIM:

1. A promoted carbon sorbent comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

2. The promoted carbon sorbent of claim 1 wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than 40 micrometers, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V halides, Group VI halides, hydrohalides, and combinations thereof.

3. The promoted carbon sorbent of claim 2 wherein the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon.

4. The promoted carbon sorbent of claim 3 further comprising an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

5. The promoted carbon sorbent of claim 4 further comprising an optional alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

6. The promoted carbon sorbent of claim 4 wherein the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

7. The promoted carbon sorbent of claim 6 wherein the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and combinations thereof.

8. The promoted carbon sorbent of claim 7 wherein the optional secondary component is selected from the group consisting of I_2, HI, and combinations thereof.

9. The promoted carbon sorbent of claim 8 wherein the promoter is substantially in vapor form when combined with the base activated carbon.

10. The promoted carbon sorbent of claim 8 wherein the promoter is combined with an

PAC ET AL. EXHIBIT 1019
Page 2065

organic solvent prior to reaction with the base activated carbon.

11. The promoted carbon sorbent of claim 8 wherein the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously.

12. The promoted carbon sorbent of claim 8 further comprising a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

13. The promoted carbon sorbent of claim 12 wherein the promoter is selected from the group consisting of Br_2, HBr, and combinations thereof.

14. The promoted carbon sorbent of claim 3 further comprising a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

15. The promoted carbon sorbent of claim 14 further comprising an optional alkaline component comprising an alkaline or alkaline earth element wherein the promoter is selected from the group consisting of Br_2, HBr, and combinations thereof.

16. A method comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream.

17. The method of claim 16 wherein the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon.

18. The method of claim 16 wherein the reaction product has an average particle size distribution greater than about 40 micrometers.

19. The method of claim 16 wherein the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof.

20. The method of claim 19 wherein the promoter is in the gas phase when contacting the activated carbon.

21. The method of claim 19 wherein the promoter is in an organic solvent when contacting the activated carbon.

PAC ET AL. EXHIBIT 1019
Page 2066

22. The method of claim 20 wherein the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

23. The method of claim 18 further comprising providing an optional alkaline component to improve the effectiveness of mercury removal.

24. The method of claim 20 further comprising reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

25. The method of claim 24 further comprising providing an optional alkaline component to improve the effectiveness of mercury removal.

26. The method of claim 24 wherein the promoter and optional secondary component are contacted simultaneously with the activated carbon.

27. The method of claim 24 wherein the optional secondary component comprises I_2 or HI.

28. The method of claim 20 further comprising adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

29. The method of claim 24 further comprising adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

30. A method for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas.

31. The method of claim 30 further comprising co-injecting an optional alkaline component into the mercury containing flue gas stream.

32. The method of claim 30 further comprising monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent.

33. The method of claim 30 wherein the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

PAC ET AL. EXHIBIT 1019
Page 2067

34. The method of claim 33 wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof.

35. The method of claim 34 wherein the promoter is selected from the group consisting of Br_2, HBr, Group V bromides, Group VI bromides, and combinations thereof.

36. The method of claim 35 wherein the promoter is reacted in the gas phase or as a vapor.

37. The method of claim 36 wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

38. The method of claim 37 wherein the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

39. The method of claim 38 wherein the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof.

40. The method of claim 39 further comprising co-injecting an optional alkaline component into the mercury containing flue gas stream.

41. The method of claim 39 wherein the optional secondary component is added at from about 1 to about 15 wt-% of the promoter content.

42. The method of claim 41 wherein the optional secondary component is selected from the group consisting of I_2, HI, and combinations thereof.

43. The method of claim 42 wherein the optional secondary component is added in the gas phase or as a vapor.

44. The method of claim 41 further comprising adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

45. The method of claim 32 further comprising using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent.

46. The method of claim 40 further comprising monitoring the mercury content of the clean

PAC ET AL. EXHIBIT 1019
Page 2068

flue gas and using the monitored mercury content to control the composition of the sorbent and the alkaline-to-sorbent injection ratio.

47. The method of claim 45 wherein the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

48. A method for reducing the mercury content of a gas stream comprising the steps of injecting a powdered activated carbon sorbent having a mass-mean particle size >40μm into a gas stream containing mercury and ash particles, capturing mercury from the gas stream on the sorbent particles, mechanically separating the sorbent particles from the ash particles, and re-injecting the separated sorbent particles into the gas stream.

49. The method of claim 48 further comprising regenerating the sorbent particles to substantially remove contaminants therefrom to recover capacity for capturing mercury.

50. The method of claim 48 further comprising co-injecting into the gas stream an alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

51. The method of claim 48 wherein the powdered activated carbon sorbent further comprises a promoter selected from the group consisting of halides, halogens, and combinations thereof.

52. The method of claim 51 further comprising co-injecting into the gas stream an alkaline component selected from the group consisting of alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

53. The method of claim 48 wherein the particulate activated carbon sorbent has a mass-mean particle size >60μm.

54. The method of claim 52 wherein the particulate activated carbon sorbent has a mass-mean particle size >60μm.

PAC ET AL. EXHIBIT 1019
Page 2069

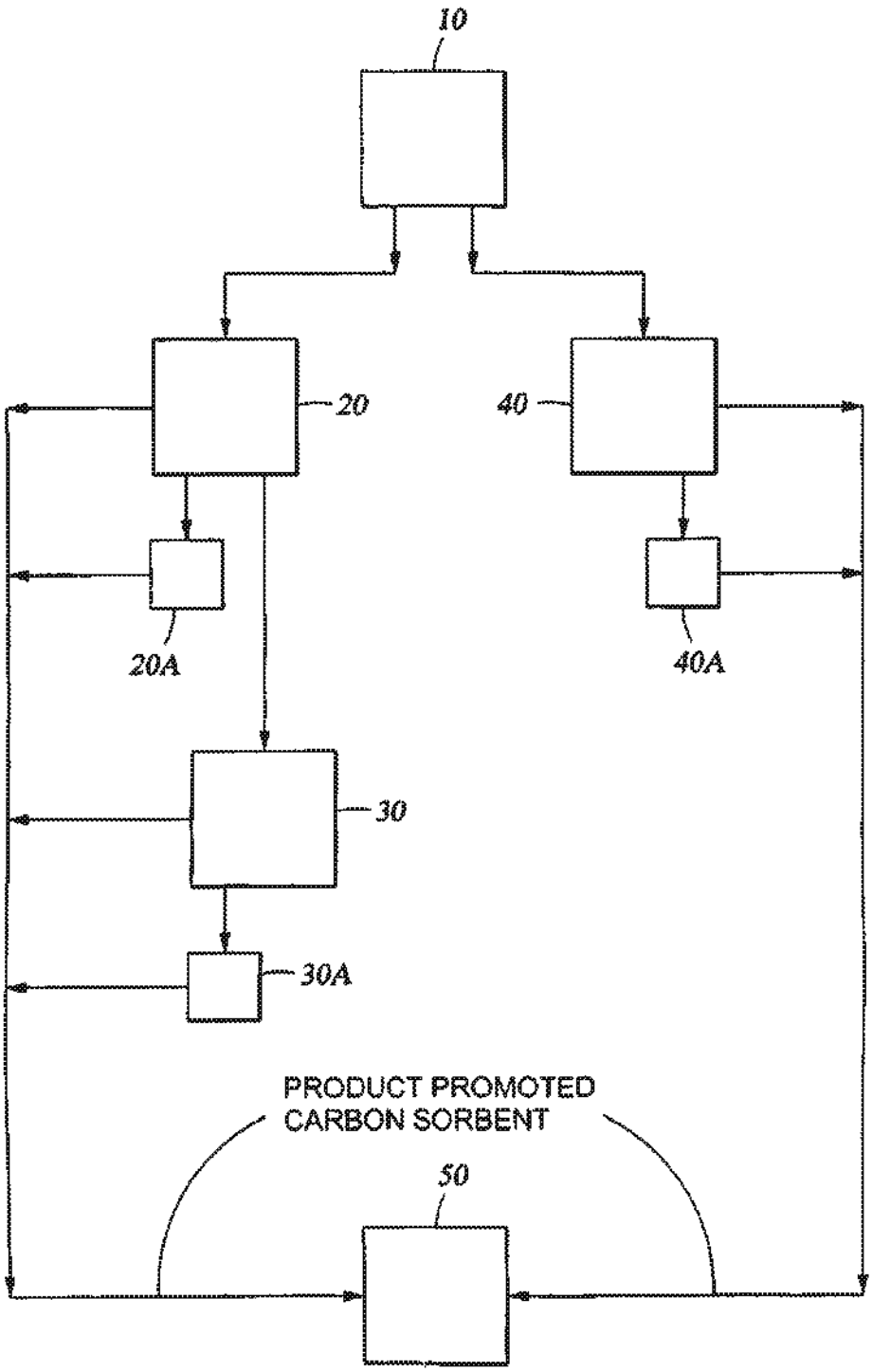


Fig. 1

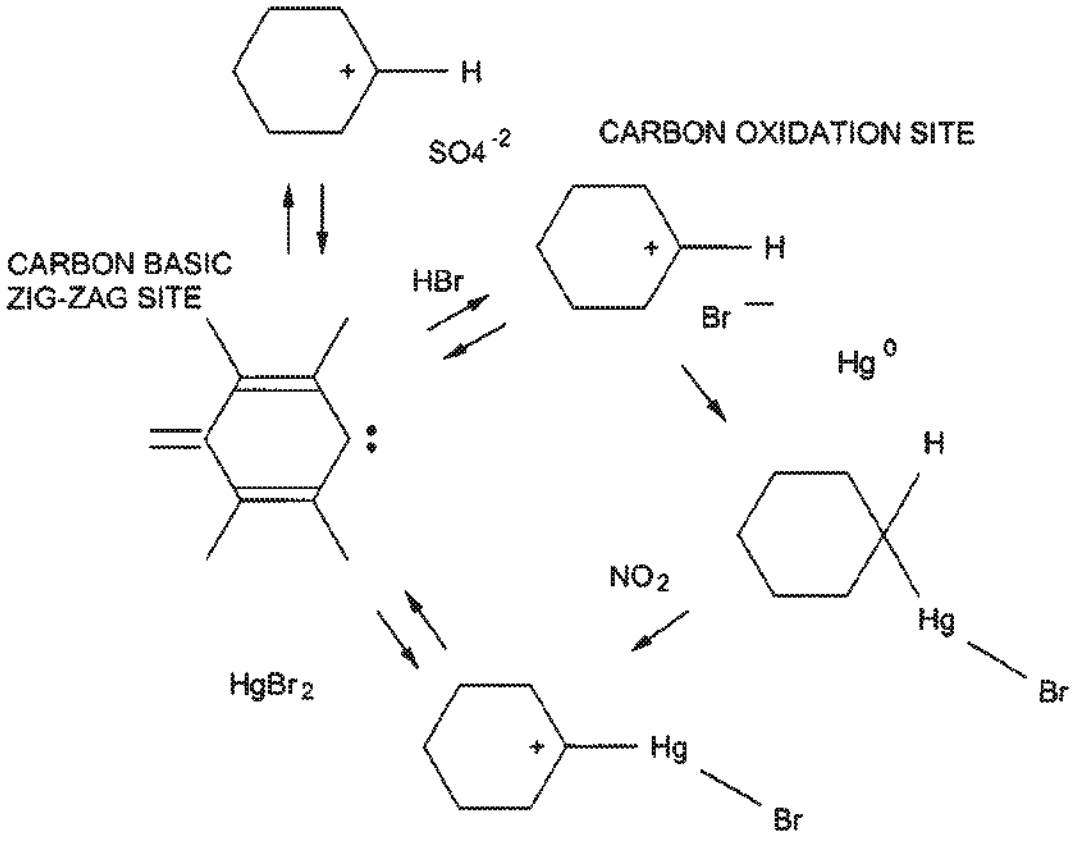

H
SO4 -2
CARBON OXIDATION SITE
CARBON BASIC
ZIG-ZAG SITE
HBr
H
Br
Hg 0
H
NO2
Hg
Br
HgBr2
Hg
Br

Fig. 2

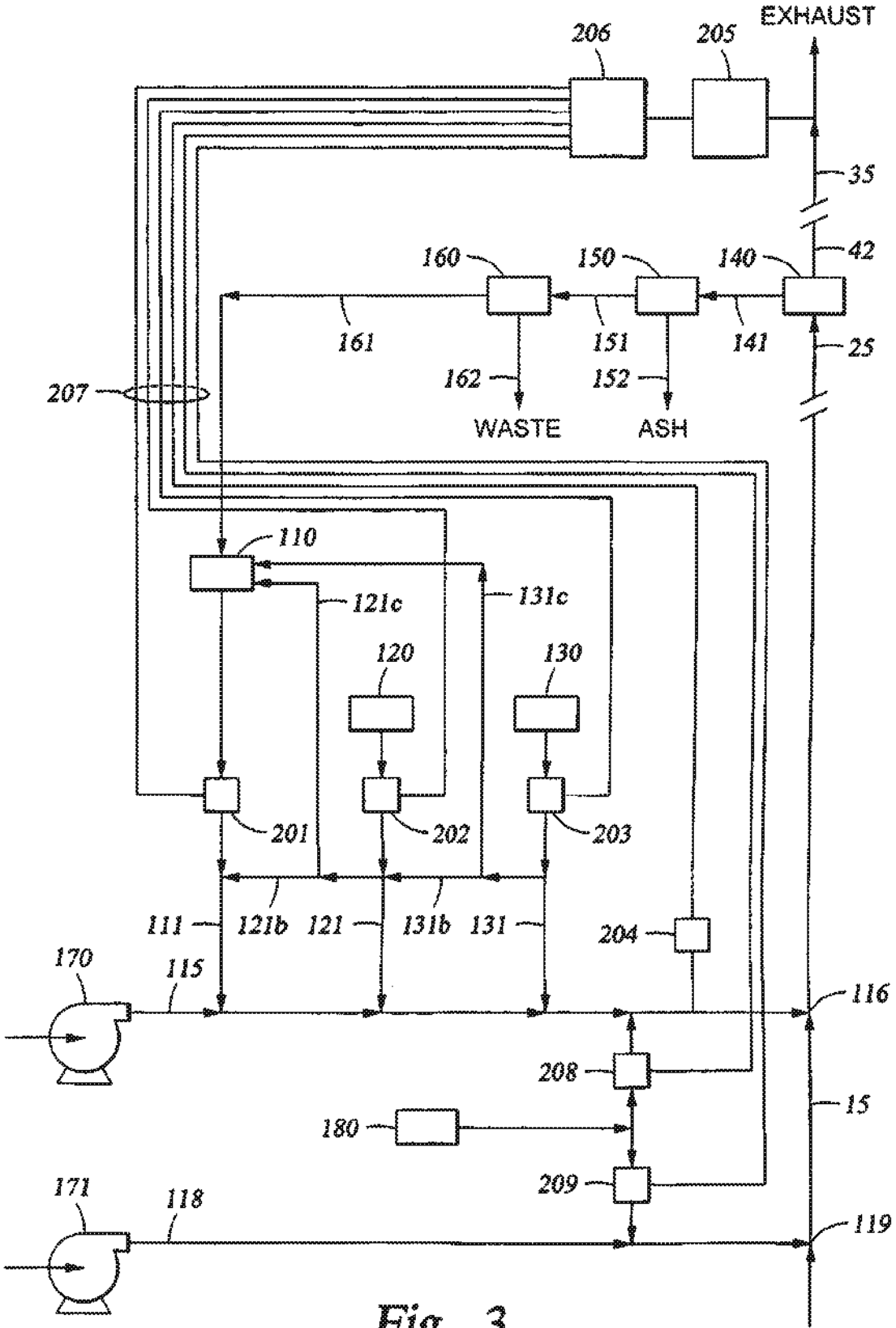


Fig. 3

PAC ET AL. EXHIBIT 1019
Page 2072

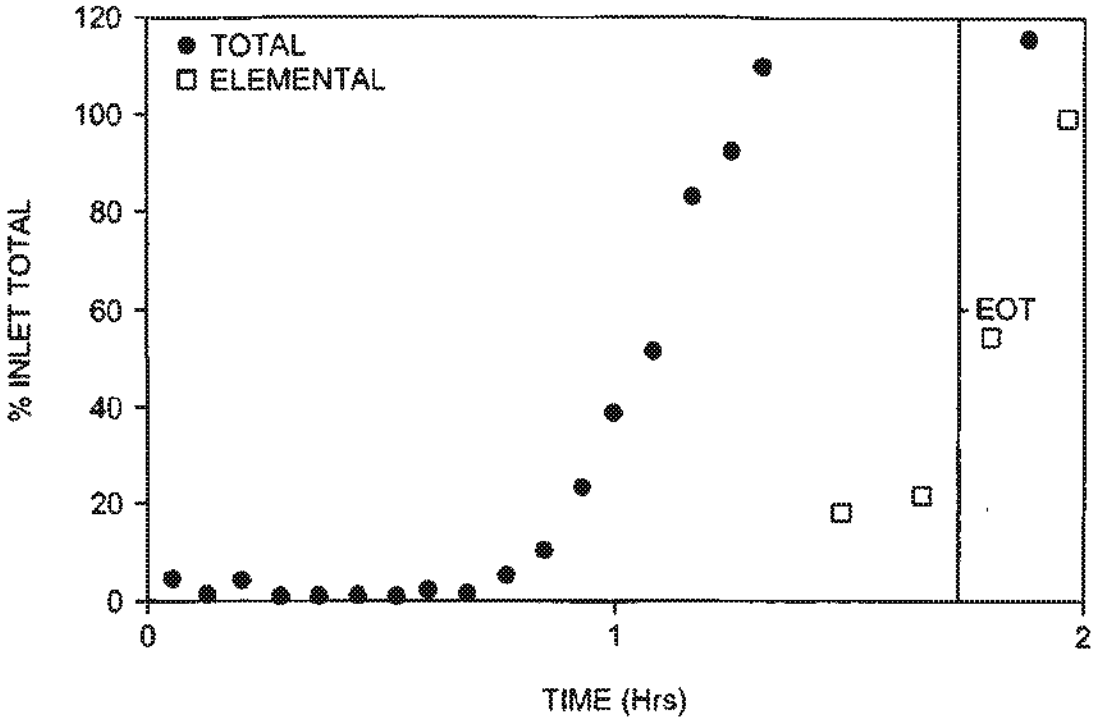


Fig. 4

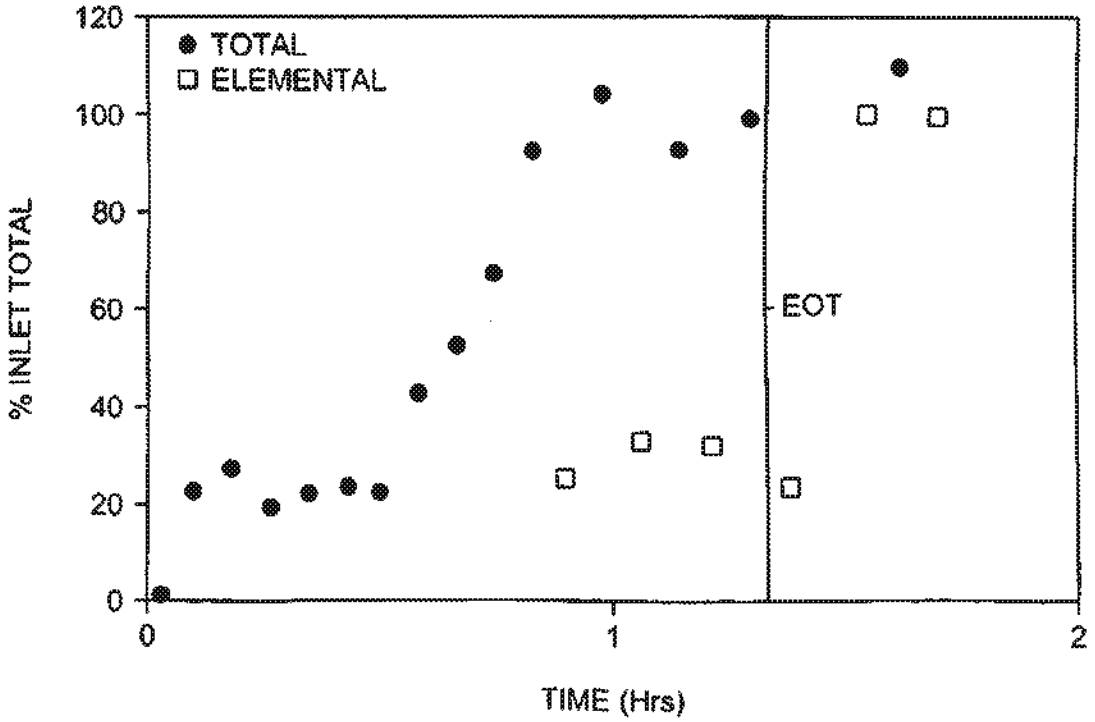


Fig. 5

PAC ET AL. EXHIBIT 1019
Page 2073

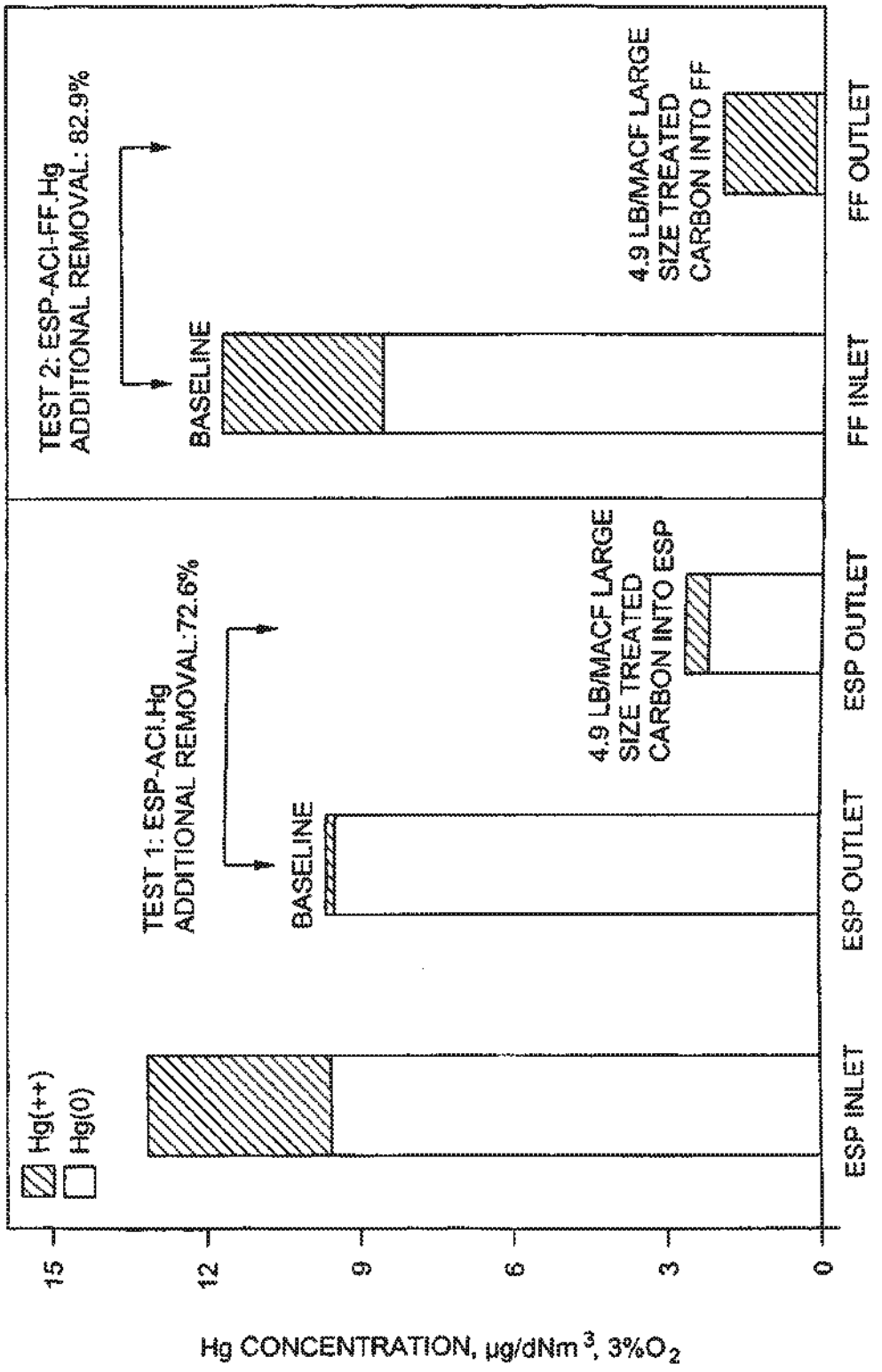

Hg(++)
Hg(0)
TEST 1: ESP-ACI.Hg
ADDITIONAL REMOVAL: 72.6%
BASELINE
4.9 LB/MACF LARGE
SIZE TREATED
CARBON INTO ESP
TEST 2: ESP-ACI-FF.Hg
ADDITIONAL REMOVAL: 82.9%
BASELINE
4.9 LB/MACF LARGE
SIZE TREATED
CARBON INTO FF
ESP INLET
ESP OUTLET
ESP OUTLET
FF INLET
FF OUTLET
15
12
9
6
3
0
Hg CONCENTRATION, µg/dNm 3, 3%O2

Fig. 6

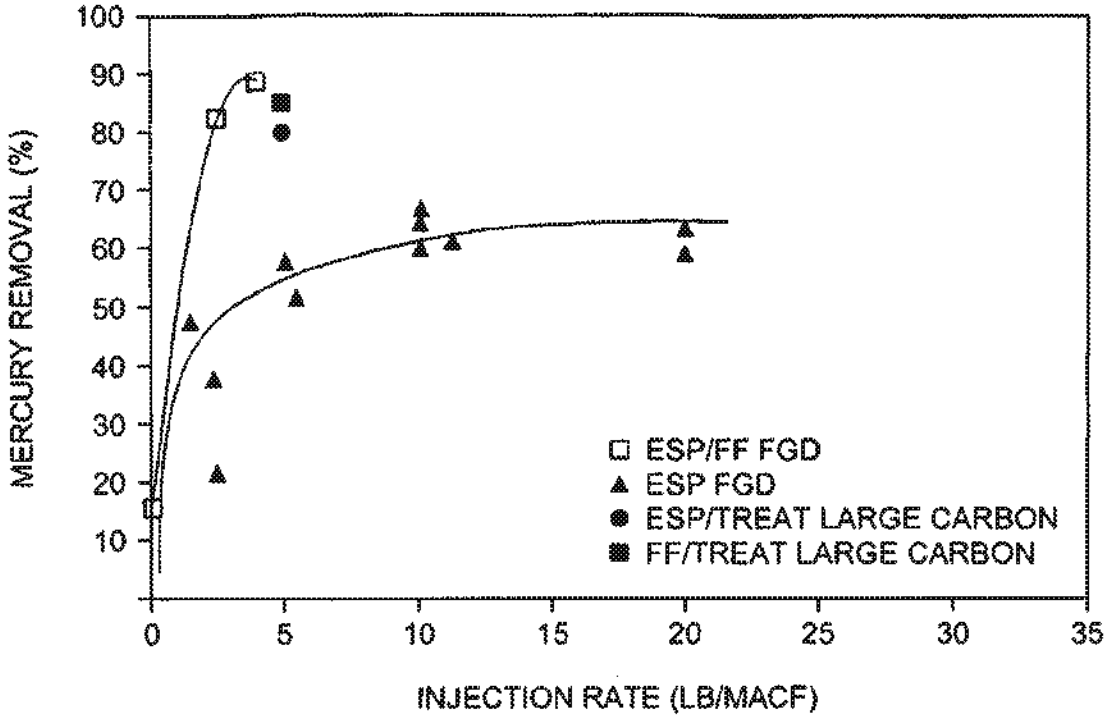

MERCURY REMOVAL (%)
100
90
80
70
60
50
40
30
20
10
0
5
10
15
20
25
30
35
INJECTION RATE (LB/MACF)
ESP/FF FGD
ESP FGD
ESP/TREAT LARGE CARBON
FF/TREAT LARGE CARBON

Fig. 7

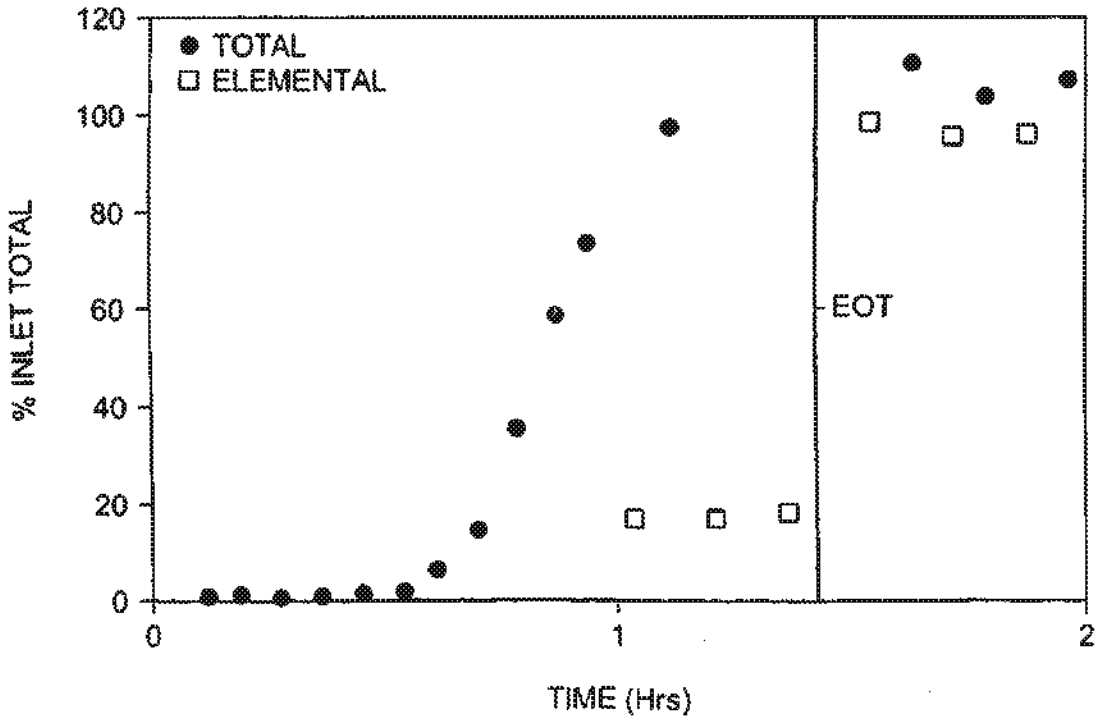

% INLET TOTAL
120
100
80
60
40
20
0
0
1
2
TIME (Hrs)
TOTAL
ELEMENTAL
EOT

Fig. 8

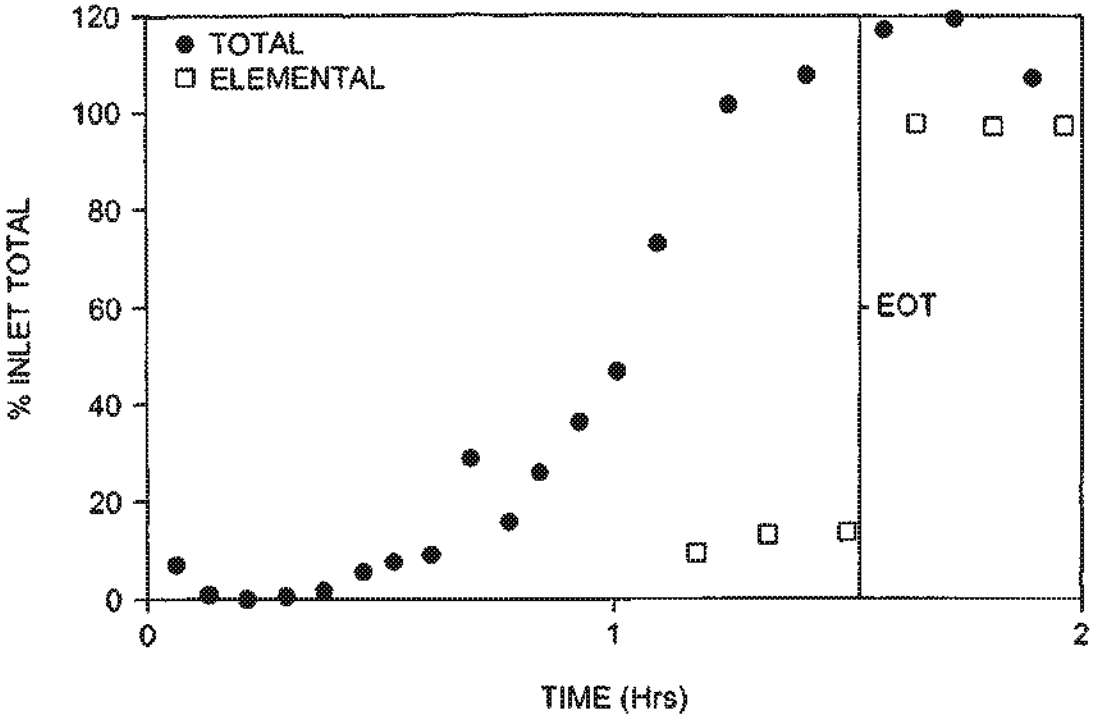

TOTAL
ELEMENTAL
EOT
% INLET TOTAL
TIME (Hrs)
0
20
40
60
80
100
120
0
1
2

Fig. 9

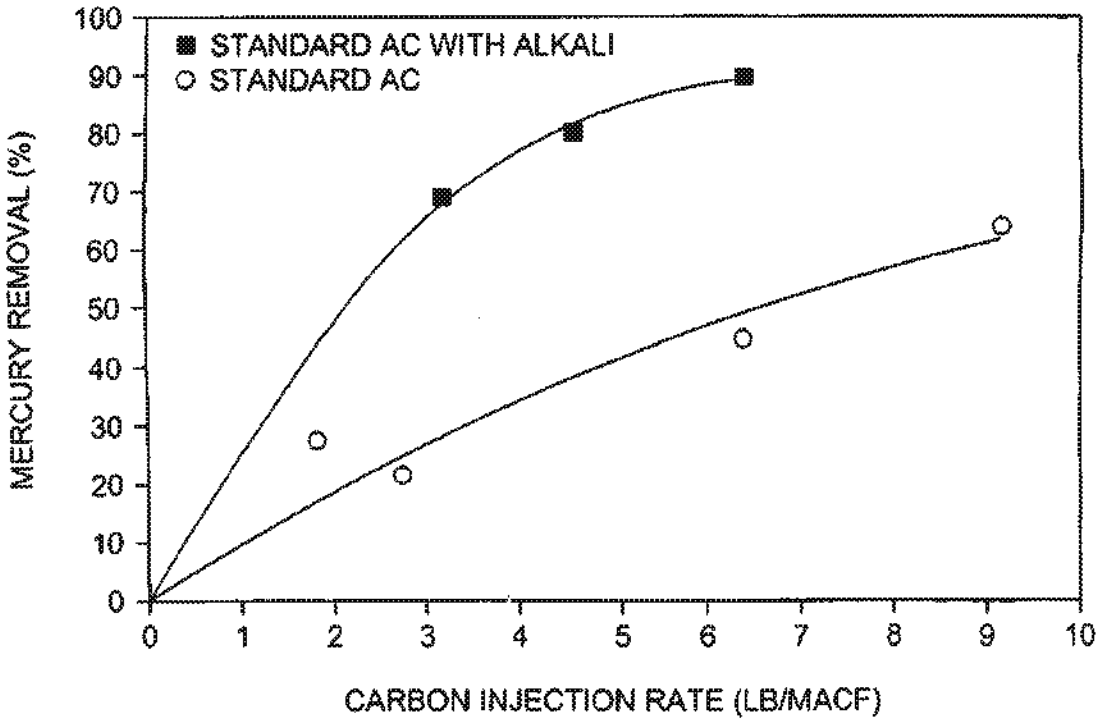

STANDARD AC WITH ALKALI
STANDARD AC
MERCURY REMOVAL (%)
CARBON INJECTION RATE (LB/MACF)
0
10
20
30
40
50
60
70
80
90
100
0
1
2
3
4
5
6
7
8
9
10

Fig. 10

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING TRANSMITTAL OF COPY OF INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (CHAPTER I OF THE PATENT COOPERATION TREATY)
(PCT Rule 44bis.1(c))

To:

MADDEN, Robert B.
Schwegman, Lundberg & Woessner
P.O. Box 2938
Minneapolis, Minnesota 55402
ETATS-UNIS D'AMERIQUE

SEP 21 2015

Date of mailing *(day/month/year)* 17 September 2015 (17.09.2015)	
Applicant's or agent's file reference 3338021WO1	IMPORTANT NOTICE

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2014/019916	03 March 2014 (03.03.2014)	06 March 2013 (06.03.2013)

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

The International Bureau transmits herewith a copy of the international preliminary report on patentability (Chapter I of the Patent Cooperation Treaty)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Philippe Bécamel
Facsimile No. +41 22 338 82 70	e-mail: pt03.pct@wipo.int

Form PCT/IB/326 (January 2004)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference 3338021WO1	**FOR FURTHER ACTION**	See item 4 below
International application No. PCT/US2014/019916	International filing date *(day/month/year)* 03 March 2014 (03.03.2014)	Priority date *(day/month/year)* 06 March 2013 (06.03.2013)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 *bis*.1(a).

2. This REPORT consists of a total of 13 sheets, including this cover sheet.

   In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☒	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☒	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☒	Box No. VII	Certain defects in the international application
☒	Box No. VIII	Certain observations on the international application

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44*bis*.3(c) and 93*bis*.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44*bis* .2).

	Date of issuance of this report 08 September 2015 (08.09.2015)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. +41 22 338 82 70	Authorized officer Philippe Bécamel e-mail: pt03.pct@wipo.int

Form PCT/IB/373 (January 2004)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2014/019916	03.03.2014	06.03.2013

International Patent Classification (IPC) or both national classification and IPC
INV. B01J20/20 B01D53/02 B01D53/10 B01J20/32 C01B31/08

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	see form PCT/ISA/210	Pöhlmann, Robert Telephone No. +49 89 2399-2059

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:

   a. (means)

      ☐ on paper

      ☐ in electronic form

   b. (time)

      ☐ in the international application as filed

      ☐ together with the international application in electronic form

      ☐ subsequently to this Authority for the purposes of search

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

☐ the entire international application

☒ claims Nos. 50-67(completely); 1-49(partially)

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search *(specify)*:

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no international search report has been established for the whole application or for said claims Nos. 50-67(completely); 1-49(partially)

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

- ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b).

☐ See Supplemental Box for further details

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has, within the applicable time limit:

   ☐ paid additional fees

   ☐ paid additional fees under protest and, where applicable, the protest fee

   ☐ paid additional fees under protest but the applicable protest fee was not paid

   ☒ not paid additional fees

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

   ☐ complied with

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

   ☐ all parts.

   ☒ the parts relating to claims Nos. 1-49(partially)

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	5-49(partially)
	No:	Claims	1-4(partially)
Inventive step (IS)	Yes:	Claims	10-15, 26-37, 40-47(all partially)
	No:	Claims	1-9, 16-25, 38, 39, 48, 49(all partially)
Industrial applicability (IA)	Yes:	Claims	1-49(partially)
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item VIII

Certain observations on the international application

1 Clarity, Article 6 PCT)

1.1 General

The terms "about" (used in claims 4-6, 18-24, 34, 50, 58, 64), "substantially" (used in claims 5, 7-9, 50, 61-64, 67) and "core" (used in claims 3, 7, 18, 19, 51, 56, 61) are vague and unclear and leave the reader in doubt as to the meaning of the technical features to which they refer, thereby rendering the definition of the subject-matter of said claims unclear, Art. 6 PCT.

1.2 Claim 4

Claim 4 does not meet the requirements of Article 6 PCT because the matter for which protection is sought is not clearly defined. The claim attempts to define the subject-matter in terms of the result to be achieved (combines with at least 70 wt%), which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result (like but not limited to volume flows, distribution of sorbent, injection of sorbent, contact times, temperatures, other components in the mercury-containing gas).

1.3 Claim 7

It is unclear (Art. 6 PCT) how the nitrogen can be homogeneously distributed in the core of the particles and how at the same time there can be a concentration profile from the surface to the core (when referring to claim 3).

1.4 Claims 8, 9

Claims 8 and 9 do not meet the requirements of Art. 6 PCT because the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

1.5 Claim 18

It is unclear in claim 18 how a core of an activated carbon sorbent particle can comprise 99 wt% nitrogen (Art. 6 PCT). The core practically would consist of nitrogen only in this case.

1.6 Claim 20

It is unclear in claim 20 how a surface layer of an activated carbon sorbent particle can comprise 99 wt% nitrogen (Art. 6 PCT). The surface would consist of nitrogen only in this cas. Also it is unclear if the technical effect related to nitrogen being present at 0.001 wt% in the surface layer is still existing (Art.6 PCT).

1.7 Claim 22

The definition of the surface layer is unclear as a thickness of 99% of the radius of the particles is in fact the complete particle and not only a "surface layer" (Art. 6 PCT).

Re Item IV

2 **Lack of unity of invention**

Notwithstanding the objections under Article 6 PCT above, the application lacks unity within the meaning of Rule 13.1 PCT.

2.1 Reference is made to the following document:

D1 YUANJING ZHENG ET AL: "Review of technologies for mercury removal from flue gas from cement production processes",PROGRESS IN ENERGY AND COMBUSTION SCIENCE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL,vol. 38, no. 5, 26 April 2012 (2012-04-26), pages 599-629, XP028415255,ISSN: 0360-1285, DOI: 10.1016/J.PECS.2012.05.001[retrieved on 2012-05-25]

D2 DE 20 2012 003747 U1 (BLUECHER GMBH [DE]) 15 November 2012 (2012-11-15)

2.2 **There are several groups of claims:**

- Group 1: Claims 1-49 (partially), in particular claims 2-9, 16-25, 38, 39, 48, 49
- Group 2: Claims 1-49 (partially), in particular claims 10-15, 26-37, 40, 41, 44, 45, claims 50-67 (completely)
- Group 3: Claims 1-49 (partially), in particular claims 42, 43
- Group 4: Claims 1-49 (partially), in particular claims claims 46, 47

2.3 **The common concept linking together the groups is the subject-matter of claim 1**. This common concept is not new over D1.

2.3.1 D1 discloses a method of reducing the mercury content in a mercury-containing gas (see page 600, para. 1.), the method comprising obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see page 615, para. 4.2.5.1 and page 616, left column, "...by impregnation of nitrogen-containing polymers or pitches ..."), contacting a pollutant-containing gas with the activated carbon sorbent to form a pollutant-sorbent composition (implicitly disclosed as for a sorbent based removal process the pollutant has to be contacted with the sorbent, the pollutant thereby always forms a pollutant-sorbent composition), and separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give a separated gas (see page 622, figure 20).

Hence, D1 discloses all the features of claim 1.

2.3.2 D1 further discloses

- claim 3: the concentration of nitrogen in the surface layer of the sorbent particles to be higher than in a core of the particles (see page 615, right column, lines 1-4, nitrogenated function introduced on carbon surface, therefrom following a lower nitrogenous concentration in the core of the particles)

- claim 5, 6: the mercury-containing gas to comprise a sulfur(VI) concentration, like SO_3 (see page 616, right column, 2nd paragraph)

2.4 **The differentiating features are**

- Group 1: applying the method for gases with a sulfur(VI) concentration of more than 3 ppm by mole
- Group 2: obtaining or providing the activated carbon sorbent comprises promoting an unpromoted carbon sorbent and/or providing or obtaining the unpromoted carbon sorbent from a carbon precursor comprising nitrogen and/or the activated carbon sorbent comprising a stabilizing agent
- Group 3: adding an alkaline component into the pollutant containing gas
- Group 4: regenerating the activated carbon sorbent

2.5 **with following resulting technical effects:**

- Group 1: no surprising and unexpected technical effect distinguishable

- Group 2: further enhancement of the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: reduction of sulfuric compounds in the pollutant containing gas
- Group 4: saving financial means for sorbent

2.6 **Thus the problems solved may be regarded as**

- Group 1: finding an alternative mercury containing gas for which the method can be applied.
- Group 2: how to modify the method of D1 in order to further enhance the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: how to modify the method of D1 in order to reduce the sulfuric compounds in the pollutant containing gas
- Group 4: how to modify the method of D1 in order to save financial means for sorbent

2.7 **The special technical features (R. 13.2 PCT) are**

- Group 1: **no** special technical feature A as the alternative gas is considered to be obvious for the skilled person.
- Group 2: differentiating feature = special technical feature B as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 3: differentiating feature = special technical feature C as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 4: **no** special technical feature D as the regeneration and reuse of the sorbent is disclosed by D1 (see page 612, left column, paragraph before 4.2.2.3).

2.8 **Groups of (alleged) inventions**

The groups of technical features do not solve any common technical problem. Thus the groups of claims are neither linked by the same nor by corresponding special technical features and define different inventions not linked by a single general inventive concept (Rule 13.1 and 13.2 PCT) and therefore **the requirement for unity of invention referred to in Rule 13 PCT is not fulfilled.**

2.9 **Consequence**

A search has been performed for the invention first mentioned in the claims, here the subject-matter of the claims forming group 1. Correspondingly, in the following this written opinion is restricted to group 1.

Group 1 : Claims 1-9, 16-25, 38, 39, 48, 49 (partially)

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

3 Novelty Claim 1

3.1 As already shown under point 2.3.1 above the subject-matter of claim 1 is not new (Article 33(2) PCT).

4 Inventive Step Claim 1

Besides D1, which is considered to be the closest prior art to the subject-matter of claim 1, also D2 could be regarded as the closest prior art the subject-matter of claim 1.

4.1.1 D2 discloses

A method of reducing the pollutant content in a pollutant-containing gas (see §0142 and 0143), the method comprising:

obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see claim 1);

4.1.2 The subject-matter of claim 1 therefore differs from this known D2 in that

a pollutant-containing gas is contacted with the activated carbon sorbent, to form a pollutant-sorbent composition; and in that at least some of the pollutant-sorbent composition is separated from the pollutant-containing gas, to give a separated gas.

4.1.3 There is no unexpected technical effect related to that difference.

4.1.4 The problem to be solved by the present invention may therefore be regarded as how to to apply the method of D2 for reducing the pollutant content in a pollutant-containing gas.

4.1.5 The solution proposed in claim 1 of the present application cannot be considered to involve an inventive step (Article 33(3) PCT) for the following reasons:

It is common general knowledge for the skilled person to contact the sorbent with the gas to form a pollutant-sorbent composition and to separate the pollutant-sorbent composition from the gas to give a separated gas. Also, amongst many other documents he finds in D1 an indication (see cited passages) with which he would contact the sorbent with the gas, thereby forming a pollutant sorbent composition and separate this composition from the gas to give a separated gas, thereby arriving at the subject-matter of claim 1 without being inventive.

5 Dependent claims

Dependent claims 2-9, 16-25, 38, 39, 48, 49 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step.

5.1 Claims 2, 3

The subject-matter of said claims is neither new (see points 2.3.1 and 2.3.2 above), nor inventive (see D2, claim 1 and §0143, mercury being an obvious toxic substance whose removal from gas streams with activated carbon is widely known in industry).

5.2 Claims 5, 6

D1 discloses a sulfur(VI) concentration in the mercury-containing gas (see 2.3.2 above) and the claimed ranges for said concentration are considered to be merely an arbitrary selection out of a variety of possible mercury containing gases without showing an unexpected technical effect. The properties of the activated carbon sorbent of D1 are considered to achieve the results claimed in claim 5 with regard to corresponding activated carbon sorbents.

5.3 Claims 16, 17, 38, 39, 48, 49

It is well-known in the art to add the sorbent into the mercury-containing gas and to remove it after a certain distance by various means like bag houses, electrostatic precipitators, cyclones or the like. As well, it is common general knowledge to contact the gas with the sorbent in a fixed bed, a dry or aqueous scrubber, a filter or a moving bed.

Claim 19, 21

D2 discloses a wide variety of possible nitrogen concentrations of the activated carbon (see claim 25), which is also considered to be applicable either to the surface and/or to the core of carbon particles. Therefore, the claimed ranges are not inventive.

Claim 24, 25

The claimed range of particle diameters is considered an arbitrary selection and activated carbon particles in this range are known to the skilled person (see for reference D2, §0106). Furthermore, every surface is considered to be continuous and therefore also a surface layer.

Re Item VII

Certain defects in the international application

6 The requirements of Rule 6.3(b) PCT (two-part form of independent claims) and Rule 5.1(a)(ii) and (iii) PCT (acknowledgement of prior art D1) are not met.

PATENT COOPERATION TREATY

Schwegman Lundberg & Woessner P.A.
JUL 24 2014
PCT RECEIVED

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SCHWEGMAN, LUNDBERG & WOESSNER, P.A.
P.O. Box 2938
Minneapolis, MN 55402
ETATS-UNIS D'AMERIQUE

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(PCT Rule 71.1)

Date of mailing *(day/month/year)*	17.07.2014
Applicant's or agent's file reference	IMPORTANT NOTIFICATION
3338016WO1	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/036964	17.04.2013	23.04.2012

Applicant
Energy & Environmental Research Center Foundation

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the International preliminary report on patentability and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:

European Patent Office P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040
Fax: +31 70 340 - 3016

Authorized Officer

Bergström, Carina

Tel. +31 70 340-2898

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 3338016WO1	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
International application No. PCT/US2013/036964	International filing date *(day/month/year)* 17.04.2013	Priority date *(day/month/year)* 23.04.2012

International Patent Classification (IPC) or national classification and IPC
INV. B01J20/12

Applicant
Energy & Environmental Research Center Foundation

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 10 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 13 sheets, as follows:
      - ☐ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions).
      - ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2).
      - ☒ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)).

   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see paragraph 3*bis* of Annex C of the Administrative Instructions).

4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☒ Box No. VII Certain defects in the international application
   - ☒ Box No. VIII Certain observations on the international application

Date of submission of the demand	Date of completion of this report
28.02.2014	17.07.2014

Name and mailing address of the international preliminary examining authority:

European Patent Office P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040
Fax: +31 70 340 - 3016

Authorized officer

Klemps, Christian

Telephone No. +31 70 340-8036

Box No. I Basis of the report

1. With regard to the **language**, this report is based on

☒ the international application in the language in which it was filed

☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:

- ☐ international search (under Rules 12.3(a) and 23.1(b))
- ☐ publication of the international application (under Rule 12.4(a))
- ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-49 as originally filed

Claims, Numbers

1-42 filed with the demand for preliminary international examination

Drawings, Sheets

1/6-6/6 as originally filed

☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/figs
- ☐ the sequence listing *(specify)*:
- ☐ any table(s) related to sequence listing *(specify)*:

4. ☒ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):

- ☐ the description, pages
- ☒ the claims, Nos. 1,38,41
- ☐ the drawings, sheets/figs
- ☐ the sequence listing *(specify)*:

5. ☐ This report has been established:

- ☐ taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-bis) and 70.2(e)).
- ☐ without taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91(Rules 66.4bis and 70.2(e)).

6. ☒ With regard to top-up searches (Rules 66.1 ter and 70.2(f)):
   - ☒ A top-up search was carried out by this Authority on 08.04.2014 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
   - ☐ No top-up search was carried out by this Authority.

7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

   ☐ the entire international application,

   ☒ claims Nos. 6-43, 46, 47, 49

   because:

   ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination *(specify)*:

   ☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

   ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*.

   ☒ no international search report has been established for the said claims Nos. 6-43, 46, 47, 49

   ☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

      ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Preliminary Examining Authority in a form and manner acceptable to it.

      ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Preliminary Examining Authority in a form and manner acceptable to it.

      ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b) and 13*ter*.2.

   ☒ See separate sheet for further details

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-5, 44, 46, 48
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-5, 44, 46, 48
Industrial applicability (IA)	Yes:	Claims	1-5, 44, 46, 48
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item I

Basis of the report

1 The International Preliminary Examining Authority considers that the following amendments to the claims go beyond the disclosure in the international application as filed:

In present claims 1 and 38, the "substrate material" is defined as "comprising at least one of diatomaceous earth, a clay, a zeolite, and a mineral". In paragraph [0061] of the description of the application as filed, however, only porous minerals are disclosed. No basis in the application as filed can be found for *any* mineral as "substrate material".

Further, in present claims 1 and 38, the "heat treatment" is defined as "comprising about 500°C to about 1200°C". In paragraph [0065] of the description of the application as filed, however, only each of the temperatures 500°C and 1200°C, respectively, are disclosed in an exemplified fashion. No basis in the application as filed can be found for a *temperature range from 500°C to 1200°C* of said "heat treatment".

Further, in present claim 1, the "promotion comprising chemical reaction with at least one of a halogen and a halide promotor" is defined as taking place "after the heat treatment". However, in none of the paragraphs [0058], [0061], [0065] or [0066] - [0074] mentioned in the applicant's letter as basis for this amendment said "promotion comprising chemical reaction with at least one of a halogen and a halide promotor" is specifically disclosed as taking place *after the heat treatment*.

The present opinion therefore has been established as if such amendments had not been made (Rule 70.2(c) PCT).

2 Claim 41 has been newly introduced. Since in the accompanying letter, the basis in the application as filed for this amendment was not indicated, this report has been established as if this amendment had not been made (Rule 70.2(c-bis).

3 Consequently, the present report has been established on the application documents as originally filed.

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

4 No opinion was established with regard to novelty, inventive step and industrial applicability on the subject-matter of claims 4-37, 40 and 42 since their subject-matter relates to inventions for which no international search report has been established (Rule 66.2(e) PCT).

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 US 2011/168018 A1 (MOHAMADALIZADEH ALI [IR] ET AL) 14 July 2011 (2011-07-14)

D2 US 2009/136401 A1 (YANG XIAOLIN DAVID [US] ET AL) 28 May 2009 (2009-05-28)

D3 US 2004/076570 A1 (JIA CHARLES Q [CA]) 22 April 2004 (2004-04-22)

D4 A. Bakandritsos ET AL: "High Surface Area Montmorillonite-Carbon Composites and Derived Carbons", Chemistry of materials, vol. 16, no. 8, 16 March 2004 (2004-03-16), pages 1551-1559, XP055072551, ISSN: 0897-4756, DOI: 10.1021/cm0350030

D5 US 2008/090951 A1 (MAO DONGSHENG [US] ET AL) 17 April 2008 (2008-04-17)

5 For the reasons mentioned under item I (see above), the present reasoned statement with regard to novelty, inventive step or industrial applicability has been established on the first (group of) inventions mentioned in the claims as originally filed. The claim numbering relates to those said claims as originally filed:

6 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-5, 44, 45 and 48 is not new in the sense of Article 33(2) PCT:

7 **D1** discloses a method for separating hydrogen sulfide (a pollutant) from a gas comprising methane, helium and hydrogen sulfide, the method comprising

providing a carbon nanocomposite sorbent of multiwall carbon nanotubes (MWCNT) with average diameters of from about 2 nm to about 5 nm and mesoporous crystalline material (MCM)-41;

contacting the said carbon nanocomposite sorbent with a flow of the gas containing 5500 ppm of hydrogen sulfide;

passing the gas flow to an outlet to give a separated gas containing 600 ppm of hydrogen sulfide (paragraph [0029]; paragraph [0062]; example 2).

D1 further discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing MWCNT as carbon precursor;

providing MCM-41 as substrate material;

mixing MWCNTs and MCM-41 and thereby contacting them;

heating the mixture for 3 hours at 110°C (paragraph [0029]; paragraph [0062]; example 2).

D1 hence discloses the subject-matter of claims 1, 2, 44, 45 and 48.

8 **D2** discloses discloses a method for separating mercury from a flue gas comprising flue gas, fly ash and mercury, the method comprising

providing as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent;

promoting the said carbon nanocomposite sorbent by impregnating it with a sodium bromide (NaBr) solution in water;

contacting the NaBr-promoted carbon nanocomposite sorbent with a flow of the gas containing mercury for one second by injecting the carbon nanocomposite sorbent into the gas in a drop tube reactor;

separating the NaBr-promoted carbon nanocomposite sorbent from the gas for analysis of mercury content (paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2; paragraph [0048] - paragraph [0050]; table 3).

D2 further discloses as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent (paragraph [0044] - paragraph [0047]; examples 8; table 1).

D2 hence discloses the subject-matter of claims 1-5, 45 and 48.

9 D3 discloses a method of separating mercury from a desiccator atmosphere that comprises mercury, the method comprising

providing treated coke (ECOcarbon), which is considered a carbon nanocomposite comprising agglomerated carbon structures of about 30 nm;

contacting the said carbon nanocomposite sorbent with a desiccator atmosphere that comprises mercury;

separating the said carbon nanocomposite sorbent comprising mercury from the desiccator atmosphere for analysis of mercury content (paragraph [0084] - paragraph [0086]; example 1; paragraph [0095] - paragraph [0099]; example 5).

D3 further discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing fluid coke as carbon precursor;

providing sulfur dioxide (SO_2) as substrate material;

contacting fluid coke and SO_2 for 10 seconds;

heating the mixture at 800°C (paragraph [0087] - paragraph [0092]; example 2).

D3 hence discloses the subject-matter of claims 1-3, 44, 45 and 48.

10 D4 discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing sucrose as carbon precursor;

providing montmorillonite as substrate material;

contacting contacting sucrose and montmorillonite;

pyrolyzing and hence heating the mixture for one hour at 600°C (Section: "Sample Preparation";page 1552, right-hand column; figure 1).

D4 hence discloses the subject-matter of claims 44, 45 and 48.

11 D5 discloses a method of making a carbon nanocomposite suitable as a sorbent and the carbon nanocomposite hence made, the method comprising

providing carbon nanotubes (CNTs) as carbon precursors,

providing epoxy as substrate material,

curing and hence heating the material for two hours at 160°C .

D5 hence discloses the subject-matter of claims 44, 45 and 48 (paragraph [0015]; figure 1).

Re Item VII

Certain defects in the international application

12 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art documents mentioned in paragraphs [0005] to [0007] of the description are not cited in a way that allows their retrieval.

Re Item VIII

Certain observations on the international application

13 For the reasons mentioned under Item I (see above), the present observations have been made with regard to the first (group of) inventions mentioned in the claims as originally filed. The claim numbering relates to those said claims as originally filed:

14 The application does not meet the requirements of Article 6 PCT for the following reasons:

15 The term "carbon nanocomposite" use in the claims is unclear, because it cannot be determined without ambiguity which further technical feature is meant to be attributed to the carbon composite by defining it as a "nano"composite. The term "nano" merely indicates a prefix in the SI and other systems of units denoting a factor of 10^{-9}. For the present purposes, any carbon composite is considered to be a "carbon nanocomposite". Insofar as

the description of the application contains a clear and unambiguous definition of the tem "carbon nanocomposite", said definition would have to be included in the claims to render the subject-matter of said claim clear.

16 The term pollutant used in claim 2 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers. Specifically, whether a compound or material is considered to be polluting or not, depends on the specific circumstances in which the compound or material is found. Since theses specific circumstances are not further defined in the claim, the said claim is unclear. Insofar as the description of the application contains a clear and unambiguous definition of the tem "pollutant", said definition would have to be included in the claims to render the subject-matter of said claim clear.

17 Claim 4 is not supported by the description as required by Article 6 PCT, as its scope is broader than justified by the description and drawings. Specific support for "promoters" can only be found for "halogen and halide" promoters (see e.g. paragraph [0009] of the description), not for any "promoter".

Claim 48 tries to define the claimed carbon nanocomposite sorbent further in that it is "in contact with mercury or oxidized mercury". This wording introduces an ambiguity as to the scope of said claim 48. The expression "in contact" seeks to define a relationship between the entities "carbon nanocomposite sorbent" and "mercury or oxidized mercury", while it cannot be determined whether one of the two or both entities fall under the scope of the claim. The subject-matter of claim 48 therefore is unclear. For the present purposes of search and examination, claim 48 is considered to be solely directed to the "carbon nanocomposite sorbent" of claim 45, upon which it depends.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Form PCT/ISA/220 as well as, where applicable, item 5 below.
3338016WO1		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US2013/036964	17 April 2013 (17-04-2013)	23 April 2012 (23-04-2012)

Applicant

ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 7 sheets.

☐ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

☒ the international application in the language in which it was filed

☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6*bis*(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box No. II)

3. ☒ **Unity of invention is lacking** (see Box No III)

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant

☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,

a. the figure of the **drawings** to be published with the abstract is Figure No. 1

☒ as suggested by the applicant

☐ as selected by this Authority, because the applicant failed to suggest a figure

☐ as selected by this Authority, because this figure better characterizes the invention

b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/036964

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-5, 44, 45, 48

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/036964

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/12 B01D53/02 B01J20/30 B01J20/32 B01D53/64
B01J20/20
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/168018 A1 (MOHAMADALIZADEH ALI [IR] ET AL) 14 July 2011 (2011-07-14) paragraph [0029] paragraph [0062]; example 2	1,2,44, 45,48
X	US 2009/136401 A1 (YANG XIAOLIN DAVID [US] ET AL) 28 May 2009 (2009-05-28) paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2 paragraph [0048] - paragraph [0050]; table 3	1-5,45, 48

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 July 2013	29/11/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Klemps, Christian

Form PCT/ISA/210 (second sheet) (April 2005)

PAGE 1 OF 2 EXHIBIT 1019
Page 2104

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/036964

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/076570 A1 (JIA CHARLES Q [CA]) 22 April 2004 (2004-04-22) paragraph [0084] - paragraph [0086]; example 1 paragraph [0087] - paragraph [0092]; example 2 paragraph [0095] - paragraph [0099]; example 5	1-3,44, 45,48
X	A. BAKANDRITSOS ET AL: "High Surface Area Montmorillonite-Carbon Composites and Derived Carbons", CHEMISTRY OF MATERIALS, vol. 16, no. 8, 16 March 2004 (2004-03-16) , pages 1551-1559, XP055072551, ISSN: 0897-4756, DOI: 10.1021/cm0350030 Section: "Sample Preparation"; page 1552, right-hand column; figure 1	44,45,48
X	US 2008/090951 A1 (MAO DONGSHENG [US] ET AL) 17 April 2008 (2008-04-17) paragraph [0015]; figure 1	44,45,48

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

PAGE ET AL EXHIBIT 1019
Page 2105

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2013/036964

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011168018 A1	14-07-2011	NONE	
US 2009136401 A1	28-05-2009	US 2009136401 A1	28-05-2009
		US 2012292564 A1	22-11-2012
US 2004076570 A1	22-04-2004	AU 2003278010 A1	04-05-2004
		CA 2408858 A1	18-04-2004
		US 2004076570 A1	22-04-2004
		WO 2004035176 A1	29-04-2004
US 2008090951 A1	17-04-2008	NONE	

Form PCT/ISA/210 (patent family annex) (April 2005)

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5, 44, 45, 48

related to a method for separating a material from a gas that comprises the material, the method comprising providing or obtaining a carbon nanocomposite sorbent, contacting at least some of the material with the sorbent, to form a material-sorbent composition, and separating at least some of the material-sorbent composition from the material-containing gas, to give a separated gas; further to a method of making a such carbon nanocomposite sorbent; further to a such carbon nanocomposite

---

2. claims: 6-42, 46, 49

related to a method for reducing the pollutant content of a pollutant-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent material, providing or obtaining a halogen or halide promotor, promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent, contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition, and separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas; further to a promoted corbon nanocomposite sorbent made by reacting a portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent

---

3. claims: 43, 47

related to a method for reducing the mercury content of a mercury-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent, the carbon nanocomposite sorbent made by steps comprising providing or obtaining a carbon precursor, providing or obtaining a substrate material, contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material, and heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent, providing or obtaining a halogen or halide promoter, promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent, contacting at least part of the promoted sorbent with the mercury, to form a mercury-sorbent composition, and separating at least some of the mercury-sorbent composition from the mercury-containing gas; further to a mercury-sorbent composition made by

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

contacting a carbon nanocomposite sorbent with a mercury-containing gas

---

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
Madden, Robert B. Reg. No. 57,521
SCHWEGMAN, LUNDBERG & WOESSNER
P.O. Box 2938
Minneapolis, MN 55402-0938
ETATS-UNIS D'AMERIQUE

INVITATION TO PAY ADDITIONAL FEES AND, WHERE APPLICABLE, PROTEST FEE

(PCT Article 17(3)(a) and Rule 40.1 and 40.2(e))

Applicant's or agent's file reference 3338016WO1	Date of mailing *(day/month/year)* 2 August 2013 (02-08-2013)
International application No. PCT/US2013/036964	**PAYMENT DUE** within **ONE MONTH** from the above date of mailing
Applicant ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION	International filing date *(day/month/year)* 17 April 2013 (17-04-2013)

1. This International Searching Authority

(i) considers that there are 3 *(number of)* inventions claimed in the international application covered by the claims indicated on an extra sheet:

(ii) therefore considers that **the international application does not comply with the requirements of unity of invention** (Rules 13.1, 13.2 and 13.3) for the reasons indicated on an extra sheet:

(iii) [X] has carried out a partial international search (see Annex) [ ] will establish the international search report on those parts of the international application which relate to the invention first mentioned in claims Nos.:

see extra sheet

(iv) will establish the international search report on the other parts of the international application only if, and to the extent to which, additional fees are paid.

2. Consequently, the applicant is hereby **invited to pay**, within the time limit indicated above, the amount indicated below:

EUR 1.875,00	x	2	=	EUR 3.750,00
Fee per additional invention		number of additional inventions		currency/total amount of additional fees

3. The applicant is informed that, according to Rule 40.2(c), **the payment of any additional fee may be made under protest**, i.e., a reasoned statement to the effect that the international application complies with the requirement of unity of invention or that the amount of the required additional fee is excessive, where applicable, subject to the payment of a protest fee.

Where the applicant pays additional fees under protest, the applicant is hereby invited, within the time limit indicated above, to pay a protest fee (Rule 40.2(e)) in the amount of EUR 830,00 *(currency/amount)*

Where the applicant has not, within the time limit indicated above, paid the required protest fee, the protest will be considered not to have been made and the International Searching Authority will so declare.

4. [ ] Claim(s) Nos. _____ have been found to be unsearchable under Article 17(2)(b) because of defects under Article 17(2)(a) and therefore have not been included within the opinion.

Schwegman Lundberg & Woessner P.A.
AUG 12 2013
PATENT DOCKETING

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016	NAMAGEMBE, Victoria Tel: +31 (0)70 340-3963

Form PCT/ISA/206 (April 2005)
Registered Mail

EXHIBIT 1019
Page 2109

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5, 44, 45, 48

related to a method for separating a material from a gas that comprises the material, the method comprising providing or obtaining a carbon nanocomposite sorbent, contacting at least some of the material with the sorbent, to form a material-sorbent composition, and separating at least some of the material-sorbent composition from the material-containing gas, to give a separated gas; further to a method of making a such carbon nanocomposite sorbent; further to a such carbon nanocomposite

---

2. claims: 6-42, 46, 49

related to a method for reducing the pollutant content of a pollutant-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent material, providing or obtaining a halogen or halide promotor, promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent, contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition, and separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas; further to a promoted corbon nanocomposite sorbent made by reacting a portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent

---

3. claims: 43, 47

related to a method for reducing the mercury content of a mercury-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent, the carbon nanocomposite sorbent made by steps comprising providing or obtaining a carbon precursor, providing or obtaining a substrate material, contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material, and heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent, providing or obtaining a halogen or halide promoter, promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent, contacting at least part of the promoted sorbent with the mercury, to form a mercury-sorbent composition, and separating at least some of the mercury-sorbent composition from the mercury-containing

gas; further to a mercury-sorbent composition made by contacting a carbon nanocomposite sorbent with a mercury-containing gas

---

The present application lacks unity of invention (Rule 13 PCT) for the following reasons:
The present application contains the following eight independent claims: claim 1 (method claim), claim 6 (method claim), claim 43 (method claim), claim 44 (method claim), claim 45 (product claim), claim 46 (product claim), claim 47 (product claim), claim 49 (product claim).
The common same or corresponding technical features among those claims are:
carbon nanocomposite sorbent; method where said carbon nanocomposite sorbent is employed with a gas; said method comprising: the step of providing or obtaining a carbon nanocomposite sorbent; the step of contacting at least part of the sorbent; the step of separating from gas.
The common same or corresponding technical feature "carbon nanocomposite" is unclear (Article 6 PCT), because it cannot be determined which further technical feature is meant to be attributed to the carbon composite by defining it as a "nano"composite. The term "nano" merely indicates a prefix in the SI and other systems of units denoting a factor of 10^-9 . For the present purposes, any carbon composite is considered to be a "carbon nanocomposite".
The document US 2011/0168018 A1 (hereinafter D1) discloses a method for separating hydrogen sulfide from a gas comprising methane, helium and hydrogen sulfide, the method comprising
providing a carbon nanocomposite sorbent of multiwall carbon nanotubes (MWCNT) with average diameters of from about 2 nm to about 5 nm and mesoporous crystalline material (MCM)-41;
contacting the said carbon nanocomposite sorbent with a flow of the gas containing 5500 ppm of hydrogen sulfide;
passing the gas flow to an outlet to give a separated gas containing 600 ppm of hydrogen sulfide (paragraph [0029]; paragraph [0062]; example 2).
Further, the document US 2009/0136401 A1 (hereinafter D2) discloses a method for separating mercury from a flue gas comprising flue gas, fly ash and mercury, the method comprising
providing as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent;
promoting the said carbon nanocomposite sorbent by impregnating it with a sodium bromide (NaBr) solution in water;
contacting the NaBr-promoted carbon nanocomposite sorbent with a flow of the gas containing mercury for one second by injecting the carbon nanocomposite sorbent into the gas in a drop tube reactor;
separating the NaBr-promoted carbon nanocomposite sorbent from the gas for analysis of mercury content (paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2; paragraph [0048] - paragraph [0050]; table 3).
All common same or corresponding technical features are known from D1 and D2. These features therefore cannot serve as "special" technical features within the meaning of Rule 13.2 PCT.
Therefore, there is no common, same or corresponding special technical feature among all independent claims and thus the requirement of Rule 13.2 PCT is not met.
Amongst the independent claims 6, 43, 46, 47 and 49, the further common

same or corresponding technical features are:
promoter; providing a halogen or halide promoter; promoting at least a portion of the carbon nanocomposite sorbent material by chemically reacting a (the) portion of the sorbent material with the halogen or halide promoter; promoted sorbent.
All common same or corresponding technical features are known from D2. These features therefore cannot serve as "special" technical features within the meaning of Rule 13.2 PCT.
Therefore, there is no common, same or corresponding special technical feature among all independent claims 6, 43, 46, 47 and 49 and thus the requirement of Rule 13.2 PCT is not met.
The separate groups of inventions are hence as mentioned above.
The common problem underlying groups 1, 2 and 3 of inventions is seen to lie in the provision of a method for the removal of a (pollutant) component of a gas from said gas and the provision of a sorbent for a such removal.
The common problem is already known from both D1 (see e.g. abstract) and D2 (see e.g. abstract). No additional problem could be identified common to these three groups of inventions which could serve as the general inventive concept as required by Rule 13.1 PCT.
The application hence does not meet the requirements of unity of invention as defined in Rule 13.1 and 13.2 PCT.

Annex to Form PCT/ISA/206
COMMUNICATION RELATING TO THE RESULTS OF THE PARTIAL INTERNATIONAL SEARCH

International Application No
PCT/US2013/036964

1. The present communication is an Annex to the invitation to pay additional fees (Form PCT/ISA/206). It shows the results of the international search established on the parts of the international application which relate to the invention first mentioned in claims Nos.:
see 'Invitation to pay additional fees'
2. This communication is not the international search report which will be established according to Article 18 and Rule 43.

3. If the applicant does not pay any additional search fees, the information appearing in this communication will be considered as the result of the international search and will be included as such in the international search report.

4. If the applicant pays additional fees, the international search report will contain both the information appearing in this communication and the results of the international search on other parts of the international application for which such fees will have been paid.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/168018 A1 (MOHAMADALIZADEH ALI [IR] ET AL) 14 July 2011 (2011-07-14) paragraph [0029] paragraph [0062]; example 2	1,2,44, 45,48
X	US 2009/136401 A1 (YANG XIAOLIN DAVID [US] ET AL) 28 May 2009 (2009-05-28) paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2 paragraph [0048] - paragraph [0050]; table 3	1-5,45, 48
X	US 2004/076570 A1 (JIA CHARLES Q [CA]) 22 April 2004 (2004-04-22) paragraph [0084] - paragraph [0086]; example 1 paragraph [0087] - paragraph [0092]; example 2 paragraph [0095] - paragraph [0099]; example 5	1-3,44, 45,48
X	A. BAKANDRITSOS ET AL: "High Surface Area Montmorillonite-Carbon Composites and Derived Carbons", CHEMISTRY OF MATERIALS, vol. 16, no. 8, 16 March 2004 (2004-03-16) , pages 1551-1559, XP055072551, ISSN: 0897-4756, DOI: 10.1021/cm0350030 Section: "Sample Preparation"; page 1552, right-hand column; figure 1	44,45,48

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

4

Annex to Form PCT/ISA/206
COMMUNICATION RELATING TO THE RESULTS
OF THE PARTIAL INTERNATIONAL SEARCH

International Application No
PCT/US2013/036964

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/090951 A1 (MAO DONGSHENG [US] ET AL) 17 April 2008 (2008-04-17) paragraph [0015]; figure 1	44,45,48

4

Form PCT/ISA/206 (Annex, continuation sheet) (July 1992; reprint January 2004)

Patent Family Annex

Information on patent family members

International Application No
PCT/US2013/036964

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011168018 A1	14-07-2011	NONE	
US 2009136401 A1	28-05-2009	US 2009136401 A1	28-05-2009
		US 2012292564 A1	22-11-2012
US 2004076570 A1	22-04-2004	AU 2003278010 A1	04-05-2004
		CA 2408858 A1	18-04-2004
		US 2004076570 A1	22-04-2004
		WO 2004035176 A1	29-04-2004
US 2008090951 A1	17-04-2008	NONE	

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

SCHWEGMAN, LUNDBERG & WOESSNER, P.A.
P.O. Box 2938
Minneapolis, MN 55402
ETATS-UNIS D'AMERIQUE

PCT

WRITTEN OPINION OF THE INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

(PCT Rule 66)

Date of mailing *(day/month/year)*	15.04.2014
Applicant's or agent's file reference: 3338016WO1	**REPLY DUE** within 1 month(s) and 15 days from the above date of mailing

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/036964	17.04.2013	23.04.2012

International Patent Classification (IPC) or both national classification and IPC
INV. B01J20/12

Applicant
Energy & Environmental Research Center Foundation

1. ☒ The written opinion established by the International Searching Authority:
   ☒ is ☐ is not
   considered to be a written opinion of the International Preliminary Examining Authority.

2. This second opinion contains indications relating to the following items:
   - ☒ Box No. I Basis of the opinion
   - ☐ Box No. II Priority
   - ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☒ Box No. VII Certain defects in the international application
   - ☒ Box No. VIII Certain observations on the international application

3. The applicant is hereby **invited to reply** to this opinion.

   When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(e).
   How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 55.3 and 66.8.
   Also: For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4*bis*. For an informal communication with the examiner, see Rule 66.6. For an additional opportunity to submit amendments, see Rule 66.4.
   If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary report on patentability (Chapter II of the PCT) must be established according to Rule 69.2 is: 23.06.2014

Schwegman Lundberg & Woessner P.A.
APR 29 2014

Name and mailing address of the international preliminary examining authority:
European Patent Office P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040
Fax: +31 70 340 - 3016

Authorized Officer
Klemps, Christian
Telephone No. +31 70 340-8036

RECEIVED

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into ,
   which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3(a) and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4(a))
   - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))

2. With regard to the elements of the international application, this opinion has been established on the basis of *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed")*:

Description, Pages

1-49 as originally filed

Claims, Numbers

1-42 filed with the demand for preliminary international examination

Drawings, Sheets

1/6-6/6 as originally filed

☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

4. ☒ This opinion has been established as if (some of) the amendments listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
   - ☐ the description, pages
   - ☒ the claims, Nos. 1-3, 38,39,41
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:

5. ☐ This opinion has been established:
   - ☐ taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 66.1(d-bis)).
   - ☐ without taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 66.4bis).

6. ☐ Supplementary international search report(s) from Authority(ies) have been received and taken into account in drawing up this opinion (Rule 45bis.8(b) and (c)).

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non- obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application

☒ claims Nos. 4-37, 40, 42

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no international search opinion has been established for the said claims Nos. 4-37, 40, 42

☐ a meaningful opinion could not be formed without sequence listing; the applicant did not, within the prescribed time limit:

☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Preliminary Examining Authority in a form and manner acceptable to it.

☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Preliminary Examining Authority in a form and manner acceptable to it.

☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b) and 13*ter*.2.

☒ See supplemental sheet for further details

Box No. V Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	No:	Claims 1-5, 44, 45, 48
Inventive step (IS)	No:	Claims 1-5, 44, 45, 48
Industrial applicability (IA)	No:	Claims

2. Citations and explanations:

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item I

Basis of the report

1 The International Preliminary Examining Authority considers that the following amendments to the claims go beyond the disclosure in the international application as filed:

In present claims 1 and 38, the "substrate material" is defined as "comprising at least one of diatomaceous earth, a clay, a zeolite, and a mineral". In paragraph [0061] of the description of the application as filed, however, only porous minerals are disclosed. No basis in the application as filed can be found for *any* mineral as "substrate material".

Further, in present claims 1 and 38, the "heat treatment" is defined as "comprising about 500°C to about 1200°C". In paragraph [0065] of the description of the application as filed, however, only each of the temperatures 500°C and 1200°C, respectively, are disclosed in an exemplified fashion. No basis in the application as filed can be found for a *temperature range from 500°C to 1200°C* of said "heat treatment".

Further, in present claim 1, the "promotion comprising chemical reaction with at least one of a halogen and a halide promotor" is defined as taking place "after the heat treatment". However, in none of the paragraphs [0058], [0061], [0065] or [0066] - [0074] mentioned in the applicant's letter as basis for this amendment said "promotion comprising chemical reaction with at least one of a halogen and a halide promotor" is specifically disclosed as taking place *after the heat treatment*.

The present opinion therefore has been established as if such amendments had not been made (Rule 70.2(c) PCT).

2 Claim 41 has been newly introduced. Since in the accompanying letter, the basis in the application as filed for this amendment was not indicated, this opinion has been established as if this amendment had not been made (Rule 70.2(c-bis).

3 Consequently, the present opinion has been established on the application documents as originally filed.

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

4 No opinion was established with regard to novelty, inventive step and industrial applicability on the subject-matter of claims 4-37, 40 and 42 since their subject-matter relates to inventions for which no international search report has been established (Rule 66.2(e) PCT).

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 US 2011/168018 A1 (MOHAMADALIZADEH ALI [IR] ET AL) 14 July 2011 (2011-07-14)

D2 US 2009/136401 A1 (YANG XIAOLIN DAVID [US] ET AL) 28 May 2009 (2009-05-28)

D3 US 2004/076570 A1 (JIA CHARLES Q [CA]) 22 April 2004 (2004-04-22)

D4 A. Bakandritsos ET AL: "High Surface Area Montmorillonite-Carbon Composites and Derived Carbons", Chemistry of materials, vol. 16, no. 8, 16 March 2004 (2004-03-16), pages 1551-1559, XP055072551, ISSN: 0897-4756, DOI: 10.1021/cm0350030

D5 US 2008/090951 A1 (MAO DONGSHENG [US] ET AL) 17 April 2008 (2008-04-17)

5 For the reasons mentioned under Item I (see above), the present reasoned statement with regard to novelty, inventive step or industrial applicability has been established on the first (group of) inventions mentioned in the claims as originally filed. The claim numbering relates to those said claims as originally filed:

6 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-5, 44, 45 and 48 is not new in the sense of Article 33(2) PCT:

7 **D1** discloses a method for separating hydrogen sulfide (a pollutant) from a gas comprising methane, helium and hydrogen sulfide, the method comprising

providing a carbon nanocomposite sorbent of multiwall carbon nanotubes (MWCNT) with average diameters of from about 2 nm to about 5 nm and mesoporous crystalline material (MCM)-41;

contacting the said carbon nanocomposite sorbent with a flow of the gas containing 5500 ppm of hydrogen sulfide;

passing the gas flow to an outlet to give a separated gas containing 600 ppm of hydrogen sulfide (paragraph [0029]; paragraph [0062]; example 2).

D1 further discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing MWCNT as carbon precursor;

providing MCM-41 as substrate material;

mixing MWCNTs and MCM-41 and thereby contacting them;

heating the mixture for 3 hours at 110°C (paragraph [0029]; paragraph [0062]; example 2).

D1 hence discloses the subject-matter of claims 1, 2, 44, 45 and 48.

8 **D2** discloses discloses a method for separating mercury from a flue gas comprising flue gas, fly ash and mercury, the method comprising

providing as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent;

promoting the said carbon nanocomposite sorbent by impregnating it with a sodium bromide (NaBr) solution in water;

contacting the NaBr-promoted carbon nanocomposite sorbent with a flow of the gas containing mercury for one second by injecting the carbon nanocomposite sorbent into the gas in a drop tube reactor;

separating the NaBr-promoted carbon nanocomposite sorbent from the gas for analysis of mercury content (paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2; paragraph [0048] - paragraph [0050]; table 3).

D2 further discloses as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent (paragraph [0044] - paragraph [0047]; examples 8; table 1).

D2 hence discloses the subject-matter of claims 1-5, 45 and 48.

9 **D3** discloses a method of separating mercury from a desiccator atmosphere that comprises mercury, the method comprising

providing treated coke (ECOcarbon), which is considered a carbon nanocomposite comprising agglomerated carbon structures of about 30 nm;

contacting the said carbon nanocomposite sorbent with a desiccator atmosphere that comprises mercury;

separating the said carbon nanocomposite sorbent comprising mercury from the desiccator atmosphere for analysis of mercury content (paragraph [0084] - paragraph [0086]; example 1; paragraph [0095] - paragraph [0099]; example 5).

D3 further discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing fluid coke as carbon precursor;

providing sulfur dioxide (SO_2) as substrate material;

contacting fluid coke and SO_2 for 10 seconds;

heating the mixture at 800°C (paragraph [0087] - paragraph [0092]; example 2).

D3 hence discloses the subject-matter of claims 1-3, 44, 45 and 48.

10 **D4** discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing sucrose as carbon precursor;

providing montmorillonite as substrate material;

contacting contacting sucrose and montmorillonite;

pyrolyzing and hence heating the mixture for one hour at 600 °C (Section: "Sample Preparation";page 1552, right-hand column; figure 1).

D4 hence discloses the subject-matter of claims 44, 45 and 48.

11 D5 discloses a method of making a carbon nanocomposite suitable as a sorbent and the carbon nanocomposite hence made, the method comprising

providing carbon nanotubes (CNTs) as carbon precursors,

providing epoxy as substrate material,

curing and hence heating the material for two hours at 160 °C .

D5 hence discloses the subject-matter of claims 44, 45 and 48 (paragraph [0015]; figure 1).

Re Item VII

Certain defects in the international application

12 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art documents mentioned in paragraphs [0005] to [0007] of the description are not cited in a way that allows their retrieval.

Re Item VIII

Certain observations on the international application

13 For the reasons mentioned under item I (see above), the present observations have been made with regard to the first (group of) inventions mentioned in the claims as originally filed. The claim numbering relates to those said claims as originally filed:

14 The application does not meet the requirements of Article 6 PCT for the following reasons:

15 The term "carbon nanocomposite" use in the claims is unclear, because it cannot be determined without ambiguity which further technical feature is meant to be attributed to the carbon composite by defining it as a "nano"composite. The term "nano" merely indicates a prefix in the SI and other systems of units denoting a factor of 10^{-9}. For the present purposes, any carbon composite is considered to be a "carbon nanocomposite". Insofar as

the description of the application contains a clear and unambiguous definition of the tem "carbon nanocomposite", said definition would have to be included in the claims to render the subject-matter of said claim clear.

16 The term pollutant used in claim 2 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers. Specifically, whether a compound or material is considered to be polluting or not, depends on the specific circumstances in which the compound or material is found. Since theses specific circumstances are not further defined in the claim, the said claim is unclear. Insofar as the description of the application contains a clear and unambiguous definition of the tem "pollutant", said definition would have to be included in the claims to render the subject-matter of said claim clear.

17 Claim 4 is not supported by the description as required by Article 6 PCT, as its scope is broader than justified by the description and drawings. Specific support for "promoters" can only be found for "halogen and halide" promoters (see e.g. paragraph [0009] of the description), not for any "promoter".

Claim 48 tries to define the claimed carbon nanocomposite sorbent further in that it is "in contact with mercury or oxidized mercury". This wording introduces an ambiguity as to the scope of said claim 48. The expression "in contact" seeks to define a relationship between the entities "carbon nanocomposite sorbent" and "mercury or oxidized mercury", while it cannot be determined whether one of the two or both entities fall under the scope of the claim. The subject-matter of claim 48 therefore is unclear. For the present purposes of search and examination, claim 48 is considered to be solely directed to the "carbon nanocomposite sorbent" of claim 45, upon which it depends.

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2013/036964	17.04.2013	23.04.2012

International Patent Classification (IPC) or both national classification and IPC
INV. B01J20/12 B01D53/02 B01J20/30 B01J20/32 B01D53/64 B01J20/20

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notifed the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Fax: +31 70 340 - 3016	see form PCT/ISA/210	Klemps, Christian Telephone No. +31 70 340-8036

Form PCT/ISA/237 (Cover Sheet) (July 2009)

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:

   a. (means)

      ☐ on paper

      ☐ in electronic form

   b. (time)

      ☐ in the international application as filed

      ☐ together with the international application in electronic form

      ☐ subsequently to this Authority for the purposes of search

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

☐ the entire international application

☒ claims Nos. 6-43, 46, 47, 49

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search *(specify)*:

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no international search report has been established for the whole application or for said claims Nos. 6-43, 46, 47, 49

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

- ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b).

☐ See Supplemental Box for further details

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has, within the applicable time limit:

   ☐ paid additional fees

   ☐ paid additional fees under protest and, where applicable, the protest fee

   ☐ paid additional fees under protest but the applicable protest fee was not paid

   ☒ not paid additional fees

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

   ☐ complied with

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

   ☐ all parts.

   ☒ the parts relating to claims Nos. 1-5, 44, 45, 48

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-5, 44, 45, 48
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-5, 44, 45, 48
Industrial applicability (IA)	Yes:	Claims	1-5, 44, 45, 48
	No:	Claims	

2. Citations and explanations

   see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Reference is made to the following documents:

D1 US 2011/168018 A1 (MOHAMADALIZADEH ALI [IR] ET AL) 14 July 2011 (2011-07-14)

D2 US 2009/136401 A1 (YANG XIAOLIN DAVID [US] ET AL) 28 May 2009 (2009-05-28)

D3 US 2004/076570 A1 (JIA CHARLES Q [CA]) 22 April 2004 (2004-04-22)

D4 A. Bakandritsos ET AL: "High Surface Area Montmorillonite-Carbon Composites and Derived Carbons", Chemistry of materials, vol. 16, no. 8, 16 March 2004 (2004-03-16), pages 1551-1559, XP055072551, ISSN: 0897-4756, DOI: 10.1021/cm0350030

D5 US 2008/090951 A1 (MAO DONGSHENG [US] ET AL) 17 April 2008 (2008-04-17)

Re Item IV

Lack of unity of invention

1 The present application lacks unity of invention (Rule 13 PCT) for the following reasons:

The present application contains the following eight independent claims: claim 1 (method claim), claim 6 (method claim), claim 43 (method claim), claim 44 (method claim), claim 45 (product claim), claim 46 (product claim), claim 47 (product claim), claim 49 (product claim).

The common same or corresponding technical features among those claims are:

carbon nanocomposite sorbent; method where said carbon nanocomposite sorbent is employed with a gas; said method comprising: the step of providing or obtaining a carbon nanocomposite sorbent; the step of contacting at least part of the sorbent; the step of separating from gas.

The common same or corresponding technical feature "carbon nanocomposite" is unclear (Article 6 PCT), because it cannot be determined which further technical feature is meant to be attributed to the carbon composite by defining it as a "nano"composite. The term "nano" merely

indicates a prefix in the SI and other systems of units denoting a factor of 10^{-9}. For the present purposes, any carbon composite is considered to be a "carbon nanocomposite".

The document US 2011/0168018 A1 (**D1**) discloses a method for separating hydrogen sulfide from a gas comprising methane, helium and hydrogen sulfide, the method comprising

providing a carbon nanocomposite sorbent of multiwall carbon nanotubes (MWCNT) with average diameters of from about 2 nm to about 5 nm and mesoporous crystalline material (MCM)-41;

contacting the said carbon nanocomposite sorbent with a flow of the gas containing 5500 ppm of hydrogen sulfide;

passing the gas flow to an outlet to give a separated gas containing 600 ppm of hydrogen sulfide (paragraph [0029]; paragraph [0062]; example 2).

Further, the document US 2009/0136401 A1 (**D2**) discloses a method for separating mercury from a flue gas comprising flue gas, fly ash and mercury, the method comprising

providing as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent;

promoting the said carbon nanocomposite sorbent by impregnating it with a sodium bromide (NaBr) solution in water;

contacting the NaBr-promoted carbon nanocomposite sorbent with a flow of the gas containing mercury for one second by injecting the carbon nanocomposite sorbent into the gas in a drop tube reactor;

separating the NaBr-promoted carbon nanocomposite sorbent from the gas for analysis of mercury content (paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2; paragraph [0048] - paragraph [0050]; table 3).

All common same or corresponding technical features are known from **D1** and **D2**. These features therefore cannot serve as "special" technical features within the meaning of Rule 13.2 PCT.

Therefore, there is no common, same or corresponding special technical feature among all independent claims and thus the requirement of Rule 13.2 PCT is not met.

Amongst the independent claims 6, 43, 46, 47 and 49, the further common same or corresponding technical features are:

promoter; providing a halogen or halide promoter; promoting at least a portion of the carbon nanocomposite sorbent material by chemically reacting a (the) portion of the sorbent material with the halogen or halide promoter; promoted sorbent.

All common same or corresponding technical features are known from **D2**. These features therefore cannot serve as "special" technical features within the meaning of Rule 13.2 PCT.

Therefore, there is no common, same or corresponding special technical feature among all independent claims 6, 43, 46, 47 and 49 and thus the requirement of Rule 13.2 PCT is not met.

The separate groups of inventions are:

Group 1: claims: 1-5, 44, 45, 48 related to a method for separating a material from a gas that comprises the material, the method comprising providing or obtaining a carbon nanocomposite sorbent, contacting at least some of the material with the sorbent, to form a material-sorbent composition, and separating at least some of the material-sorbent composition from the material-containing gas, to give a separated gas; further to a method of making a such carbon nanocomposite sorbent; further to a such carbon nanocomposite.

Group 2: claims: 6-42, 46, 49 related to a method for reducing the pollutant content of a pollutant-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent material, providing or obtaining a halogen or halide promotor, promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent, contacting at least part of the promoted sorbent with the pollutant in the pollutant-containing gas, to form a pollutant-sorbent composition, and separating particulates from the pollutant-containing gas, the particulates comprising at least some of the pollutant-sorbent composition, to give a cleaned gas; further to a promoted corbon nanocomposite sorbent made by reacting a portion of the sorbent material with a halogen or halide promoter to form the promoted sorbent.

Group 3: claims: 43, 47 related to a method for reducing the mercury content of a mercury-containing gas, the method comprising providing or obtaining a carbon nanocomposite sorbent, the carbon nanocomposite sorbent made by steps comprising providing or obtaining a carbon precursor,

providing or obtaining a substrate material, contacting the carbon precursor and the substrate material, to provide a nanocomposite starting material, and heating the nanocomposite starting material, to provide the carbon nanocomposite sorbent, providing or obtaining a halogen or halide promoter, promoting at least a portion of the sorbent material by chemically reacting the portion of the sorbent material with the halogen or halide promoter to form a promoted sorbent, contacting at least part of the promoted sorbent with the mercury, to form a mercury-sorbent composition, and separating at least some of the mercury-sorbent composition from the mercury-containing gas; further to a mercury-sorbent composition made by contacting a carbon nanocomposite sorbent with a mercury-containing gas.

The common problem underlying groups 1, 2 and 3 of inventions is seen to lie in the provision of a method for the removal of a (pollutant) component of a gas from said gas and the provision of a sorbent for a such removal.

The common problem is already known from both **D1** (see e.g. abstract) and **D2** (see e.g. abstract). No additional problem could be identified common to these three groups of inventions which could serve as the general inventive concept as required by Rule 13.1 PCT.

The application hence does not meet the requirements of unity of invention as defined in Rule 13.1 and 13.2 PCT.

In accordance with Article 17(3) PCT the international search report is established on those parts of the international application which relate to the invention first mentioned in the claims, i.e. the above mentioned Group 1.

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

2 The present application further does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-5, 44, 45 and 48 is not new in the sense of Article 33(2) PCT:

3 **D1** discloses a method for separating hydrogen sulfide (a pollutant) from a gas comprising methane, helium and hydrogen sulfide, the method comprising

providing a carbon nanocomposite sorbent of multiwall carbon nanotubes (MWCNT) with average diameters of from about 2 nm to about 5 nm and mesoporous crystalline material (MCM)-41;

contacting the said carbon nanocomposite sorbent with a flow of the gas containing 5500 ppm of hydrogen sulfide;

passing the gas flow to an outlet to give a separated gas containing 600 ppm of hydrogen sulfide (paragraph [0029]; paragraph [0062]; example 2).

D1 further discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing MWCNT as carbon precursor;

providing MCM-41 as substrate material;

mixing MWCNTs and MCM-41 and thereby contacting them;

heating the mixture for 3 hours at 110°C (paragraph [0029]; paragraph [0062]; example 2).

D1 hence discloses the subject-matter of claims 1, 2, 44, 45 and 48.

4 **D2** discloses discloses a method for separating mercury from a flue gas comprising flue gas, fly ash and mercury, the method comprising

providing as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent;

promoting the said carbon nanocomposite sorbent by impregnating it with a sodium bromide (NaBr) solution in water;

contacting the NaBr-promoted carbon nanocomposite sorbent with a flow of the gas containing mercury for one second by injecting the carbon nanocomposite sorbent into the gas in a drop tube reactor;

separating the NaBr-promoted carbon nanocomposite sorbent from the gas for analysis of mercury content (paragraph [0044] - paragraph [0047]; examples 8, 16; tables 1, 2; paragraph [0048] - paragraph [0050]; table 3).

D2 further discloses as-mined kaolin containing about 2% naturally intercalated carbon (Kaolin-1), which is considered as a carbon nanocomposite sorbent (paragraph [0044] - paragraph [0047]; examples 8; table 1).

D2 hence discloses the subject-matter of claims 1-5, 45 and 48.

5 **D3** discloses a method of separating mercury from a desiccator atmosphere that comprises mercury, the method comprising

providing treated coke (ECOcarbon), which is considered a carbon nanocomposite comprising agglomerated carbon structures of about 30 nm;

contacting the said carbon nanocomposite sorbent with a desiccator atmosphere that comprises mercury;

separating the said carbon nanocomposite sorbent comprising mercury from the desiccator atmosphere for analysis of mercury content (paragraph [0084] - paragraph [0086]; example 1; paragraph [0095] - paragraph [0099]; example 5).

D3 further discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing fluid coke as carbon precursor;

providing sulfur dioxide (SO_2) as substrate material;

contacting fluid coke and SO_2 for 10 seconds;

heating the mixture at 800°C (paragraph [0087] - paragraph [0092]; example 2).

D3 hence discloses the subject-matter of claims 1-3, 44, 45 and 48.

6 **D4** discloses a method of making a carbon nanocomposite sorbent and the carbon nanocomposite sorbent hence made, the method comprising

providing sucrose as carbon precursor;

providing montmorillonite as substrate material;

contacting contacting sucrose and montmorillonite;

pyrolyzing and hence heating the mixture for one hour at 600°C (Section: "Sample Preparation"; page 1552, right-hand column; figure 1).

D4 hence discloses the subject-matter of claims 44, 45 and 48.

7 **D5** discloses a method of making a carbon nanocomposite suitable as a sorbent and the carbon nanocomposite hence made, the method comprising

providing carbon nanotubes (CNTs) as carbon precursors,

providing epoxy as substrate material,

curing and hence heating the material for two hours at 160°C .

D5 hence discloses the subject-matter of claims 44, 45 and 48 (paragraph [0015]; figure 1).

Re Item VII

Certain defects in the international application

8 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art documents mentioned in paragraphs [0005] to [0007] of the description are not cited in a way that allows their retrieval.

Re Item VIII

Certain observations on the international application

9 The application does not meet the requirements of Article 6 PCT for the following reasons:

10 The term "carbon nanocomposite" use in the claims is unclear, because it cannot be determined without ambiguity which further technical feature is meant to be attributed to the carbon composite by defining it as a "nano"composite. The term "nano" merely indicates a prefix in the SI and other systems of units denoting a factor of 10^9. For the present purposes, any carbon composite is considered to be a "carbon nanocomposite".

11 The term pollutant used in claim 2 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers. Specifically, whether a compound or material is considered to be polluting or not, depends on the specific circumstances in which the compound or material is found. Since theses specific circumstances are not further defined in the claim, the said claim is unclear.

12 Claim 4 is not supported by the description as required by Article 6 PCT, as its scope is broader than justified by the description and drawings. Specific support for "promoters" can only be found for "halogen and halide" promoters (see e.g. paragraph [0009] of the description), not for any "promoter".

13 Claim 48 tries to define the claimed carbon nanocomposite sorbent further in that it is "in contact with mercury or oxidized mercury". This wording introduces an ambiguity as to the scope of said claim 48. The expression "in

contact" seeks to define a relationship between the entities "carbon nanocomposite sorbent" and "mercury or oxidized mercury", while it cannot be determined whether one of the two or both entities fall under the scope of the claim. The subject-matter of claim 48 therefore is unclear. For the present purposes of search and examination, claim 48 is considered to be solely directed to the "carbon nanocomposite sorbent" of claim 45, upon which it depends.

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
Madden, Robert B. Reg. No. 57,521
SCHWEGMAN, LUNDBERG & WOESSNER
P.O. Box 2938
Minneapolis, MN 55402-0938
ETATS-UNIS D'AMERIQUE

INVITATION TO PAY ADDITIONAL FEES AND, WHERE APPLICABLE, PROTEST FEE

(PCT Article 17(3)(a) and Rule 40.1 and 40.2(e))

Applicant's or agent's file reference 3338021WO1	Date of mailing *(day/month/year)* 30 May 2014 (30-05-2014) **PAYMENT DUE** within ONE MONTH from the above date of mailing
International application No. PCT/US2014/019916	International filing date *(day/month/year)* 3 March 2014 (03-03-2014)
Applicant ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION	

1. This International Searching Authority

(i) considers that there are 4 *(number of)* inventions claimed in the international application covered by the claims indicated on an extra sheet:

(ii) therefore considers that the international application does not comply with the requirements of unity of invention (Rules 13.1, 13.2 and 13.3) for the reasons indicated on an extra sheet:

(iii) [X] has carried out a partial international search (see Annex) [ ] will establish the international search report on those parts of the international application which relate to the invention first mentioned in claims Nos.:

see extra sheet

(iv) will establish the international search report on the other parts of the international application only if, and to the extent to which, additional fees are paid.

2. Consequently, the applicant is hereby invited to pay, within the time limit indicated above, the amount indicated below:

EUR 1.875,00 (Fee per additional invention) x 3 (number of additional inventions) = EUR 5.625,00 (currency/total amount of additional fees)

3. The applicant is informed that, according to Rule 40.2(a), the payment of any additional fee may be made under protest, i.e., a reasoned statement to the effect that the international application complies with the requirement of unity of invention or that the amount of the required additional fee is excessive, where applicable, subject to the payment of a protest fee.

Where the applicant pays additional fees under protest, the applicant is hereby invited, within the time limit indicated above, to pay a protest fee (Rule 40.2(e)) in the amount of EUR 865,00 *(currency/amount)*

Where the applicant has not, within the time limit indicated above, paid the required protest fee, the protest will be considered not to have been made and the International Searching Authority will so declare.

4. [ ] Claim(s) Nos. _____ have been found to be unsearchable under Article 17(2)(b) because of defects under Article 17(2)(a) and therefore have not been included with any invention.

Name and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016	Authorized officer SLOAN, Mary Tel: +49 (0)89 2399-2608

Schwegman Lundberg & Woessner P.A.
JUN 09 2014

Form PCT/ISA/206 (April 2005)
Registered Mail

RECEIVED

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and applying the method for gases with a sulfur(VI) concentration of more than 3 ppm by mole

---

2. claims: 50-67(completely); 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and obtaining or providing the activated carbon sorbent comprises promoting an unpromoted carbon sorbent and/or obtaining the unpromoted carbon sorbent from a carbon precursor comprising nitrogen and/or the activated carbon sorbent comprising a stabilizing agent

---

3. claims: 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and adding an alkaline component into the pollutant containing gas

---

4. claims: 1-49(partially)

Pollutant removal from a gas by contacting with an activated carbon sorbent comprising nitrogen and regenerating the activated carbon sorbent

---

The common concept linking together the groups is the subject-matter of claim 1 . This common concept is not new over D1.
D1 discloses a method of reducing the mercury content in a mercury-containing gas (see abstract), the method comprising obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see page 615, para. 4.2.5.1 and page 616, left column, "...by impregnation of nitrogen-containing polymers or pitches ..."), contacting a pollutant-containing gas with the activated carbon sorbent to form a pollutant-sorbent composition (implicitly disclosed as for a sorbent based removal process the pollutant has to be contacted with the sorbent, the pollutant thereby always forms a pollutant-sorbent composition), and separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give a separated gas (see page 622, figure 20).
Hence, D1 discloses all the features of claim 1.

D1 further discloses

PAC ET AL. EXHIBIT 1019
Page 2140

- claim 3: the concentration of nitrogen in the surface layer of the sorbent particles to be higher than in a core of the particles (see page 615, right column, lines 1-4, nitrogenated function introduced on carbon surface, therefrom following a lower nitrogenous concentration in the core of the particles)
- claim 5, 6: the mercury-containing gas to comprise a sulfur(VI) concentration, like SO 3 (see page 616, right column, 2nd paragraph)

The differentiating features are
- Group 1: applying the method for gases with a sulfur(VI) concentration of more than 3 ppm by mole
- Group 2: obtaining or providing the activated carbon sorbent comprises promoting an unpromoted carbon sorbent and/or providing or obtaining the unpromoted carbon sorbent from a carbon precursor comprising nitrogen and/or the activated carbon sorbent comprising a stabilizing agent
- Group 3: adding an alkaline component into the pollutant containing gas
- Group 4: regenerating the activated carbon sorbent

with following resulting technical effects:
- Group 1: no surprising and unexpected technical effect distinguishable
- Group 2: further enhancement of the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: reduction of sulfuric compounds in the pollutant containing gas
- Group 4: saving financial means for sorbent

Thus the problems solved may be regarded as
- Group 1: finding an alternative mercury containing gas for which the method can be applied.
- Group 2: how to modify the method of D1 in order to further enhance the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: how to modify the method of D1 in order to reduce the sulfuric compounds in the pollutant containing gas
- Group 4: how to modify the method of D1 in order to save financial means for sorbent

The special technical features (R. 13.2 PCT) are
- Group 1: no special technical feature A as the alternative gas is considered to be obvious for the skilled person.
- Group 2: differentiating feature = special technical feature B as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 3: differentiating feature = special technical feature C as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 4: no special technical feature D as the regeneration and reuse of the sorbent is disclosed by D1 (see page 612, left column, paragraph before 4.2.2.3).

Groups of (alleged) Inventions
The groups of technical features do not solve any common technical problem. Thus the groups of claims are neither linked by the same nor by corresponding special technical features and define different inventions not linked by a single general inventive concept (Rule 13.1 and 13.2 PCT)

and therefore the requirement for unity of invention referred to in Rule 13 PCT is not fulfilled .

PAC ET AL. EXHIBIT 1019
Page 2142

Annex to Form PCT/ISA/206
COMMUNICATION RELATING TO THE RESULTS
OF THE PARTIAL INTERNATIONAL SEARCH

International Application No
PCT/US2014/019916

1. The present communication is an Annex to the invitation to pay additional fees (Form PCT/ISA/206). It shows the results of the international search established on the parts of the international application which relate to the invention first mentioned in claims Nos.:
see 'Invitation to pay additional fees'.
2. This communication is not the international search report which will be established according to Article 18 and Rule 43.

3. If the applicant does not pay any additional search fees, the information appearing in this communication will be considered as the result of the international search and will be included as such in the international search report.

4. If the applicant pays additional fees, the international search report will contain both the information appearing in this communication and the results of the international search on other parts of the international application for which such fees will have been paid.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YUANJING ZHENG ET AL: "Review of technologies for mercury removal from flue gas from cement production processes", PROGRESS IN ENERGY AND COMBUSTION SCIENCE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 38, no. 5, 26 April 2012 (2012-04-26) , pages 599-629, XP028415255, ISSN: 0360-1285, DOI: 10.1016/J.PECS.2012.05.001 [retrieved on 2012-05-25]	1-9, 16-25, 38,39, 48,49
Y	page 600, paragraph 1 page 615, paragraph 4.2.5.1 page 615, right-hand column, line 1 - line 4 "...by impregnation of nitrogen-containing polymers or pitches ..."; page 616, left-hand column 2nd paragraph; page 616, right-hand column page 622; figure 20 paragraph before 4.2.23; page 612, left-hand column	5-9, 16-25, 38,39, 48,49
X	DE 20 2012 003747 U1 (BLUECHER GMBH [DE]) 15 November 2012 (2012-11-15)	1-4
Y	claims 1, 25 paragraphs [0106], [0142], [0143]	5-9, 16-25, 38,39, 48,49

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

4

Form PCT/ISA/206 (Annex, first sheet) (July 1992; reprint January 2004)

Patent Family Annex

Information on patent family members

International Application No
PCT/US2014/019916

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 202012003747 U1	15-11-2012	DE 102012007392 A1	08-05-2013
		DE 202012003747 U1	15-11-2012
		WO 2013068060 A1	16-05-2013

Electronic Acknowledgement Receipt

EFS ID:	32667989
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
Filer Authorized By:	Jordan Rivard Golomb
Attorney Docket Number:	4820.001US9
Receipt Date:	18-MAY-2018
Filing Date:	
Time Stamp:	17:20:33
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Foreign Reference	0005_ca2584327a1.pdf	6083082 6e542d3a6e0461bc042423cc82aa0a857b5f5031	no	45

Warnings:

Information:					
2	Foreign Reference	0014_cn104619410b.pdf	6086694 6a6ba8e16c3bedd4977fa59f0955c6a57d3d6a44	no	34
Warnings:					
Information:					
3	Foreign Reference	0016_cn105188910a.pdf	701890 a7c8b7963ba1ab0356ce87282bfd166c5d2bf2ca	no	32
Warnings:					
Information:					
4	Foreign Reference	0017_cn107661744a.pdf	773323 3188e2617eb02e123909c81658bb8afb8cb6e70f	no	31
Warnings:					
Information:					
5	Foreign Reference	0021_de3816600a1.pdf	1520044 7fe37d80c7cfdf65ed2f115edc64d76029bfdab6	no	13
Warnings:					
Information:					
6	Foreign Reference	0023_ep1386655a1.pdf	2891160 22a19582bf4d1cd52b1e5a983f1697ec5b729f79	no	23
Warnings:					
Information:					
7	Foreign Reference	0024_ep1458474a1__espacenet_description.pdf	76346 2a8b1f3a6e6207630d9f75c7e4e9aefcdc0b603b	no	22
Warnings:					
Information:					
8	Foreign Reference	0032_jps50145324a.pdf	1398456 5ba601e59da903e378e6a35e1bc31058c4a597b7	no	9
Warnings:					
Information:					

9	Foreign Reference	0036_kr20027006149a.pdf	406096 b06ccb29ee93c1c8100a1cd88d0bd5a0ac54400e	no	15
Warnings:					
Information:					
10	Foreign Reference	0038_su732207a1.pdf	727306 6e94f35b66ba32716cc80f22c5e6d093e246b124	no	11
Warnings:					
Information:					
11	Foreign Reference	0045_wo2006039007a9.pdf	5793502 a0a59374ec9d5e0348384bedf9593c058358d677	no	42
Warnings:					
Information:					
12	Non Patent Literature	0126_3338021us1_cnoa_022717.pdf	273818 41541b12c4bf21559c463cd8525063e5d123d419	no	2
Warnings:					
Information:					
13	Non Patent Literature	0127_3338021us1_cnoa_032917.pdf	280726 11c4d54fc5268d73d78a9ebd211ca708e26e0cdb	no	2
Warnings:					
Information:					
14	Non Patent Literature	0130_pages_from_14195360oarmnonfinal_office_action_received20160620.pdf	1174774 2bd463f10b67194d831633595c436702bc77722b	no	11
Warnings:					
Information:					
15	Non Patent Literature	0137_3338005us6_adar_021717.pdf	597844 b294389deb6de67ff2d1309c995e732d86037cef	no	4
Warnings:					
Information:					

16	Non Patent Literature	0138_3338005us6_cnoa_052217.pdf	281053 cbe958de9371b8038861970 9b83ab8039da0703f	no	2
Warnings:					
Information:					
17	Non Patent Literature	0141_3338005us6_noar_051517.pdf	1217856 0f17716c26973d502e105a963f19b14497ccd6d6	no	8
Warnings:					
Information:					
18	Non Patent Literature	0147_3338016us2_foar_111716.pdf	462324 f697abb917eac88912c09c3af631ef70be61ab1c	no	4
Warnings:					
Information:					
19	Non Patent Literature	0148_3338016us2_oarn_071216.pdf	721717 b71a977c8af77ea4b7915bb574a074e51ede1eba	no	6
Warnings:					
Information:					
20	Non Patent Literature	0149_3338016us2_noar_013017.pdf	1001446 3bd6a233135986f7caeb711aadf0b66ccd2c3190	no	6
Warnings:					
Information:					
21	Non Patent Literature	0153_3338016us2_rerr_031616.pdf	617747 933f5235c8100badabe5d43d723e058ddd990a36	no	5
Warnings:					
Information:					
22	Non Patent Literature	0154_4820001us7_adar_021218.pdf	974674 7f0732a2bff33f278a4223c1196262a0070a9f15	no	8
Warnings:					
Information:					

23	Non Patent Literature	0155_4820001us7_exir_030518.pdf	290772 7b7feede8ce3e09ae27c3bf860cc99061b2cf709	no	3
Warnings:					
Information:					
24	Non Patent Literature	0156_4820001us7_foar_120617.pdf	1013589 a4746675f884dbddceb77e98b036e36a4fc46293	no	9
Warnings:					
Information:					
25	Non Patent Literature	0157_4820001us7_oarn_070617.pdf	775286 0dbdcf5d642cadaeb57c948d4b2fe0065f0ab65c	no	7
Warnings:					
Information:					
26	Non Patent Literature	0166_4820005us1_adar_04242018.pdf	392844 72756a3b2d0eb2eadc8ff6b3475e93e731e307f0	no	3
Warnings:					
Information:					
27	Non Patent Literature	0167_4820005us1_foar_021518.pdf	1325353 e276ff447552558 2d388e61f89264b33c96b88ae	no	13
Warnings:					
Information:					
28	Non Patent Literature	0168_4820005us1_oarn_092717.pdf	1793034 54ec81d4c344881e5fd00d4f6df19af5e864694d	no	17
Warnings:					
Information:					
29	Non Patent Literature	0173_4820003us2_oarn_022118.pdf	1546672 7c143c515d54c319b73a267c8790c7f4ed6fc4da	no	15
Warnings:					
Information:					

30	Non Patent Literature	0176_3338021wo1_p326_091715.pdf	1749339 cbc37e098d4d4a45b5571df71c571d9838ffe17b	no	14
Warnings:					
Information:					
31	Non Patent Literature	0191_4820006ca1_oarmisc_083117.pdf	311032 4f6a5c19c87fa1829334664614861 54e1224b1c4	no	4
Warnings:					
Information:					
32	Non Patent Literature	0193_3338016ca1_oarmisc_122216.pdf	1805782 617c36492c1081db114b2816a68bcd1255ad64c7	no	5
Warnings:					
Information:					
33	Non Patent Literature	0194_2871422aarmisc_022718_20180226.pdf	493492 d34437dc1d4cb8d0ad1c33100cfbd51dce99758b	no	53
Warnings:					
Information:					
34	Non Patent Literature	0195_2871422aarmisc20170621_response_as_filed_00406200 4220170621.pdf	2186747 81153d94d87b997d5dfdb9ff1a220309f6cbf749	no	41
Warnings:					
Information:					
35	Non Patent Literature	0198_cn_response_1_20_12.pdf	163517 50229b25801fc453111b2122ff04dcb86cb183c1	no	10
Warnings:					
Information:					
36	Non Patent Literature	0203_4820003cn1_oarmisc_071217.pdf	577839 cdac1873f2a92079499e2d31cec18300102 34aca	no	8
Warnings:					
Information:					

37	Non Patent Literature	0205_3338021cn1_oarmisc_122316.pdf	3071500 8f5068b30bc12c0d992aaacad89e1ae7a230412c	no	39
Warnings:					
Information:					
38	Non Patent Literature	0209_norit_darco_fgd_product_sheet.pdf	6905 be548c8109ed35cec0550d2137848eda3646bf31	no	2
Warnings:					
Information:					
39	Non Patent Literature	0250_4820006ep1_oarmisc_042417.pdf	655151 2b9e03b133bf38e0fc82729e4b9a4c3b39b32468	no	8
Warnings:					
Information:					
40	Non Patent Literature	0251_3338016ep1_oarmisc_051217.pdf	702332 39b5bae5aa81e1ab4863a0da719c11815f19655e	no	6
Warnings:					
Information:					
41	Non Patent Literature	0254_3338021ep1_e2001_022217.pdf	655001 edac181f6d36bc4e53fd3742fc08d343b75d3ca1	no	6
Warnings:					
Information:					
42	Non Patent Literature	0263_3338016wo1_p326_071714.pdf	1867110 8bba347872462fbd2c1e73f0991b005e716dbc15	no	11
Warnings:					
Information:					
43	Non Patent Literature	0264_3338016wo1_p210_112913.pdf	804642 37637610eba16727784b76d1f6773b68508ff926	no	7
Warnings:					
Information:					

44	Non Patent Literature	0265_3338016wo1_p206_080213.pdf	1096404 4f73a57f27cd6357dfa9a394f07baae27111b001	no	7
Warnings:					
Information:					
45	Non Patent Literature	0266_3338016wo1_p237_041514.pdf	1414324 e160735752cb93f61a7786d1374c27cc0ac3e7e5	no	10
Warnings:					
Information:					
46	Non Patent Literature	0267_3338016wo1_p237_112913.pdf	1600046 28c71f171eb9a09c60339d98f183a058d819189f	no	13
Warnings:					
Information:					
47	Non Patent Literature	0269_3338021wo1_p206_053014.pdf	967792 4937489a3d6398b410981a0de35931a4331a37dc	no	6
Warnings:					
Information:					
48	Non Patent Literature	0275_bakandritsos_2004.pdf	814947 035502ff6fb4f8ab61ba5532f297270cf24cb2eb	no	9
Warnings:					
Information:					
49	Non Patent Literature	0298_49_2_philadelphia_1004_1107.pdf	134177 e8184730499064e381ed9cbd22687aa220d71c91	no	2
Warnings:					
Information:					
50	Non Patent Literature	0300_nguyen_thanh_etal_2006.pdf	106723 b2ff02bf1068dee116770afd0c7b1a48eee83181	no	2
Warnings:					
Information:					

51	Non Patent Literature	0301_nguyen_thanh_bandosz_2006.pdf	1310722 428d7cdcf1e9189feeb0f2f2a83578fda8813cff	no	9
Warnings:					
Information:					
52	Non Patent Literature	0302_141953604.pdf	1783543 f5465935959639791d0e3136e3bdc5d7dc65f1ef	no	36
Warnings:					
Information:					
53	Non Patent Literature	0303_3338013us1_olson_reduction_111808.pdf	913696 ab983bce541533694b0c5cb4d7029df50e8078ac	no	13
Warnings:					
Information:					
54	Non Patent Literature	0304_olson_2000.pdf	6533383 7282bfdc61a421d64782fa37b70d0b946e8bf593	no	13
Warnings:					
Information:					
55	Non Patent Literature	0305_olson_etal_2005.pdf	2299530 c66722b1aa0049cd7b63085a858ddcfe2c0442a09	no	8
Warnings:					
Information:					
56	Non Patent Literature	0306_154491121.pdf	112331 352559e93fa23ad8349ead7121a9ef3b1770302e	no	1
Warnings:					
Information:					
57	Non Patent Literature	0307_15449112.pdf	68265 626d47152bb32cf977974bff269f4fd2ff9f5adf	no	1
Warnings:					
Information:					

58	Non Patent Literature	0308_141953603.pdf	577480 2c7ffe87145df8ba2fd42b6e0b97fbde1dc4342e	no	7
Warnings:					
Information:					
59	Non Patent Literature	0309_14195360_structural_characterization_of__n_taining.pdf	888482 abaf1f1d6e2569eeaf69f60cf4cb8752a7cac772	no	12
Warnings:					
Information:					
60	Non Patent Literature	0310_alternatives_to_activated_carbon_for_mercury_trol__power_engineering.pdf	2034520 8261e45c38a75b88de4bc9459a7aeccde5cdf11a	no	10
Warnings:					
Information:					
		Total Files Size (in bytes):	78906182		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

Patent Translate
Powered by EPO and Google

Notice

This translation is machine-generated. It cannot be guaranteed that it is intelligible, accurate, complete, reliable or fit for specific purposes. Critical decisions, such as commercially relevant or financial decisions, should not be based on machine-translation output.

ABSTRACT DE202012003747

Nitrogen-Modified and / or stickstofffunktionalisierte activated carbon, in particular with catalytic and / or reactive properties, preferably activated carbon with nitrogen as the catalytically active hetero atom, obtainable by a process, in which method, an activated carbon used as the starting material ("output active carbon"), first a surface oxidation using and / or in the presence of at least one oxidizing reagent ("OR") is subjected, and the thus obtained, on the surface of oxidized activated carbon following a gear, in particular modification and / or functionalization to nitrogen, especially with nitrogen-containing functional groups, using, and / or in the presence of at least one Stickstoffmodifizierungsreagenzes ("SMR") is subjected.

Europäisches Patentamt
European Patent Office
Office européen des brevets

Patent Translate
Powered by EPO and Google

Notice

This translation is machine-generated. It cannot be guaranteed that it is intelligible, accurate, complete, reliable or fit for specific purposes. Critical decisions, such as commercially relevant or financial decisions, should not be based on machine-translation output.

DESCRIPTION DE202012003747

[0001]

The present invention relates to the technical field of adsorptive materials based on activated carbon, which in particular catalytic and / or reactive properties, and in particular a nitrogen base modification and / or Stickstofffunktionalisierung, preferably using nitrogen as the catalytically active heteroatom having.

[0002]

In particular, the present invention relates to a nitrogen-modified and / or stickstofffunktionalisierte activated carbon, in particular with catalytic and / or reactive properties, preferably an activated carbon with catalytically active nitrogen as hetero atom, which is obtainable by a method for their preparation.

[0003]

Furthermore, the present invention relates to protective materials, which are prepared using the activated carbon according to the invention and having the activated carbon according to the invention.

[0004]

Moreover, the present invention also relates to filters or

Filter materials that are prepared using the activated carbon according to the invention and having the activated carbon according to the invention.

[0005]

Activated carbon is the most widely used adsorbent fairly unspecific adsorptive properties.

Legal requirements, but also to the rising awareness of environmental responsibility, leading to a growing demand for activated carbon.

[0006]

Activated carbon is generally obtained by carbonization (also referred to synonymously as smoldering, pyrolysis, burn, etc.) and subsequent activation of carbonaceous starting materials.

The nature of the activated carbon produced - finely or coarsely porous, firm or brittle, finely divided or granular shaped, etc. - depends on the particular starting material - in addition to the process conditions for the carbonization and activation.

Customary starting materials are especially coconut shells, charcoal and wood (eg.

As wood waste), peat, bituminous coal, pitches, but also particular plastics or organic polymers, which play a certain part in the production of activated carbon fabrics.

For further details on the activated carbon production may be particularly referred to H. v.

Kienle and E. baths, "activated carbon and its industrial application", Enke Verlag Stuttgart., 1980

[0007]

Activated carbon is used in various forms: pulverized carbon, splint coal or

Grain, molded carbon and since the late 1970s, spherical activated carbon ("carbon spherules").

Spherical activated carbon has over other forms of activated carbon, such as powder, shaifer, grain and form carbon and the like, a number of benefits, they useful or even indispensable makes for certain applications: it is free flowing, abrasion-resistant and dust-free and hard.

Spherocarbon is in high demand because of their particular shape, but also because of high abrasion resistance, for example, for special applications.

[0008]

Spherocarbon is still mostly produced by multistage and very costly process.

The most common method consists in producing spherules from coal tar pitch and suitable asphaltic residues from the petrochemical industry, which is oxidized - thus they are infusible - and smouldered and subsequently activated.

For example, can be produced from bitumen spherocarbon also in a multistage process starting.

These multistage processes are very cost-intensive, and the associated high cost of these carbon spherules prevents many applications where spherocarbon would have to be due to their characteristics actually preferred.

[0009]

In WO 98/07655 A1 a process for producing activated carbon beads is described in which first a mixture, which is processed into free-flowing beads one derived from the diisocyanate production distillation residue, a carbon-containing processing aid and optionally comprises one or more further additives, and then the carbonized beads obtained in this manner and are then activated.

[0010]

Known from the prior art is also the production of spherical carbon by carbonization and subsequent activation of new or used ion exchangers containing sulfonic acid groups, or by smoldering ion exchanger precursors in the presence of sulfuric acid and subsequent activation, the sulfonic acid or sulfuric acid function have a cross-linker.

Such methods are described for example in DE 43 28 219 A1 and DE 43 04 026 A1 and DE 196 00 237 A1 including the German additional application DE 196 25 069 A1.

[0011]

Furthermore, methods are known from the prior art in which the production of activated carbon, in particular carbon spherules, sulfonated by carbonization and subsequent activation divinylbenzolvernetzter polystyrenes (ie, sulfonated styrene (divinylbenzene copolymers) is carried out (see. Eg.

B. DE 10 2007 050 971 A1).

[0012]

For special applications, however, is not only the geometry or outer shape of the activated carbon is of crucial importance but also the porosity thereof, in particular the total pore volume, and the adsorption capacity of one hand, and the distribution of the

pores, ie, the proportion of micro-, meso- and macro-pores in relative to the total pore volume, on the other hand; in particular, the porosity can be selectively controlled by the selection of raw materials and the process conditions.

In the present invention, the term of the micropores refer to those pores with pore diameters of less than 2 nm, whereas the term of the mesopores (ie 2 nm inclusive) designates such pores having pore diameters in the range of 2 nm to 50 nm inclusive, and the term of the macropores refers to those pores having pore diameters greater than 50 nm (ie,> 50 nm).

[0013]

Because of their good adsorptive properties is activated carbon for a variety of applications: For example, activated carbon is used in medicine or pharmacy, but also in the food industry.

For filtering applications found charcoal far-reaching applications (eg.

B. filtration of gases and liquids, removal of unwanted or harmful or toxic gases, etc.).

[0014]

In particular, activated carbon adsorption filter, in particular, especially in protective materials to poisons such as chemical and biological warfare agents, such as NBC protective clothing, are used.

To this end, in particular air and water vapor permeable protective suits against chemical warfare agents are known; Such air and water vapor permeable protective suits often have an adsorption filter layer with activated carbon, which adsorb the chemical poisons.

[0015]

To increase the adsorption performance of activated carbon is often equipped with a catalytically active or reactive component by the activated carbon, for example, with a biocide or biostatic acting catalyst, in particular based on metals or metal compounds, impregnated.

Such activated carbon can particularly be used in insulation materials, such as are described for example in DE 195 19 869 A1, which includes a multi-ply, textile, gas-permeable filter material having an adsorption layer based on activated carbon, in particular in the form of carbonized fibers, which is provided with a catalyst from the group of copper, cadmium, platinum, palladium, mercury and zinc in amounts of 0.05 to 12 wt .-%, based on the activated carbon material impregnated.

[0016]

A special, coming in this context to use impregnation is for example a so-called ABEK-impregnation, which is opposed to specific toxic substances having a catalytic or degrading effect.

In this connection, type A refers to certain organic gases and vapors with a boiling point> 65 ° C, for example, cyclohexane.

Type B refers to certain inorganic gases and vapors, such as hydrogen cyanide.

Type E refers to a degrading or protective effect against sulfur dioxide and other acidic gases and vapors.

Type K finally refers to a protective function against ammonia and organic ammonia derivatives.

For further information, reference may be made to the relevant European Standard EN 14387 (January 2004).

[0017]

A disadvantage of conventional impregnation of activated carbon with metals or

Metal salts is in particular the fact that by impregnating a part of the adsorption capacity of the activated carbon, which is required for the adsorption and thus for the neutralization of chemical pollutants is lost.

By impregnation processes known from the prior art, the activated carbon with metals or

Metal salts thus the performance of the activated carbon is adversely affected.

Furthermore, it is not always achieved by a conventional impregnation, the desired efficacy.

PAC ET AL. EXHIBIT 1019

Also the problem of strike through of toxic or

Warfare agents at high concentrations is not always solved by this principle; on the other hand at very low concentrations (for example to remove contaminants or to interfering gases.

Example, in the air conditioning for clean room conditions) does not often reach the desired efficiency, since an adsorption begins only at higher concentrations.

Finally, the conventional impregnation process required with metals or

Metal salts, relatively large amounts of impregnating material, since a large part of the present as a solid impregnating material is not in the adsorption available, especially not if thicker layers of impregnating material in the pore system of the activated carbon, in particular in the form of crystallites are present.

[0018]

Another disadvantage of the equipment of active carbon with metals or

Metal salts is that conventional activated carbon is formed non-polar or hydrophobic on its surface and in particular has no significant affinity for the impregnating agents used, which are used for the reactive or catalytic equipment of active carbon.

As a result, a large excess of impregnating agents must be used in order to ensure at all a certain amount of loading of the activated carbon.

The impregnating generally adhere only on purely physical interactions and may be undesirably removed at least to a predominant part again in contact with liquids.

[0019]

Moreover, it is in the prior art especially with regard to the adsorption of acidic gases such as sulfur dioxide and the like, provided a subsequent impregnation of the activated carbon with especially basic nitrogen-containing Imprägnierreagenzien, in particular amines perform.

They embark on equally the above-described disadvantages, particularly as regards the use of a large excess of impregnating, the poor durability of the impregnation and the clogging of the pore system of the activated carbon.

[0020]

Moreover, it was also tried in the prior art, an equipment or

To realize impregnation based on the nitrogen-containing Imprägnierreagenzien insofar as the Imprägnierreagenz as part of the manufacturing process of the activated carbon, in particular in the activation, is added to the substrate to be treated.

In this regard, in the prior art ammonia and

NH_3 used as appropriate Imprägnierreagenz, particularly in the form of ammonia water.

However, the underlying approach, according to which namely Imprägnierreagenz during the activation process and is therefore added as such during the preparation of activated carbon is especially disadvantageous that needs to be worked on Imprägnierreagenz with a large excess, since a majority of the Imprägnierreagenes not for actual impregnation is used, but rather is part of the activation process.

Furthermore, with this approach is disadvantageous in that the actual impregnation may be only poorly controlled since the addition of Imprägnierreagenzes takes place in the context of actual activation, in which namely the same time is also an erosion of the activated carbon, which of a homogeneous loading of the activated carbon with high amounts Imprägnierungsreagenz is detrimental.

In this context it is also necessary to state that the presence of Imprägnierungsreagenzes equally controlled and precisely reproducible implementation of the activation process difficult or impossible, especially as regards the formation of a defined pore structure and the like.

Furthermore, it is not with respect to the previously described procedure with the addition of Imprägnierreagenzes sealing agent during the activation process possible chemical bonding or

To achieve integration of the nitrogen component of the activated carbon skeleton, in particular because the underlying active carbon substrate is non-polar or hydrophobic in terms of its surface texture, corresponding to a contacting or an interaction with the Impragnierreagenz is detrimental.

Based on this procedure, it is thus the result is not possible to enable effective impregnation with a catalytically active component, because both the equipment with the underlying reactive component either is continuous or in large quantities or homogeneous and moreover at the same time the activation process as Such is adversely affected.

[0021]

It is therefore an object of the present invention to provide adsorptive materials with reactive and / or catalytic properties in the form of activated carbon, the above-described disadvantages of the prior art should be at least largely avoided or at least mitigated.

[0022]

In particular, should be provided in the context of the present invention, an activated carbon having a reactive or catalytic equipment based on nitrogen as catalytically active hetero atom and which are particularly suitable for adsorption or

Neutralization of acidic pollutants and in particular

Noxious gases is, the present invention provided the activated carbon should be compared with the prior art and, in particular improved BEYOND should also have chemisorptive properties.

In particular, an efficient method must be within the scope of the present invention can be used which enables the provision of an active carbon which is equipped in an efficient manner with a reactive or catalytically active component in the form of nitrogen, which is to be ensured at the same time that the underlying equipment with the catalytically active component is permanent and results in excellent reactive or catalytic properties of the resulting activated carbon.

[0023]

As the applicant has now been found in a completely surprising manner, the previously mentioned and the present object underlying the invention in any unexpected way be achieved in that in the present invention, a nitrogen-modified or stickstofffunktionalisierte activated carbon is provided which is obtainable by a process after which activated carbon is used as such as a raw material, which ("OR") surface oxidation is first subjected to a surface oxidation using at least one oxidizing reagent and that the activated carbon thus obtained, oxidized on its surface below an equipment with nitrogen or with nitrogen-containing functional groups using at least one Stickstoffmodifizierungsreagenzes ("SMR") is subjected.

[0024]

To achieve the above-described object, the present invention thus proposes - in accordance with a first aspect of the present invention - the invention nitrogen-modified or stickstofffunktionalisierte activated carbon, especially with catalytic or reactive properties, preferably an activated carbon with nitrogen as catalytically active heteroatom, which by a process is provided for their preparation, according to claim 1..

Further, particularly advantageous embodiments of the present invention carried out method are the subject of the respective dependent claims.

[0025]

Another object of the present invention - according to a second aspect of the present invention - is the nitrogen-modified or stickstofffunktionalisierte activated carbon according to the invention, which in particular catalytic or reactive properties and which is preferably nitrogen comprises as catalytically active heteroatom, according to this respect independent claims.

Further, particularly advantageous embodiments of the activated carbon according to the invention are subject of the respective dependent claims.

[0026]

PAC ET AL. EXHIBIT 1019

In addition, another object of the present invention - according to a third aspect of the present invention - the protective materials according to the invention, in particular for the civil or military sector, in particular protective clothing, according to the independent claim in this regard.

[0027]

Finally, another object of the invention - in accordance with a fourth aspect of the present invention - filters and filter materials, in particular for the removal of pollutants, odors and toxins of all kinds, according to independent claim in question.

[0028]

It goes without saying that in the following description of the present invention include those embodiments, embodiments, advantages, examples or the like, which subsequently - be carried out on a single aspect of the invention, of course, also in terms remaining on the - for the purpose of avoiding unnecessary repetition aspects of the invention apply mutatis mutandis, without the requirement of an explicit mention.

[0029]

Furthermore, it goes without saying that with the following details of values, numbers and areas in this respect of values, numbers and ranges are not limiting; It should be understood by those skilled saying that single case or application based on the specified areas or

Information may be waived, without the context of the present invention is to leave.

[0030]

In addition, is that all of values listed below or

Parameter information or the like basically with standardized or standardized or explicitly indicated methods of determination or otherwise with the person skilled in the art is familiar per se destination or

Can be calculated or determined measurement methods.

[0031]

In other respects, that is to be observed in all the following relative or percentage, especially weight-related quantitative data, that this information in the context of the present invention by those skilled select such or to combine that in the sum - optionally with the inclusion of additional components or.

Ingredients, in particular as defined below - always 100% and

100 wt .-% result.

This is obvious to the skilled person but from itself.

[0032]

That said, in the following, the present invention will be described in more detail:

According to a first aspect of the present invention, the present invention relates to a nitrogen-modified or stickstofffunktionalisierte activated carbon which is obtainable by a process for the preparation thereof, wherein the activated carbon produced by the method used in the invention comprises catalytic or reactive properties.

When activated carbon produced by the method employed in this invention, in particular an activated carbon with nitrogen as catalytically active heteroatom.

The inventively performed process is distinguished by the fact that one used as starting material activated carbon ("output activated carbon") is first subjected to a surface oxidation using or in the presence of at least one oxidizing reagent ("OR") and oxidized on its surface obtained in this way activated carbon ("intermediate") below a gear, in particular modification or

Functionalization, is subjected to nitrogen, especially with nitrogen-containing functional groups, using or in the presence of at least one Stickstoffmodifizierungsreagenzes ("SMR").

[0033]

As indicated above, the basic idea of the present invention is therefore to provide an activated carbon based on a method, based on which it is possible to modify an activated carbon as a starting material in an optimized manner with nitrogen or to functionalize with nitrogen active as catalytically hetero atom acts and nitrogen being especially coupled in a controlled manner to the surface structure of the activated carbon used or chemically bonded or permanently immobilized in the form of nitrogen-containing functional groups on the one hand, or the manner of a doping with nitrogen or an N-type doping under integration or

Recessed in the carbon skeleton of the activated carbon (ie, immobilization or

Inclusion of the nitrogen in or on the carbon skeleton of the final product) on the other.

[0034]

In this context, it is quite surprising in the context of the present invention that by the actual nitrogen fixation or modification upstream surface oxidation of the activated carbon used as the starting material a significant improvement in nitrogen or modification

Stickstofffunktionalisierung the activated carbon is achieved.

Without wishing to limit or define in this theory, it is through the targeted and purposeful oxidation of the surface of the activated carbon used using specific oxidation reagents ("OR"), the surface structure of the activated carbon with respect to the modification or

Functionalization with nitrogen insofar optimized created as to a hydrophilic structures or the hydrophilicity of the activated carbon is increased as such, which improves the interaction with the Stickstoffmodifizierungsreagenz ("SMR").

Secondly, in particular those functional chemical groups are created by the selective oxidation of the surface of the activated carbon, which are the Stickstoffmodifizierungsreagenz ("SMR") to interact in particular with the formation of chemical bonds or to respond capable what the chemical bond or

Improved integration of nitrogen with respect to the activated carbon or permits.

Based on the present invention carried out the oxidation in terms of a pre-treatment of the activated carbon, the affinity of the activated carbon is to Stickstoffmodifizierungsreagenz ("SMR") increases.

[0035]

As will be described in detail, it is possible due to the specific process version, the resulting nitrogen-modified or stickstofffunktionalisierte charcoal or equipped with nitrogen activated carbon customize or tailor what both at the level of oxidation of the (initial) activated charcoal as well in view of the subsequent nitrogen modification is possible, as a result, on the basis of the inventive method performed activated carbons are provided which are accessible to a wide range of applications in total or in particular for the adsorption or

Rendering harmless of specific toxic substances are optimized.

[0036]

Another key advantage of the present invention conducted process management can be seen in the fact that a variety of commercially available or commercially available activated carbons as the raw material for the inventively provided guidance or procedures

Modification can be used, so that the inventively performed process can be universally used with regard to the starting materials based on activated carbon, for example, with variable porosity or the like, so to speak.

Due to the modification or downstream, so to speak

Equipment with nitrogen are not affected under the activated carbon production as such present processes such as carbonization and activation.

[0037]

Due to the inventively realized process control with the functionalization of the activated carbon with nitrogen-containing functional groups or with the targeted integration of nitrogen in the carbon surface or in the framework of the activated carbon special nitrogen-modified or stickstofffunktionalisierte activated carbons thus be obtained, which has a catalytic activity or

Reactivity and thus chemisorptive properties against different substances, particularly toxic gaseous substances exhibit.

In this regard, the obtained by the method according to the invention carried out nitrogen or nitrogen-functionalized modified activated carbons on a high suitability for the particular catalytic or reactive degradation of various toxic gases.

This may be, for example, and in non-limiting manner to so-called Chemical Warfare Agents (CWAs), Toxic Industrial Materials (TIMs) such as larger molecules, such as ethylene oxide or the like to Toxic Industrial Chemicals (TICs), such as NH3, SO2, H2S, Cl2, HCl or the like, act.

In particular, the stickstofffunktionalisierte or nitrogen-modified activated carbon or nitrogen equipped with activated carbon obtained by the present invention carried out method is suitable for the adsorption or

Neutralization of particular acidic toxic gases such as H2S, SO2 or

HCl.

[0038]

Without wishing to restrict or specify to this theory, is in particular a reduction of such toxic gases or even

Noxious gases through an oxidation on the carbon surface of the modified activated carbon possible, as it is possible, for example, in non-limiting manner for SO2, H2S, AsH3 and DMS.

This is particularly the case when the nitrogen, as previously described, is integrated or incorporated into the carbon skeleton of the inventively modified activated carbon in the manner of an N-type impurity, that is, the nitrogen is immobilized, so to speak, in particular by chemical and / or covalent binding in the carbon skeleton of the inventively modified activated carbon.

[0039]

Moreover, the available based on the method employed in this invention nitrogen or modified stickstofffunktionalisierte activated carbon - to equally without intending to be limited or defined in this theory - a catalytic activity or reactive properties against such toxic substances or

Gases, which are to react with the formed nitrogen-containing functional groups on the surface of the modified activated carbon according to the invention capable of for example formaldehyde and NOx compounds.

[0040]

An activated carbon is based on the present invention underlying concept with the specific equipment of activated carbon with nitrogen thus in a completely surprising manner provided by the invention which of excellent properties in terms of (chemicals) sorption or the catalytic and / or reactive degradation different pollutants and toxic gases, such as chemical toxicant or

Warfare agents, has.

For example, the resultant treated activated carbon is also suitable for the particular oxidative degradation of particular sulfur-containing components.

Similarly, the activated carbons thus obtained can through a purposeful optimization of related equipment for broadband applications, for example in the context of respiratory protection applications, are used.

In this context, a use in ABEK-Filter comes, especially in combination with other adsorbents into consideration.

[0041]

In general, the activated carbon of the invention is, for example, to gas adsorption and more particularly to the adsorption of sulfur containing gases (such as sulfur oxides and / or hydrogen sulfide), nitrogen-containing gases (such as nitrogen oxides and / or nitrogen hydrogens, such as ammonia) and by halogen-containing gases (such as hydrogen chloride gas).

Similarly, the activated carbon of the invention is also to adsorb organic based harmful substances such as formaldehyde, or the like.

In particular, the activated carbon of the invention has particularly good properties in respect of the sorption, particularly physisorption and / or chemisorption of sulfur and nitrogen oxides, hydrogen halides, cyanogen, hydrogen cyanide, hydrogen sulfide, chlorine gas, arsine and / or ammonia.

[0042]

Due to the inventive design of the method according to the invention used with it were upstream surface oxidation or surface oxidation downstream equipment with nitrogen, the activated carbon to be treated as a starting material is a particularly homogeneous or uniform and equipment

Canister load - in particular over the entire pore spectrum - to be incorporated with the.

Achieved nitrogen because the Stickstoffmodifizierungsreagenz ("SMR") may very well penetrate into the pore system and there or due to the upstream oxidation with the high affinity of the reaction parameters to each other, a uniform loading of the activated carbon to form nitrogen-functional groups or integration

Immobilization of nitrogen ensured in the carbon skeleton.

[0043]

The inventively performed process distinguishes itself by a somewhat two-stage process procedure from which namely first conventional activated carbon is subjected as the starting material to surface oxidation and subsequently the activated carbon thus obtained, oxidised at their surface below in purposeful manner using a Stickstoffmodifizierungsreagenzes ("SMR") with Nitrogen is equipped, on the basis of nitrogen-containing functional groups and / or based on the incorporation and the incorporation of nitrogen in terms of a nitrogen dopant (N-type impurity) in the carbon skeleton, in particular in the material forming the outer and inner surface of the carbon skeleton.

[0044]

In this context, it is according to the invention also completely surprising that the pore system of the activated carbon used as the starting material is at least substantially not affected by the equipment with the nitrogen.

In other words, it is ensured according to the invention that the pore system of the activated carbon is not or at least substantially not adversely affected in terms of the adsorption of pollutants.

The available based on the inventively performed process activated carbon thus has even after equipment or

Functionalization with nitrogen for.

B. high, the adsorption of pollutants accessible BET surface area, so that the basic properties of the activated carbon are retained as such even when fitted with nitrogen, which could not be foreseen.

Thus, the procedure of the invention, in contrast to the known prior art impregnation with the associated advantage that no loss of specific surface or

Total pore volume is present and also the pore structure is, as such, does not change at least substantially in terms of their distribution in the form of micro-, meso- and macropores.

[0045]

In this regard, it was completely surprising in the context of the present invention that by the targeted equipment of activated carbon with nitrogen - in fundamental contrast to the methods of the prior art - does not lead to clogging of the pore system, because the nitrogen component permanently to form chemical bonds in the carbon structure the activated carbon is integrated, either on the basis of nitrogen-functional groups or integration into the carbon matrix of the treated or modified activated carbon.

In particular, a crystallization or a crystallization within the pore system is prevented due to the inventively realized lawsuit, the performance of the activated carbon according to the invention further improved.

Herein also can be seen a significant difference to the impregnation method known in the art, in which micro-porous activated carbon particular leads to an occurrence of clogging with respect to the pore structure of the activated carbon.

[0046]

Due to the specific equipment of the activated carbon with nitrogen as the catalytically active heteroatom the activated carbon produced by the invention process carried out as indicated above has, so to speak, a reactive or catalytic surface in addition to the chemisorptive and / or physisorptive properties of the activated carbon as such on.

Accordingly, the obtainable with the present invention conducted processes activated carbon combines chemisorptive as physisorptive properties in a single material and is thus capable of sorbates or to be sorbed substances - in contrast to non-catalytic or non-reactive activated carbon - also reliably and irreversibly and retain suitably or degrade.

[0047]

Also, by particularly homogeneous and uniform equipment of activated carbon obtainable by the invention process carried out with the nitrogen component of the performance of the thus obtained nitrogen-modified or nitrogen-functionalized activated carbon is increased in view of the sorption, and the reduction to be removed substances again especially as the so available activated carbon based on reactive or catalytic properties on the other hand has a certain extent over a large part of its surface on the combined characteristics of physisorption on the one hand and the chemisorption, which is also amplify about the sum of the individual measures, which are regarded as evidence of the existence of a synergistic effect needs.

[0048]

In the present invention, an efficient method is therefore used, which leads to an optimized adsorption system with the combined and complementary characteristics of physisorption and chemisorption on the one hand on the other.

[0049]

As indicated above, according to the invention results in a functionalized activated carbon, which in contrast to the prior art, however, at least substantially no significant adverse effect on other physicochemical parameters, such as porosity, pore volume, pore distribution and the like.

[0050]

In the present invention, it is also completely surprising that activated carbon as such at all or in an effective way with regard to the inventively provided nitrogen modification

Stickstofffunktionalisierung suitable.

For thus activated carbon has hydrophobic properties such fundamentally what an efficient treatment or

Interaction with the Stickstoffmodifizierungsreagenz ("SMR") for the formation of functional groups or to integrate nitrogen is generally detrimental.

In particular, however, it is due to the particular invention conducted procedure with the purposeful upstream surface oxidation of the activated carbon used as the starting material managed in a completely surprising and unforeseeable manner, the compatibility of activated carbon on the one hand and Stickstoffmodifizierungsreagenz ("SMR") to increase the other hand, activated carbon as such in effective way to functionalize with nitrogen or modified, which leads to the above mentioned positive characteristics with respect to sorption of pollutants.

[0051]

In summary, the inventively realized process management characterized thus by the fact that a specially modified with nitrogen or functionalized activated carbon is obtained, which has based on a combination of physical adsorption and chemisorption excellent adsorption properties.

In particular, occurs in conventional activated carbon, for example.

B. frequently occurring in fatigue or excessive loading or release

Absorption already sorbed substances in the inventive activated carbon is not or not to any significant extent.

Due to the inventive concept of providing an activated carbon, which in addition to its inherent adsorptive properties equally reactive or catalytic properties, a durable and generally irreversible binding or an efficient degradation of sorbed substances ensures that equally as those at issue in decreased desorption substances and leads to an increase of the total adsorption capacity.

Due to the solid chemical bonding of nitrogen to the carbon structure also exists a permanent and stable modification of activated carbon with nitrogen.

In particular, the permanently immobilized nitrogen can not be removed by washing or the like again by the activated carbon.

[0052]

According to the invention, the method used further are collectively so far characterized, as initially under the procedures implementing an output activated carbon or a Basisadsorbens a chemical or thermal oxidation to obtain an oxidized on the surface of activated carbon (oxidized Basisadsorbens) is subjected, the intermediate thus obtained below is modified or functionalized, or in a subsequent step, the oxidation or in a separate step with nitrogen.

For this purpose, the oxidative intermediate with the Stickstoffmodifizierungsreagenz ("SMR") is first brought into contact, for example using a urea solution, wherein the oxidative intermediate as part of a dipping method or the like with the Stickstoffmodifizierungsreagenz ("SMR") are brought into contact in such a case, can.

Similarly, a contacting is also within the scope of an air stream, for example using ammonia (NH3) or the like, is possible.

This is followed by an appropriate thermal treatment for the formation of nitrogenous functionalization or to dope the carbon skeleton with nitrogen (ie, for the immobilization of nitrogen).

[0053]

As regards the term "surface oxidation", as used in the present invention, so here under particular oxidation of such surfaces of the activated carbon used as the starting material to understand which are in contact with the particular Oberflächenreagenz ("OR") containing environment, or which as it were from the outside for the inventively used oxidizing reagent ("OR") are accessible.

This is in particular also to the pore system of the activated carbon based on macro, meso and micropores.

[0054]

Without wishing to restrict or specify to this theory, based on results of the inventively realized process control to a certain extent an oxidized layer with respect to the activated carbon, which generally has the following still listed oxygen-containing functional groups.

The the surface oxidation occurs subsequent equipment with the nitrogen then - to equally without intending to be limited or defined in this theory - particularly in the oxidized (border) layer, wherein the oxygen-containing functional groups as a kind of Eindungs- or

Anchor points or

Reactants for the inventively used Stickstoffmodifizierungsreagenz ("SMR") act.

[0055]

Thus, activated carbons are generated with reactive or catalytically active surfaces through which the oxidation subsequent equipment of the activated carbon within the process carried out with nitrogen as catalytically active heteroatom.

[0056]

Next, regarding the method according to the invention carried out, it can be provided that the surface oxidation is carried out to form a hydrophilic surface of the activated carbon.

According to the invention it is equally possible that the surface oxidation leads to the formation of oxygen-containing functional groups at the surface of the activated carbon.

In this regard, the oxygen-containing functional groups may be selected from acidic and basic oxygen-containing functional groups and combinations thereof, in particular, acidic and basic surface oxides.

In particular, the oxygen-containing functional groups may be selected from the group of hydroxyl, carboxyl, carbonyl, anhydride, lactone, quinone, pyrone, chromene and ether groups, and combinations thereof.

Such groups are suitable in a special way to interact with the Stickstoffmodifizierungsreagenz ("SMR").

[0057]

As indicated above, lead to the surface of activated carbon in particular by reaction of oxidizing reagent ("OR") with the activated carbon used as the starting material ("output activated carbon") resulting oxygen-containing functional groups to increase the hydrophilicity or the hydrophilic properties of the treated activated carbon , which interact with the Stickstoffmodifizierungsreagenz used below ("SMR") and improved in a corresponding manner to an improved functionalization or

Modification of the activated carbon with nitrogen leads.

In particular, the generated in this manner the oxygen-containing functional groups, as reaction partners for the Stickstoffmodifizierungsreagenz ("SMR") can act so as to chemical bonding or implementation or

To improve integration of nitrogen in the activated carbon to be modified or permit.

The inventively performed and upstream surface oxidation thus serves in a sense to prepare for the subsequent nitrogen modification or functionalization of the activated carbon.

In this connection, in particular also the surface hydrophilicity of the carbon skeleton, the activated carbon increases to be treated by the surface oxidation according to the invention realized, resulting in the foregoing advantages.

[0058]

Next, regarding the present invention process carried out, it can be adjusted by the purposeful surface oxidation and the pH-value, in particular the surface pH value of the oxidized at its surface activated charcoal, as compared to the starting active carbon at a value of at least 0 , 25, especially at least 0.5, preferably at least 0.75, preferably at least 1, more preferably at least 1.5, changed.

In particular, it can be provided that the acidity of the oxidized at its surface activated carbon is increased and / or the pH-value, in particular the surface pH value is reduced to its surface oxidized activated carbon by carried out the oxidation of the active carbon, in particular a value of at least 0.25, especially at least 0.5, preferably at least 0.75, preferably at least 1, more preferably at least 1.5, or that increased by the oxidation of the activated carbon made the basicity of the activated carbon oxidized on their surface and / or the pH-value, in particular the surface pH value is increased at the surface thereof oxidized activated carbon, in particular to a value of at least 0.25, especially at least 0.5, preferably at least 0.75, preferably at least 1, more preferably at least 1.5.

By purposeful adjustment of the pH value on the basis of the present invention to be carried out surface oxidation of the starting activated carbon can, in particular the affinity to used below Stickstoffmodifizierungsreagenz ("SMR") will be further optimized, which are available to an even further increase in efficiency in terms of equipment on the basis of the inventive method performed activated carbon with nitrogen leads.

Particularly when using output activated carbons with a relatively high pH or alkalinity output activated carbons results in an induced surface oxidation reducing the surface pH value.

[0059]

According to the invention it can also be provided that the surface oxidation is carried out in such a way that the activated carbon obtained in this manner, oxidized at its surface has a content of oxygen-containing functional groups, calculated and / or

expressed as a volatile content ("FB") and to the on the dry weight of the oxidized at its surface activated charcoal, wt .-% of at least 1, especially at least 2 wt .-%, preferably at least 3 wt .-%, preferably at least 4 wt .-%, and / or in the range of 1 wt .-% to 30 wt .-%, in particular 1.5 wt .-% to 25 wt .-%, preferably wt .-% 2 to 20 wt .-%, preferably 3 wt .-% to 15 wt .-% having.

[0060]

In this context, can be set in the context of the present invention implemented process management, the content of oxygen-containing functional groups, for example, by appropriate selection of the temperature and / or time period and / or type and / or concentration of oxidizer ("OR").

In this way can be carried out in particular with regard to the following Stickstofffunktionalisierung a tailoring or modification of the oxidation process.

In the context of the present invention implemented process management is thus the oxygen content of the oxidized on the surface of activated carbon compared to the starting activated carbon employed - which is generally related an oxygen content of less than 1 wt .-%, expressed as a quantity of volatile substances ("FB") and on the dry weight of the starting activated carbon, which - significantly increased.

[0061]

The volatiles content ("FB") acts generally as a measure of oxidation, and particularly relates to formed by the oxidation of surface oxides.

In particular, the quantity of volatile substances on the basis of ISO 562: are determined 1981st

In particular, the volatile content ("FB") to the previously dried, oxidized on the surface of activated carbon at an appropriate heating for a period of 7 minutes 900 ° C can be determined under inert conditions.

[0062]

By adjusting the content of oxygen-containing functional groups can also be installed below the amount of nitrogen to be determined or influenced in particular by an appropriate setting of the number of reactants.

The recorded amount of nitrogen according to the invention provided nitrogen or nitrogen-functionalized modified activated carbon thus correlated with the content or the amount of surface oxides or with the volatile constituents of the oxidized base in the form of oxidized on the surface of activated carbon.

[0063]

As to the oxidizing reagent used in the context of surface oxidation ("OR"), then this may include a variety of reagents, or

Compounds.

Basically, while the oxidation process is carried out, as described below, for a defined period of time especially under heat or

Influence of temperature.

[0064]

In general, the oxidation reagent ("OR") can be selected from the group consisting of oxygen, ozone, inorganic or organic oxides and peroxides, as well as inorganic or organic acids and peracids and combinations thereof.

In accordance with the invention preferably, the oxidizer is selected from the group consisting of oxygen, hydrogen peroxide (H_2O_2), nitric acid (HNO_3) and ammonium ($(NH_4)_2S_2O_8$) and combinations thereof.

In the context of the present invention is in particular in the use of oxygen which can be fed to be oxidized activated carbon, in particular in the form of atmospheric air, even speak of a so-called thermal oxidation, since this takes place usually by heating, whereas when using the other oxidation reagents, especially of H_2O_2 or

HNO_3 according to the invention is generally spoken of a chemical oxidation, no additional heat is in this case depending on the reagent used sometimes required, although this may also be performed here in general.

In particular, the aforementioned oxidizing reagents ("OR") can be used in gaseous and / or liquid form, and in particular preferably in the form of aqueous solutions or the like, which is in principle known to the skilled person as such.

[0065]

In general, the surface oxidation can be carried out under heating.

Here, the surface oxidation can be carried out at such temperatures that a reaction of the oxidizing reagent ("OR") with the activated carbon with the formation of oxygen-containing functional groups is carried out on the surface of activated carbon.

In particular, in this connection, the surface oxidation in the temperature range from -20 ° C to 1,000 ° C, especially 0 ° C to 800 ° C, preferably 20 ° C to 600 ° C, preferably 30 ° C to 500 ° C, can be performed.

In particular, in this connection, the surface oxidation for a period of time ranging from 1 minute to 600 minutes, especially 5 minutes to 500 minutes, preferably 10 minutes to 400 minutes is performed.

Sufficiently, the degree of surface oxidation, and in particular the number and the content of oxygen-containing groups on the activated carbon surface, can be specified.

[0066]

According to a first invention particularly preferred embodiment, the oxidation reagent ("OR") may be selected from the group consisting of inorganic or organic oxides and peroxides and inorganic or organic acids and peracids, and combinations thereof, preferably from the group of hydrogen peroxide (H_2O_2) and nitric acid (HNO_3), preferably nitric acid (HNO_3).

In particular, then, the surface oxidation in the temperature range from -20 ° C to 500 ° C, especially -10 ° C to 400 ° C, preferably 0 ° C to 350 ° C, preferably 10 ° C to 300 ° C, particularly preferably 15 ° C to 250 ° C, most preferably 20 ° C to 200 ° C, performed.

This is, as described above, so to speak, a chemical oxidation, which can be performed in principle, and depending of the oxidizing reagent used also at room temperature.

[0067]

According to a second invention particularly preferred embodiment, the oxidation reagent ("OR") can be selected from the group consisting of oxygen and ozone, preferably oxygen.

In particular, the surface oxidation should be in the temperature range from 100 ° C to 1000 ° C, in particular 150 ° C to 900 ° C, preferably 200 ° C to 750 ° C, preferably 225 ° C to 600 ° C, more preferably 250 ° C to 500 ° C, most preferably 250 ° C to 450 ° C, performed.

As indicated above, these are to a certain extent by thermal oxidation.

[0068]

Can be With regard to the inventively provided surface oxidation of the activated carbon, so, these are summarized for a specific variable or adjustable process that based on the way the employed oxidizing reagent ("OR"), the oxidation time and / or temperature controlled ,

As indicated above, is determined by the selective oxidation, the oxidized in this manner on the surface of activated carbon for the subsequent functionalization or

Modifying optimized with nitrogen.

For example, to be increased as a measure of the degree of oxidation in function of the oxidation time, the content of volatile constituents.

In addition, the pH-value, in particular the surface-pH of the oxidized activated carbon on their surface can be adjusted and tailored by choice of the oxidation conditions, for example the duration of the oxidation.

Thus, in the chemical oxidation described above, in particular the formation of surface oxides is preferably acidic, whereas during the thermal oxidation previously described in particular, the formation of basic surface oxides is preferred.

Similarly, has an increasing oxidation time with respect to the oxidized activated carbon at their surface an influence on the so-called tap density of the activated carbon, which in general with increasing oxidation time at least slightly decreases.

Similarly, the oxidation also has an impact on the total pore volume, in particular the total pore volume according to Gurvich, the activated carbon, which is increased, for example, with increasing oxidation time at least slightly.

As a result, therefore, the surface properties of the activated carbon are set in a specific manner with regard to the following modification with nitrogen or tailored based on the oxidation.

[0069]

As part of the method according to the invention realized guide, it may also be provided that after the surface oxidation, and in particular in front of the equipment, in particular, modification and / or functionalization, with a nitrogen purification or

Done drying the oxidised at their surface active carbon.

In this connection, the purification by means of at least one washing operation in a liquid, in particular water, take place.

Similarly, the drying under heating of the oxidized activated carbon at their surface, in particular to temperatures in the range from 40 ° C to 200 ° C, particularly 50 ° C to 150 ° C, preferably 60 ° C to 120 ° C, take place.

By carefully drying the oxidised at their surface of activated carbon is the intermediate product thus obtained or

BEYOND intermediate for the subsequent modification or

Functionalization with nitrogen optimized, especially since the access for the Stickstoffmodifizierungsreagenz ("SMR") is improved.

[0070]

What the the surface oxidation of the activated carbon subsequent equipment, in particular modification or

Functionalization of the oxidized activated carbon with nitrogen regards to its surface, this should contacting the surface obtained by the oxidation with the active carbon Stickstoffmodifizierungsreagenz ("SMR"), in particular followed by a heat treatment, comprise.

In this way, the chemical attachment or

Integration and the formation of nitrogen-containing functional groups at the surface of previously oxidized active carbon guarantees.

As previously indicated, interacts the Stickstoffmodifizierungsreagenz ("SMR"), in particular with the oxygen-containing surface functionality which have been generated as part of the preceding oxidation step in a controlled manner on the activated carbon.

[0071]

By contacting the oxidized on the surface of activated carbon with the Stickstoffmodifizierungsreagenz ("SMR") is especially the with the environment in connection pore system of the activated carbon filled or contacted with the Stickstoffmodifizierungsreagenz what in this way the subsequent chemical reactions oxygenates especially with the allows functional groups of the oxidised at their surface active carbon.

[0072]

In particular, carried out as part of the modification or

Functionalization with nitrogen, a reaction of the Stickstoffmodifizierungsreagenzes ("SMR") with the oxygen-containing functional groups, as defined above, with this regard, a key advantage is to be seen in that the pore volume of the activated carbon will not significantly, or at most only changed slightly.

According to the invention is to a certain extent before a chemical bonding of nitrogen to the oxygen-containing functional groups which can be optionally modified BEYOND, as will be mentioned.

[0073]

What the present invention for the equipment, in particular modification and / or functionalization of the oxidized on the surface of activated carbon with nitrogen used Stickstoffmodifizierungsreagenz ("SMR") is concerned, this may be according to the invention is selected from the group consisting of urea, ammonia, melamine and amino acids as well as their combinations, especially urea and ammonia, and combinations thereof, preferably urea.

[0074]

According to a preferred embodiment according to the invention can be used as the equipment for the particular modification and / or functionalization of the oxidized at its surface activated carbon used with nitrogen Stickstoffmodifizierungsreagenz ("SMR") urea.

In this connection, the urea in the form of a preferably aqueous solution, are preferably used in the form of an at least substantially saturated solution of urea.

Generally, the amount and concentration of the urea solution can be varied accordingly, depending on the desired degree of Stickstofffunktionalisierung what lies in technically customary skill of the art.

In this context, according to the invention can be, for example, the procedure is such that the oxidized at its surface activated carbon is firstly immersed in the urea solution, the excess urea solution is then decanted and subsequently a thermal treatment takes place in particular in an inert gas stream.

[0075]

According to a further embodiment of the invention it can also be provided that as Stickstoffmodifizierungsreagenz ("SMR") Ammonia (NH_3) is used.

In this connection, ammonia in the form of gas and / or ammonia water, in particular in the form of gas, can be used.

In this connection, the to be treated and oxidized at its surface an ammonia activated charcoal or

NH_3 gas stream or an NH_3-containing gas stream are subjected under appropriate warming.

[0076]

What equipment, in particular modification or

Functionalization of the oxidized activated carbon with nitrogen continue terms on their surface, this may in the context of the inventive method performed by the reaction, in particular chemical reaction, preferably with the formation of covalent bonds, the Stickstoffmodifizierungsreagenzes ("SMR") with the oxidized at its surface activated carbon, in particular with the oxygen-containing functional groups at the surface of the activated carbon, effected.

In this context, it can be inventively provided that the equipment, in particular modification and / or functionalization of the oxidized on the surface of activated carbon with nitrogen to form nitrogen-containing functional groups, in particular selected from the group of amines, in particular primary, secondary, tertiary and quaternary amines, imines and azines and their combinations is carried out, in particular to amine, imine, azine, pyrrole, nitrile, nitro, nitroso, pyridine, imide, amide, lactam and / or Pyridongruppen and their combinations can be formed.

According to the invention thus at least initially be a chemical bonding of nitrogen to form nitrogen-containing functional groups, wherein the chemical connection is localized in particular at the surface of previously oxidized active carbon and in particular due to a chemical reaction to form covalent bonds with the previously-formed oxygen-containing functional groups results.

[0077]

According to the invention it can, however, also be provided that the equipment, in particular, modification and / or functionalization, the oxidized at its surface activated carbon with nitrogen integration and / or installation, in particular with the formation of chemical bonds, preferably formation of covalent chemical bonds, particularly between nitrogen on the one hand and carbon on the other hand, takes place in the carbon skeleton and / or in the carbon matrix of the oxidized activated carbon on their surface.

In this way, the nitrogen is as it were integrated or built directly into the carbon skeleton of the activated carbon.

This corresponds to a doping nitrogen (N-doping).

The integration of nitrogen in the carbon skeleton may, starting from the above-described connection of the nitrogen or of the Stickstoffmodifizierungsreagenzes ("SMR") made to the oxygen-containing functional groups, in particular as part of a subsequently yet specified thermal treatment, which on the basis of the resulting nitrogen-containing functional groups to an integration of the nitrogen into the carbon skeleton of the activated carbon in particular based on a pyrolysis.

[0078]

Next, regarding the inventively realized process control, so it may be provided in the context of the present invention that the apparatus and particularly the modification and / or functionalization of the oxidized on the surface of activated carbon with nitrogen is carried out under heating, particularly at temperatures above the decomposition temperature of Stickstoffmodifizierungsreagenzes ("SMR").

In this connection, the equipment, and in particular modification or

Functionalization which take place on its surface oxidized activated carbon with nitrogen at such temperatures that a reaction of the Stickstoffmodifizierungsreagenzes ("SMR") with the oxidized at its surface activated carbon, particularly with the oxygen-containing functional groups at the surface of the activated carbon, is carried out.

In particular, in this regard be taken in such a way that the equipment, in particular modification or

Functionalization of the oxidized activated carbon on the surface thereof with nitrogen in the temperature range of 200 ° C to 1200 ° C, in particular 300 ° C to 1000 ° C, preferably 500 ° C to 950 ° C is carried out.

As regards the duration of the heat treatment, so it can be inventively provided also that the equipment, in particular modification or

Functionalization which is on its surface oxidized activated carbon with nitrogen for a period of time ranging from 0.1 hours to 15 hours, preferably 0.2 hours to 10 hours, preferably 0.5 hour to 8 hours is performed.

In particular, with respect to the use of urea as Stickstoffmodifizierungsreagenz ("SMR") will proceed at temperatures above 180 ° C, whereby the above-mentioned temperature of the decomposition temperature of urea equivalent.

[0079]

What according to another preferred embodiment further regards to connect the Stickstoffmodifizierungsreagenzes ("SMR") to the oxygen-containing groups to form the nitrogen-containing functional groups and for integration of the nitrogen in the carbon skeleton or grille heat treatment carried out the oxidized on the surface of activated carbon, so it can be inventively provided that the equipment, in particular modification and / or functionalization of the oxidized on the surface of activated carbon with nitrogen while heating takes place in the form of a single-stage heat treatment.

[0080]

In this regard, it may in particular be provided that the equipment, in particular modification or

Functionalization of the oxidized at its surface activated carbon with nitrogen while heating to a temperature range of 300 ° C to 700 ° C, in particular 400 ° C to 600 ° C, preferably 400 ° C to 550 ° C, carried out, in particular for a time period in the range of from 0.1 hours to 15 hours, preferably 0.2 hours to 10 hours, preferably 0.5 hour to 8 hours.

In this manner, in particular are nitrogen-containing functional groups, as they have been previously defined, is formed.

[0081]

According to the invention it can also be provided that the equipment, in particular, modification and / or functionalization, the oxidized at its surface activated carbon with nitrogen while heating to a temperature range of 750 ° C to 1200 ° C, in particular 800 ° C to 1,100 ° C, preferably 850 ° C to 1,050 ° C is carried out.

In this regard, in particular for a period ranging from 0.1 hours to 15 hours, preferably 0.2 hours to 10 hours, preferably 0.5 hour to 8 hours, A method.

As part of the heat treatment described above, in particular an integration or incorporation of the nitrogen in the carbon skeleton and the carbon matrix of the oxidized activated carbon at their surface, in particular as defined above.

Thus takes priority immobilization of nitrogen as a result of chemical bonding Based on this procedure, with a heat treatment at higher temperatures or

Integration of nitrogen on or in the carbon skeleton, or

Carbon lattice of activated carbon, which in this respect - without restricting or being bound to this theory - first nitrogen-containing functional groups can be formed, which are subsequently decomposed to convert the nitrogen in the carbon structure to some extent thermally or based on pyrolysis, so that incorporated in the final product of reactive or catalytic nitrogen directly into the carbon skeleton of the so treated activated carbon or incorporated present.

[0082]

According to a further preferred embodiment according to the equipment can, in particular modification or

Functionalization, which take place on its surface oxidized activated carbon with nitrogen under heating in the form of a multistage, in particular two-stage heat treatment.

[0083]

In this context, it can be inventively provided in particular that the equipment, in particular modification and / or functionalization of the oxidized on the surface of activated carbon with nitrogen in a first heat treatment by heating to a temperature range of 300 ° C to 700 ° C, in particular 400 ° C to 600 ° C, preferably 400 ° C to 550 ° C, and a subsequent second heat treatment by heating to a temperature range of 750 ° C to 1200 ° C, in particular 800 ° C to 1,100 ° C, preferably 850 ° C to 1050 ° C, is performed.

In particular, the respective heat treatments, independently of one another, be up to 6 hours, carried out for a period of time ranging from 0.1 hours to 15 hours, preferably 0.2 hours to 10 hours, preferably 0.5 hours.

In particular, the nitrogen-containing functional groups are in this manner in the first step are formed, which are then decomposed in a second step under pyrolysis, where the nitrogen is transferred or incorporated into the carbon skeleton.

[0084]

The temperature of the heat treatment thus has a significant effect on the chemical constitution of the charged activated carbon in the nitrogen.

At low temperatures the heat treatment, as defined above, primarily results in the formation of nitrogen-containing functional groups, and at higher temperatures, as defined above, particular priority or a built-in or an integration of the nitrogen in the backbone structure of the activated carbon.

[0085]

In this context, it can also be provided that the connection is made to the equipment, in particular modification and / or functionalization, with nitrogen purification and / or drying of the resulting charcoal.

In this connection, the purification by means of at least one washing operation in a liquid, in particular water, take place.

In addition, a drying under heating of the equipped with nitrogen, activated carbon, in particular to temperatures in the range from 40 ° C to 200 ° C, particularly 50 ° C to 150 ° C, preferably 60 ° C to 120 ° C can take place.

By purification or

Washing process to remove combustion residues from the particular modified with nitrogen activated carbon.

[0086]

Due to the inventively realized procedure guiding the nitrogen content of treated activated carbon can be significantly increased, which for the obtained and with nitrogen-modified product of the content of volatile components ("FB") of the activated carbon as a measure for the content of nitrogen groups after nitrogen modification or - Functionalization can be used, in particular in view

of the above defined nitrogen-containing functional groups: Thus, the equipped with nitrogen, activated carbon has a volatiles content ("TB"), based on the dry weight of the finished with nitrogen activated carbon of at least 0.1 .-%, in particular at least 0.2 wt .-%, preferably at least 0.3 wt .-%, preferably at least 0.5 wt .-%, particularly 1 wt .-% preferably at least, even more preferably at least 2 wt. -%, and / or in the range of 0.1 wt .-% to 20 wt .-%, in particular 0.2 wt .-% to 15 wt .-%, preferably 0.3 wt .-% to 12 wt. -%, preferably 0.5 wt .-% to 10 wt .-%, more preferably 1 wt .-% to 10 wt .-%, have.

In this respect, the volatiles ("FB") may, based on the ISO 562: to be determined at a temperature of 900 ° C under an inert atmosphere or under heating for 7 1981 minutes, in particular, be based on the dry matter.

[0087]

Moreover, the nitrogen equipped with activated carbon has a nitrogen content (ie,

Total nitrogen content), based on the dry weight of the activated carbon fitted with nitrogen, of at least 0.1 wt .-%, in particular at least 0.2 wt .-%, preferably at least 0.3 wt .-%, preferably at least 0.5 wt. -%, more preferably 1 wt .-% at least, very particularly preferably at least 2 wt .-%, and / or in the range of 0.1 wt .-% to 30 wt .-%, in particular 0.2 wt .-% to 25 wt .-%, preferably 0.3 wt .-% to 20 wt .-%, preferably 0.5 wt .-% to 15 wt .-%, more preferably 1 wt .-% to 15 wt .-% having.

In this context, at least 50%, especially at least 60%, preferably at least 70%, preferably at least 80% of the nitrogen, based on the total nitrogen content, are present chemically bonded in the fitted with nitrogen activated carbon and / or incorporated and / or not in the form of volatiles ("FB") are in the equipped with nitrogen activated carbon.

Similarly, should in this context, 50% to 99.9%, in particular 60% to 99%, preferably 70% to 95%, preferably 80% to 90%, of the nitrogen, based on the total nitrogen content, chemically bonded in the fitted with nitrogen charcoal and / or integrated presence and / or non-volatile components in the form of ("FB") are in the nitrogen equipped with activated charcoal.

In other words, the nitrogen should be integrated on the basis of the above, or the above amounts in the carbon skeleton or grids of the activated carbon, in which case the remaining portion of nitrogen in the form of nitrogen-containing functional groups present, in particular as defined above.

This provides a particularly good catalytic activity or

Reactivity coupled with excellent resistance of the equipment achieved with nitrogen.

[0088]

In this context, the higher values for the integrated in the carbon skeleton or grids of the activated carbon nitrogen are generally achieved when the equipment, in particular, modification and / or functionalization, the oxidized at its surface activated carbon with nitrogen while heating to a temperature range of 750 ° C to 1200 ° C, in particular as defined above, is performed.

The nitrogen is then at best before only to a small extent in the form of nitrogen-containing functional groups.

In contrast, in general, lower values for the integrated in the carbon skeleton or grids of the activated carbon nitrogen can be achieved when the equipment, in particular, modification and / or functionalization, the oxidized at its surface activated carbon with nitrogen while heating to a temperature range of 300 ° C to 700 ° C, in particular as defined above, is performed.

As explained previously, the nitrogen is then present in a greater proportion in the form of nitrogen-containing functional groups.

In this way, in particular an improved breakdown performance compared to certain substances, such as in particular formaldehyde, can be achieved.

[0089]

Furthermore, the activated carbon fitted with nitrogen according to the invention may have a content in the carbon skeleton built-in or integrated (that is, so to speak immobilized) nitrogen, based on the dry weight of the activated carbon fitted with nitrogen, of at least 0.05 wt .-%, in particular at least 0.1 wt .-%, preferably at least 0.2 wt .-%, preferably at least 0.3 wt .-%, particularly preferably at least 0.5 wt .-%, even more preferably 1 wt .-% at least, and in the range wt .-% of 0.05 to 30 wt .-%, particularly 0.1 wt .-% to 25 wt .-%, preferably 0.2 wt .-% to 20 wt .-%, preferably 0.5 wt .-% to 15 wt .-%, have.

[0090]

In this context, the respective nitrogen content of activated carbons invention are determined by methods known per se.

The total nitrogen content can be determined by means of known per se elemental analysis, while the identification of volatiles ("FB") according to the ISO 562: can be done 1981st

From the difference of certain means of elemental analysis total nitrogen content on the one hand and according to the ISO 562: 1981 certain content of volatile constituents (ie volatile nitrogen-containing functional groups), the content of immobilized or built in the carbon skeleton nitrogen can then be determined.

[0091]

Below are additional characteristics or

Parameters of activated carbon obtainable by the method according to the invention carried out defined.

The following information relating to the parameters available in the context of the inventive method performed nitrogen or nitrogen-functionalized modified activated carbon are determined using standardized or explicitly indicated methods of determination or the skilled person per se determination methods.

In particular, the parameter data concerning the characterization of porosity, pore size distribution and other adsorption properties result in general each of the respective nitrogen sorption isotherms of the respective activated carbon or the measured products.

[0092]

In particular, in the context of the present invention equipped with nitrogen activated carbon or a nitrogen-modified or stickstofffunktionalisierte activated carbon is obtained, which has a total pore volume, in particular a total pore volume according to Gurvich, in the range of 0.4 to 4 cm <3> / g, more preferably 0.5 to 3.5 cm <3> / g, preferably 0.6 to 3 cm <3> / g, particularly preferably 0.7 to 2.5 cm <3> / g.

In this context should 30 to 99%, in particular 40% to 99%, preferably 50% to 95%, of the total pore volume, in particular of the total pore volume according to Gurvich, which equipped with nitrogen, activated carbon, by pores having pore diameters of ≤ 50 nm, in particular by micro- - and / or mesopores can be formed.

Similarly, should in this context, 10% to 85%, in particular 20% to 80%, preferably 30% to 75%, of the total pore volume, in particular of the total pore volume according to Gurvich, which equipped with nitrogen, activated carbon, up by pores having pore diameters in the range of from 2 nm 50 nm, in particular by mesopores are formed.

[0093]

As regards the determination of the total pore volume according to Gurvich, so it is a the person skilled in the art per se known measurement method of determination.

For further details regarding the determination of the total pore volume according to Gurvich, for example, be made to L. Gurvich (1915), J. Phys.

Chem.

Soc.

Russ. 47, 805, and on S. Lowell et al, Characterization of Porous Solids and Powders:. Surface Area Pore Size and Density, Kluwer Academic Publishers, Article Technology Series, pages 111 et seq.

[0094]

In particular, it can be provided in the context of the present invention that the equipped with nitrogen, activated carbon, a by pores having pore diameters of ≤ 2 nm formed pore volume, especially micropore volume after carbon black, especially by analysis using t-plot, is in the range of 0.05 to 2 cm <3> / g, especially 0.1 to 1.5 cm <3> / g, preferably 0.2 to 1.1 cm <3> / g, particularly preferably 0.3 to 1 cm <3> / g having.

Similarly, it may be provided that 10% to 95%, in particular 20% to 95%, preferably 30% to 90%, of the total pore volume of the equipped with nitrogen activated charcoal, formed by pores having pore diameters of ≤ 2 nm, in particular by micro pores.

[0095]

The determination method of carbon black is known in the art per se, so that in this respect there is no need for further details.

In addition, to further details of the determination of the pore surface area and pore volume by carbon black, for example, referred to RW Magee, Evaluation of the External Surface Area of Carbon Black by Nitrogen adsorption, Presented at the Meeting of the Rubber Division of the American Chem.

Soc., October 1994 z.

B. gives a lecture in: Quantachrome Instruments, AUTOSORB-1, AS1 WinVersion 1.50 Operating Manual, OM, 05061, Quantachrome Instruments in 2004, Florida, USA, pages 71 et seq.

[0096]

In the present invention, it is equally advantageous when the nitrogen-modified or stickstofffunktionalisierte with nitrogen equipped activated carbon has an average pore diameter in the range of 1 to 60 nm, especially 1 to 55 nm, preferably 1.5 to 50 nm, more preferably 2 to 45 nm.

[0097]

To obtain or to ensure the sorption of available with the inventively performed process equipped with nitrogen activated carbon, which equipped with nitrogen activated carbon has a BET specific surface area in the range of 500 m <2> / g to 3,500 m <2> / g should , in particular 600 to 3,000 m <2> / g, preferably 700-2750 m <2> / g, particularly preferably 800 to 2,500 m <2> / g.

[0098]

The determination of the BET specific surface area is principle to the expert known as such, so that need to be carried out in this respect no further details.

All BET surface area figures relate to the determination according to ASTM D6556-04.

In the context of the present invention is to determine the BET surface area - in general and if not expressly indicated otherwise hereinafter - the so-called multi-point BET method of determination (MP-BET) in a partial pressure p / p0 of 0.05 to 0.1 applied.

[0099]

With regard to further details concerning the determination of the BET surface area or to the BET method can in the aforementioned ASTM D6556-04 and to Römpp Chemie Lexikon, 10th

Edition, Georg Thieme Verlag, Stuttgart / New York, keyword: "BET method", including the references cited therein, and to Winnacker-Kuchler (. 3

Edition), Volume 7, pages 93 et seq., As well as Z. Anal.

Chem.

238, pages 187-193 (1963), directed.

[0100]

Furthermore, it is an advantage if the nitrogen-modified or stickstofffunktionalisierte or equipped with nitrogen, activated carbon has a formed by micro pore surface area of 400-2500 m <2> / g, more preferably 500 to 2,300 m <2> / g, preferably 600 to 2,100 m <2> / g, more preferably from 700 to 1,900 m <2> / g.

[0101]

The nitrogen or stickstofffunktionalisierte modified or equipped with nitrogen, activated carbon should also a density of 1.1 to 3.5 g / ml, in particular of 1.5 to 3 g / ml, preferably 1.75 to 2.75 g / ml, preferably from 2 to 2.5 g / ml, comprise.

[0102]

Similarly, should the modified or nitrogen stickstofffunktionalisierte equipped with nitrogen or the activated carbon has a bulk density of 0.1 to 1.5 g / ml, in particular from 0.15 to 1 g / ml, preferably from 0.2 to 0.8 g / ml, preferably from 0.3 to 0.6 g / ml, comprise.

[0103]

In addition, it is advantageous when the nitrogen-modified or stickstofffunktionalisierte or equipped with nitrogen activated carbon has a pressure and / or bursting strength (resistance to weight loading) per activated carbon grain, in particular per activated carbon spherule, of at least 5 newtons, in particular at least 10 Newtons, preferably at least 15 Newtons preferably at least 20 Newtons, and / or in that the activated carbon has a pressure and / or bursting strength (resistance to weight loading) per activated carbon grain, in particular per activated carbon beads, in the range of 5 to 50 newtons, in particular 10 to 45 Newtons, preferably 15 to 40 Newton has, ,

[0104]

What beyond the activated carbon used in the context of the inventive method performed or

Output activated carbon is concerned, which is first oxidized at its surface and subsequently modified with nitrogen and equipped, is concerned, this can be done with respect to a variety of activated carbons, for example, with different pore structure with regard to the distribution of micro, meso and macro pores, are used.

In particular, commercially available or commercially available activated carbons can be used.

In the context of the present invention to use activated carbons coming for example from Blucher GmbH, Erkrath, Germany or the AdsorTech GmbH, Premnitz, Germany expelled.

[0105]

What the activated carbon used in the invention or

Output activated carbon still concerned, in this regard, in particular a granular, in particular spherical activated carbon are used.

The activated carbon used or

Output activated carbon, especially granular carbon or carbon spherules, may be obtained by known processes of the state: Normally, for this purpose, grain or spherical sulfonated organic polymers, in particular based on divinylbenzolvernetztem polystyrene, carbonized and then activated to the respective activated carbon.

For further details in this regard, for example, to the publications DE 43 28 219 A1, DE 43 04 026 A1, 196 00 237 A1 and EP 1918022 A1 or referenced parallel, belonging to the same patent family US 7,737,038 B2 DE.

Similarly, also activated carbon based on other raw materials such as pitch or the like, are used.

Such activated carbons are known in the art as such.

[0106]

In particular, in the context of the present invention, an activated carbon is used as a starting material, which particle sizes, in particular particle diameter is in the range of 0.001 to 2 mm, in particular 0.01 to 1 mm, preferably 0.05 to 0.8 mm, preferably 0.1 to 0.7 mm, particularly preferably 0.15 to 0.6 mm.

This should, based on the activated carbon, at least 80 wt .-%, in particular at least 90 wt .-%, preferably at least 95 wt .-% having the activated carbon used particle sizes, in particular particle diameter, within the aforementioned ranges.

Furthermore, it is according to the invention advantageous if the activated carbon used as a starting material mean particle sizes (D50), in particular median particle diameter (D50), ranging from 0.01 to 1 mm, in particular 0.05 to 0.8 mm, preferably 0.1 to 0.6 mm, preferably 0.15 to 0.5 mm, particularly preferably 0.2 to 0.4 mm.

The corresponding particle size or diameter can be 04 determined, for example, based on the ASTM D2862-97 method according to /.

In addition to the aforementioned variables with determination methods based on a sieve analysis, be determined on the basis of X-ray diffraction, laser diffraction or the like.

The respective determination methods are in the art as such well-known, so that it does not require further explanations in this respect.

The specified parameters of the starting activated carbon can be found in a corresponding manner in the nitrogen or nitrogen-functionalized modified activated carbon again.

[0107]

The inventively performed process is associated with a variety of benefits, as they have already stated previously.

Due to the outstanding sorption properties of the obtained or obtainable by the method according to the invention carried out charcoal is a broad Conditions and

Possible use of spectrum, as is mentioned below in more detail.

[0108]

Another object of the present invention - according to a second aspect of the present invention - the invention is nitrogen or modified stickstofffunktionalisierte activated carbon as such, in particular with catalytic or reactive properties, preferably using nitrogen as the catalytically active heteroatom.

[0109]

The nitrogen-modified or stickstofffunktionalisierte activated carbon according to the invention is characterized by surface oxidation of activated carbon used as the starting material ("output activated carbon") using or in the presence of at least one oxidizing reagent ("OR") and subsequent equipment, in particular modification or

Functionalization, with nitrogen, the thus-obtained oxidized at their surface by using activated carbon or in the presence of at least one Stickstoffmodifizierungsreagenzes ("SMR") available.

[0110]

Thus, the present invention relates, according to this aspect of the invention, the nitrogen-modified active carbon or stickstofffunktionalisierte as such according to the invention, in particular with catalytic or reactive properties, preferably using nitrogen as the catalytically active heteroatom.

The activated carbon according to the invention is characterized in that nitrogen is attached to form chemical bonds, preferably with the formation of covalent chemical bonds, to the activated carbon.

[0111]

What as such continues to regard the activated carbon of the invention or the equipped with nitrogen activated carbon according to the invention, it can be inventively provided that nitrogen in the form of at least one nitrogen-containing functional group, in particular selected from the group of amines, in particular primary, secondary, tertiary and quaternary amines, imines and azines and combinations thereof occurs.

In particular, the nitrogen in the form of amine, imine, azine, pyrrole, nitrile, nitro, nitroso, pyridine, imide, amide, lactam and Pyridongruppen and combinations thereof, are present.

Here, the nitrogen is preferably bonded to the nitrogen-modified and / or nitrogen-functionalized activated carbon, preferably bonded chemically and / or covalent.

[0112]

Similarly, it can be inventively provided that preferably with the formation of covalent chemical bonds, particularly between nitrogen on the one hand and carbon with respect to the nitrogen-modified and / or stickstofffunktionalisierte activated carbon

according to the invention nitrogen in the carbon skeleton or in the carbon matrix of nitrogen-modified or nitrogen-functionalized activated carbon on the other hand is integrated or installed.

[0113]

In the present invention, it may be provided that the nitrogen-modified and / or stickstofffunktionalisierte activated carbon has a volatiles content ("FB"), based on the dry weight of the finished with nitrogen activated carbon of at least 0.1 wt .-%, in particular at least 0.2 wt .-%, preferably at least 0.3 wt .-%, preferably at least 0.5 wt .-%, more preferably at least 1 wt .-%, most preferably at least 2 wt .-%, and / or in the range of 0.1 wt .-% to 20 wt .-%, in particular 0.2 wt .-% to 15 wt .-%, preferably 0.3 wt .-% to 12 wt .-%, preferably 0 , 5 wt .-% to 10 wt .-%, more preferably 1 wt .-% to 10 wt .-%, has.

As indicated above, can the volatiles ("FB") as a measure of the content of nitrogen in terms of the presence in the form of nitrogen-containing functional groups, in particular as defined above, are used.

For the relevant methods of determination may be made to the above statements.

[0114]

Furthermore, it is within the scope of the present invention advantageous if the nitrogen-modified active carbon stickstofffunktionalisierte or a nitrogen content, based on the dry weight of the activated carbon fitted with nitrogen, of at least 0.1 wt .-%, in particular at least 0.2 wt .-% , preferably at least 0.3 wt .-%, preferably at least 0.5 wt .-%, particularly 1 wt .-% preferably at least, even more preferably at least 2 wt .-%, and / or in the range of 0.1 .-% to 30 wt .-%, in particular 0.2 wt .-% to 25 wt .-%, preferably 0.3 wt .-% to 20 wt .-%, preferably 0.5 wt .-% to 15 wt .-%, more preferably 1 wt .-% to 15 wt .-%, has.

In this regard, at least 50%, especially at least 60%, preferably at least 70%, preferably at least 80% of nitrogen, based on the total nitrogen content, present in the nitrogen-modified or nitrogen-functionalized activated carbon chemically bonded or integrated and / or in the form of volatile components ("FB") are in the nitrogen-modified and / or nitrogen-functionalized activated carbon.

In this context should 50% to 99.9%, in particular 60% to 99%, preferably 70% to 95%, preferably 80% to 90%, of the nitrogen, based on the total nitrogen content, chemically bonded in the nitrogen-modified or nitrogen-functionalized activated carbon or be integrated and / or in the form of volatile constituents ("FB") are in the nitrogen-modified and / or nitrogen-functionalized activated carbon.

[0115]

Furthermore, the activated carbon fitted with nitrogen according to the invention may have a content in the carbon skeleton built-in or integrated (that is, so to speak immobilized) nitrogen, based on the dry weight of the activated carbon fitted with nitrogen, of 0.05 wt .-%, in particular at least 0.1 .-%, preferably at least 0.2 wt .-%, preferably at least 0.3 wt .-%, particularly preferably at least 0.5 wt .-%, even more preferably 1 wt .-% at least, or in the range of 0.05 wt .-% to 30 wt .-%, particularly 0.1 wt .-% to 25 wt .-%, preferably 0.2 wt .-% to 20 wt .-%, preferably 0.5 wt. -% to 15 wt .-% have.

[0116]

In particular, the inventive activated carbon with nitrogen or modification is distinguished

Stickstofffunktionalisierung also characterized by the following parameters; for the relevant assay method can be equally referred to the above statements:

According to the invention should have the nitrogen-modified and / or stickstofffunktionalisierte activated carbon has an overall pore volume, in particular a total pore volume according to Gurvich, in the range of 0.4 to 4 cm <3> / g, especially 0.5 to 3.5 cm <3> / g, preferably 0 6 to 3 cm <3> / g, particularly preferably 0.7 to 2.5 cm <3> / g.

[0117]

In this regard, should be at least 30% to 99%, in particular 40% to 99%, preferably 50% to 95%, of the total pore volume, in particular of the total pore volume according to Gurvich, the nitrogen-modified and / or nitrogen-functionalized activated carbon by pores having pore diameters of ≤ 50 nm, in particular be by micro- and / or mesopores formed.

In particular, can be 10% to 85%, in particular 20% to 80%, preferably 30% to 75%, of the total pore volume, in particular of the total pore volume according to Gurvich, the nitrogen-modified and / or nitrogen-functionalized activated carbon, up by pores having pore diameters in the range of from 2 nm 50 nm, to be, in particular formed by mesopores.

[0118]

Furthermore, should the nitrogen-modified and / or stickstofffunktionalisierte activated carbon according to the invention a formed by pores having pore diameters of ≤ 2 nm pore volume, especially micropore volume after carbon black, especially by analysis using t-plot, is in the range of 0.05 to 2 cm <2> / g, especially 0.1 to 1.5 cm <3> / g, preferably 0.2 to 1.1 cm <3> / g, particularly preferably 0.3 to 1 cm <3> / g.

This should 10% to 95%, in particular 20% to 95%, preferably 30% to 90%, of the total pore volume of the nitrogen-modified and / or nitrogen-functionalized activated carbon to be formed by pores having pore diameters of ≤ 2 nm, in particular by micro pores.

[0119]

Furthermore, it should have a mean pore diameter in the range of 1 to 60 nm, especially 1 to 55 nm, preferably 1.5 to 50 nm, more preferably 2 to 45 nm, which have nitrogen-modified and / or stickstofffunktionalisierte activated carbon according to the invention.

[0120]

According to the invention should have the nitrogen-modified and / or stickstofffunktionalisierte activated carbon according to the invention further has a BET specific surface area ranging from 500 m <2> / g to 3,500 m <2> / g, in particular 600 to 3,000 m <2> / g, preferably 700 to 2,750 m <2> / g, more preferably from 800 to 2,500 m <2> / g.

[0121]

Furthermore, the equipped with nitrogen activated carbon should have a formed by micropores surface area of 400 to 2,500 m <2> / g, in particular 500 to 2,300 m <2> / g, preferably from 600 to 2100 meters <2> / g, more preferably 700 to 1,900 m <2> / g.

[0122]

In addition, the nitrogen equipped with activated carbon should have a density of 1.1 to 3.5 g / ml, in particular of 1.5 to 3 g / ml, preferably 1.75 to 2.75 g / ml, preferably according to the invention from 2 to 2.5 g / ml, comprise.

[0123]

Furthermore, the activated carbon should be equipped with nitrogen according to the invention has a bulk density of 0.1 to 1.5 g / ml, in particular from 0.15 to 1 g / ml, preferably from 0.2 to 0.8 g / ml, preferably from 0.3 to 0.6 g / ml have.

[0124]

According to the invention equipped with nitrogen activated carbon should also a pressure and / or bursting strength (resistance to weight loading) per activated carbon grain, in particular per activated carbon spherule, of at least 5 newtons, in particular at least 10 Newtons, preferably at least 15 Newtons, preferably at least 20 Newton exhibit.

In addition, should the activated carbon has a pressure and / or bursting strength (resistance to weight loading) per activated carbon grain, in particular per activated carbon beads, in the range of 5 to 50 newtons, in particular 10 to 45 Newtons, preferably 15 to 40 Newton exhibit.

[0125]

Next, regarding the nitrogen-modified and / or stickstofffunktionalisierte activated carbon, it can be self-supporting or is in the form of a loose bed in particular.

[0126]

Alternatively, it is also possible that the activated carbon is supported on a carrier material.

[0127]

In this context, the support material may be gas-permeable, in particular, be air permeable formed.

[0128]

What the carrier material terms as such in this context, so should this gas permeability, in particular air permeability of at least 10 l · m <-2> · s <-1>, in particular at least 30 l · m <-2> · s <- 1>, preferably at least 50 l · m <-2> · s <-1>, more preferably at least 100 l · m <-2> · s <-1>, most preferably at least 500 l · m <-2> · s <-1>, and / or a gas permeability, in particular air permeability of up to 10,000 l · m <-2> · s <-1>, in particular up to 20,000 l · m <-2> · s <-1 > having at a flow resistance of 127 Pa.

[0129]

According to one embodiment of the present invention, the support material used in the invention have a three-dimensional structure.

In particular, the support material used in the invention according to this embodiment as preferably open-pored foam, particularly preferably as a polyurethane foam formed.

[0130]

According to an alternative embodiment, however, the support material used in the invention comprise a two-dimensional or two-dimensional structure.

Particularly in this embodiment may be formed as a preferably textile fabric, the support material used in the invention.

For example, the carrier material as a textile fabric, preferably an air-permeable textile material, preferably a woven, knitted or crocheted fabrics, scrim or nonwoven fabric, in particular woven (nonwoven) may be formed.

Similarly, the carrier material has a basis weight of 5 to 1,000 g / m <2>, particularly 10 to 500 g / m <2>, preferably 25 to 450 g / m <2> having.

[0131]

In this embodiment, the carrier material can be a natural fiber and / or synthetic fibers (chemical fibers) containing or consisting thereof be textile fabric.

In this context, the natural fibers from the group of wool fibers and cotton fibers (CO) may be selected.

In addition, the synthetic fibers may be selected from the group of polyester (PES); Polyolefins, in particular polyethylene (PE) and / or polypropylene (PP); Polyvinyl chlorides (CLF); Polyvinylidene chloride (CLF); Acetates (CA); Triacetates (CTA); Polyacrylic (PAN); Polyamides (PA), in particular aromatic, preferably flame-resistant polyamides; Polyvinyl alcohols (PVOH); Polyurethanes; Polyvinyl; (Meth) acrylates; Polylactic acids (PLA); Activated carbon; and mixtures thereof.

[0132]

Typically, the nitrogen-modified active carbon stickstoffunktionalisierte or is fixed to the invention, at or on the support material.

This can, for example by means of adhesive (eg.

B. be made by means of an adhesive) or as a result of tackiness or Eigenadhäsion, in particular the support material.

[0133]

The activated carbon according to the invention with the nitrogen or modification

PAC ET AL. EXHIBIT 1019

Stickstofffunktionalisierung is associated with a variety of benefits, as they have already stated previously.

[0134]

The activated carbon according to the invention can be used for numerous uses.

[0135]

Thus, the nitrogen-modified or stickstofffunktionalisierte activated carbon for the production of filters and filtering materials of any kind, in particular for the removal of pollutants, odors and toxins of all kinds, in particular from air and / or gas streams, such as NBC protective mask filters, odor filters, sheet filters, air filters , in particular filters for indoor air cleaning, adsorption-capable support structures and filters for the medical sector, are used.

[0136]

In addition, the inventive nitrogen-modified or stickstofffunktionalisierte activated carbon for the production of protective materials of any kind, especially protective clothing, in particular for the civil or military sector, such as protective suits, protective gloves, protective footwear, protective socks, head protective apparel and the like, and of protective coverings of any kind, preferably all aforementioned Protection materials are used for NBC deployment.

[0137]

Here, the inventive nitrogen-modified or activated carbon stickstofffunktionalisierte excellent sorption properties, in particular with respect to sulfur-containing or nitrogen-containing gases such as hydrogen sulphide, in particular hydrogen sulfide (H2S), and to ammonia (NH3).

[0138]

In particular, the inventive nitrogen-modified or stickstofffunktionalierte charcoal is also suitable for use as sorption of gases or liquids.

In addition, the activated carbon of the invention with or Stickstofffunktionalisierung

Find nitrogen modification as a catalyst or catalyst support use.

Is the high specific surface area and the excellent reactivity and catalytic activity of the modified nitrogen or nitrogen-functionalized activated carbon according to the invention is crucial for the aforementioned applications.

[0139]

Furthermore, the inventive nitrogen-modified active carbon or stickstofffunktionalisierte for chemical catalysis, in particular for the catalysis of chemical reactions and processes may be used.

[0140]

Another possible application of nitrogen or nitrogen-functionalized modified activated carbon according to the invention is the use in or as gas sensors or in fuel cells.

[0141]

Furthermore, another possible application of the active carbon is according to the invention with nitrogen modification or

Stickstofffunktionalisierung in the use for sorptive, in particular adsorptive applications, particularly preferably as a reactive and / or catalytic adsorbent.

[0142]

Furthermore, the inventive activated carbon with nitrogen or modification is

Stickstofffunktionalisierung for use in gas purification and for gas processing.

[0143]

Another use of nitrogen or nitrogen-functionalized modified activated carbon according to the invention can be seen in the context of the removal of pollutants, especially gaseous pollutants, or environmental pollutants, harmful or toxic substances or gases.

[0144]

Finally, the inventive nitrogen-modified or stickstofffunktionalisierte activated carbon is also suitable for use in the treatment and / or provision of clean room atmospheres, in particular for the electrical industry, in particular for semiconductor or chip manufacturing.

[0145]

According to a third aspect of the present invention - - insulation materials, in particular for the civil or military sector, in particular protective clothing, such as protective suits, protective gloves, protective footwear, protective socks protective clothing and the like, as well as protective covers, preferably all aforementioned protective materials for NBC Moreover, the present invention relates to deployment, which are prepared using the above-defined nitrogen-nitrogen-functionalized or modified activated carbon according to the invention or which have the above defined nitrogen-modified active carbon or stickstofffunktionalisierte according to the invention.

[0146]

Moreover, further object of the present invention - in accordance with a fourth aspect of the present invention - filters and filter materials, in particular for the removal of pollutants, odors and toxins of all kinds, in particular from air and / or gas streams, such as NBC protective mask filters, odor filters , surface filters, air filters, in particular filters for indoor air cleaning, adsorption-capable supporting structures and filters for the medical sector, produced using the previously defined active carbon according to the invention with nitrogen or modification

Stickstofffunktionalisierung or having the previously defined nitrogen-modified or stickstofffunk-tionalisierte activated carbon according to the invention.

[0147]

The following describes the present invention based representative of preferred embodiments and drawings

Figure representations explained in more detail.

In connection with the explanation of these preferred embodiments of the present invention, but which are by no means limiting with respect to the present invention, even further advantages, features, aspects and features of the present invention will be described.

[0148]

In the figure representations showing:

[0149]

FIG. 1aeine graphical representation of the influence of the thermal oxidation of the activated carbon used as the starting material selected oxidation time on various parameters and on the textural properties of the obtained as an intermediate, oxidized on the surface of activated carbon;

[0150]

1beine graphical representation of the dependency of various parameters or the textural properties of the oxidized at its surface activated carbon of the content of volatile constituents ("FB") of the oxidized at its surface activated carbon as a measure of the content of oxygen-containing functional groups or as a measure of the degree of oxidation of the resulting as an intermediate at its surface oxidized activated carbon;

[0151]

1ceine graphic representation for analyzing the chemical nature of the oxidized activated carbon on the surface thereof in terms of acidity and basicity of the surface oxides formed, wherein the underlying determination was carried out by potentiometric titration.

The figure display shows the formation of surface oxides using (atmospheric) oxygen as oxidizer ("OR") under variable temperature oxidation (thermal oxidation).

In the figure, the letter "a", the basic surface oxides indexing curve peak;

[0152]

1deine graphical display for further analysis of the chemical nature of the surface oxides formed, or the oxygen-containing functional groups at the surface of the activated carbon in accordance with the embodiments in Figure 1c.

As oxidizer ("OR"), however, were different concentrated urea solutions or

Hydrogen peroxide used in different concentrations (chemical oxidation).

In the figure, the letter "b", the acidic surface oxides indexing curve peak;

[0153]

1eeine graph for analysis of the chemical composition in terms of basicity or

Acidity of the resulting oxidation within the oxygen-containing functional groups, with the data by means of TPD-MS (Temperature Programmed Desorption coupled to mass spectroscopy) have been determined.

The desorption of carbon dioxide (CO_2) indicated thereby, the present during the oxidation formation of acidic surface oxides whereas the desorption of carbon monoxide (CO) caused indexed under the oxidation formation of basic surface oxides groups.

The oxidation was carried out on the basis of the aforementioned in 1d chemical oxidation.

[0154]

1feine graphical representation pursuant to 1e, with the data obtained or

Measured values in contrast to a obtained by thermal oxidation, on its surface oxidized activated carbon, as indicated in Figure 1c, refer;

[0155]

2aeine graphical represeniation of Wasserdampfisothermen of oxidised at their surface activated carbons which or under oxidant (air) oxygen at variable temperatures

Obtained durations (thermal oxidation), compared to a non-oxidized starting material or a starting activated carbon;

[0156]

2beine graphical representation of Wasserdampfisothermen of oxidised at their surface activated carbons, which to this effect as oxidizer ("OR") and hydrogen peroxide

Was nitric acid (HNO_3) used in each variable oxidation time (oxidation) compared to a non-oxidized starting activated carbon;

[0157]

3eine graphical representation of Wasserdampfisothermen of nitrogen-modified or nitrogen-functionalized activated carbon with the influence of the members elected at the nitrogen equipment temperature on the final product, the respective rights adsorption branch of the tested activated carbon is the adsorption and the respective left adsorption branch of the tested activated carbon desorption of water;

[0158]

3bgrafische representations of the influence of the performed oxidation with subsequent Stickstofffunktionalisierung or modification to the relevant parameters and textural properties of the resulting activated carbon and the related influence of or in the functionalization

Modifying selected with nitrogen temperature, which in the graphical representation the symbol ① the base or

The icon ② obtained after surface oxidation, on its surface oxidized activated carbon (intermediate), which therefore is not nitrogen-modified or is -funktionalisiert, and the symbol ③ the nitrogen functionalized or modified activated carbon in the form of the final product represent output activated carbon;

[0159]

4aeinen the inventively performed process underlying the invention process carried out but in non-limiting manner characterizing reaction sequence for obtaining a nitrogen-modified or nitrogen-functionalized activated carbon, based on an oxidized on the surface of activated carbon using urea as Stickstoffmodifizierungsreagenz ("SMR");

[0160]

4bein XPS spectrum (X-ray photoelectron spectroscopy, X-ray photoelectron spectroscopy) for the detection of nitrogen-containing functional groups for various heat treatment steps for obtaining the nitrogen-functionalized or nitrogen-modified activated carbons;

[0161]

5 shows a graphical representation in the form of a bar graph with the determined for different activated carbons breakthrough times in relation to different Sorptionssubstanzen (NH_3, H_2S and SO_2), in 5 the symbol ① represents an unoxidized starting activated carbon and the other activated carbons according to the symbols ② to ④ each based nitrogen-modified urea or represent stickstofffunktionalisierte activated carbons.

In this context, the symbols ② or ③ nitrogen is modified or stickstofffunktionalisierte activated carbons which or on the basis of a with (air) oxygen at temperatures of 400 ° C

450 ° C were obtained on its surface oxidized activated carbons (thermal oxidation).

The symbol ③ also represents a nitrogen or stickstofffunktionalisierte modified activated carbon which has been obtained on the basis of a means of nitric acid (HNO_3) at its surface oxidized activated carbon (oxidation);

[0162]

6aeine graphical representation of breakthrough experiments using Schwefeldioxid (SO_2) as to sorbing gas based on a comparison of output activated carbon ("feedstock") on the one hand and a nitrogen-modified or nitrogen-functionalized activated carbon ("final") on the other hand;

[0163]

6beine graphical representation of breakthrough experiments in accordance with the embodiments to 6, wherein, in contrast to this, hydrogen sulfide (H_2S) was used as a sorbent for gas;

[0164]

7sein XPS spectrum of a C 1 s-range scans an oxidized at its surface, but not yet nitrogen modified or nitrogen-functionalized activated carbon with the representation of the measured values obtained ("measurement data") and the corresponding data adjustment for the purposes of surface analysis and the chemical structure the surface of oxidized activated carbon as an intermediate of the present invention carried out the process;

[0165]

7bein further XPS spectrum of O 1s region scans the determined in this way measurement data ("data") and the corresponding data adjustment for oxidised at their surface but not yet nitrogen or nitrogen-functionalized modified activated carbon.

[0166]

The figure representation according to Figure 1a illustrates the effect of oxidation time on different parameters or to the textural properties of the obtained on the basis of the present invention carried out oxidation, oxidized on the surface of activated carbon, with (air) oxygen as oxidizer ("OR") was used (thermal oxidation) and which on the one hand a low activated charcoal and, secondly, a highly activated charcoal has been used as the starting activated carbon.

The figure shows that as the oxidation time, the content of volatile components ("FB") for both activated carbon significantly increases.

As indicated above, provides the volatile content of the activated carbon on its surface is a measure of the content of oxygen-containing functional groups as they are formed during the oxidation.

Thus, an increase in the content of oxygen-containing functional groups is observed for both active carbons with increasing oxidation number which can act in the course of the invention implemented process management as a reactant for the Stickstoffmodifizierungsreagenz ("SMR"). 1a further illustrates that under the given process conditions with increasing oxidation time the surface pH value of the activated carbon of a slightly basic range falls into a slightly acidic range.

Finally, the graphical representation of Figure 1a shows that the total pore volume (Vtot) and the tap density (RD) are modified slightly for both activated carbons in the course of the thermal oxidation, with respect to the total pore volume is present even a slight increase.

[0167]

1bzeigt to further illustrate the dependence of the surface pH value of the oxidized at its surface activated carbon on the one hand, and the tap density and the total pore volume on the other hand by the content of volatile components as a measure of the content of oxygen-containing functional groups of the oxidized at its surface activated carbon as a intermediate of reacted according process management. 1b shows likewise that slightly decreases with increase of the content of oxygen-containing functional groups and thus the degree of oxidation, the pH and the tap density of the oxidized activated carbon on their surface, while in terms of the pore volume, an increase is observed.

[0168]

Furthermore, the figure diagram illustrates according 1c that within the thermal oxidation using (atmospheric) oxygen as oxidizer ("OR") (oxidation), the formation of basic surface oxides is preferred.

In contrast, the figure shows representation 1d according to that using urea or

Hydrogen peroxide (chemical oxidation) equally acidic surface oxides are formed.

In this context, the figure representations according confirm 1e and 1f the previously mentioned experimental findings: So shows 1f that the above-mentioned thermal oxidation decisive for desorption of carbon monoxide (CO) leads as a measure of the formation of basic surface oxides during the formation of acidic surface oxides, which is indicated by the desorption of carbon dioxide (CO2), occurs only in a limited volume.

In this context shows 1e that under oxidation conditions as an intermediate an oxidized on the surface of activated carbon is obtained in the context of the present invention implemented process management, which has an increased content of acidic surface oxides.

[0169]

Overall, the figure diagram illustrates under 1a to 1e so that it or in accordance with the invention implemented process management with the targeted selection

Tuning the oxidation conditions to form the oxidized at its surface activated carbon is a controllable or adjustable individually process, on the basis of the intermediate thus obtained can be formed individually, in particular in view of the following equipment or

Modification with nitrogen.

As in this regard in the context of variable oxidation process parameters are in particular the one employed oxidizer ("OR") and questioned for different temperature and oxidation time.

The benefits provided under the inventively realized process control oxidative pretreatment for obtaining the oxidized on the surface of activated carbon as an intermediate therefore constitutes an adjustable or individually tunable process, in particular the intensity and the degree of oxidation by process parameters such as oxidation time, oxidation temperature and concentration of oxidizing reagent used ("OR") and controlled the type of surface oxides formed on the choice of the oxidizing agent and can be tailored.

[0170]

Furthermore, show the character illustrations in Figures 2a and 2b the Wasserdampfisothermen below on several ways on its surface oxidized activated carbon as compared to a non-oxidized starting activated carbon, 2 to thermal oxidation using (atmospheric) oxygen as oxidizer ("OR") various temperatures (thermal oxidation) and 2b stop the use of oxidizing reagents ("OR") based on hydrogen peroxide and nitric acid oxidation at different times (oxidation).

It can be seen in both figures that the processing performed oxidation leads to a shift of the adsorption of water in the direction of smaller p / p0-values, which corresponds to an increase in the capacity as a result of the performed oxidation create hydrophilic surfaces, which in turn in view of the following Connecting the Stickstoffmodifizierungsreagenzes ("SMR") is of relevance.

2a shows in this connection that an increase in the temperature of a part, and the oxidation time and duration on the other hand hydrophilic to a higher capacity or to an increased formation surfaces of the thus treated activated carbon leads.

Accordingly, 2b be seen that under the present conditions nitric acid leads to a greater increase in capacity and a higher content of hydrophilic surfaces when compared to hydrogen peroxide, it also being possible here to further increase the respective values can be observed with the increase of the oxidation time.

[0171]

The figure representation according to Figure 3a shows the Wasserdampfisothermen obtained for using ammonia nitrogen modified or stickstofffunktionalisierte at different temperatures activated carbon, at a lower Funktionalisierungstemperatur of 500 ° C compared to a higher Funktionalisierungstemperatur of 920 ° C a larger shift in the adsorption to smaller p can be observed / P0 values, which speaks to a higher functionality, especially with regard to the formation of hydrophilic surfaces, the active carbon obtained at lower temperatures or an integration of nitrogen in the carbon skeleton at higher temperatures.

In this context, the figure display shows 3b according to the underlying parameters and textural properties of the activated carbon are not adversely affected on the basis of the implemented process management according to the invention with the oxidation of starting activated carbon and subsequent nitrogen modification or functionalization.

Rather, both in terms of the total pore volume according to Gurvich (Vtot), the micropore volume (VMIC) and the MP-BET surface area is observed that the processing performed oxidation to form functional oxygen-containing groups on the surface of the activated carbon, even a slight increase, and the subsequent nitrogen modification or functionalization at best leads to a slight decrease in the values in question, which however still lie above the values of the appropriate starting material.

The inventively realized process control thus resulting in any way to a deterioration of the listed parameters of the underlying activated carbon, in this respect also be no significant differences in the temperature selected at the Stickstofffunktionalisierung or modification.

The investigated in 3b activated carbons were equally equipped using ammonia nitrogen.

[0172]

The figure representation according 4a again shows an exemplary, the present invention conducted processes underlying reaction sequence wherein Figure A represents the carbon skeleton of the oxidized on the surface of activated carbon (intermediate) with the trained oxygenated functional groups.

With the addition of urea as Stickstoffmodifizierungsreagenz ("SNR") is subsequently obtained the illustrated in Figure B intermediate having tailed urea component.

Figure C shows at a temperature treatment of 500 ° C obtained (intermediate) product of the reaction of urea to give the corresponding nitrogen-containing functional groups at the surface of the carbon matrix, whereby in this respect cyclic urea derivatives, nitriles, amides, or primary amines are formed.

By a further heat treatment at 920 ° C integration of the nitrogen is as shown below degradation of nitrogen-containing functional group in Figure D in the carbon skeleton or in the carbon matrix of nitrogen or nitrogen-functionalized modified activated carbon.

[0173]

In this figure the representation Zusammenhag illustrated according 4b based on an XPS spectrum of the presence of various species of nitrogen-containing functional groups at different time points or at different temperatures during the process of modification or nitrogen functionalization.

While at low temperatures, in particular nitrogen-containing functional groups on the basis of amides or

Pyrroles are present at higher temperatures of 500 ° C., a conversion and a shift to particular quaternary nitrogen-containing groups, while at even higher temperatures of 920 ° C, the content of the abovementioned groups significantly declining, suggesting an integration of nitrogen in the carbon skeleton or suggesting in the carbon matrix of the treated activated carbon.

[0174]

As regards the character representation in accordance with 5, this shows a comparison of the penetration times by three different inventive activated carbon with respect to the sorption of ammonia (NH3), hydrogen sulfide (H2S) and sulfur dioxide (SO2) as compared to a starting active carbon.

For this purpose, the appropriate activated carbons were exposed to a continuous flow of being rich in failure with the respective harmful gas atmosphere under defined conditions for a specified period and determines the respective breakthrough times.

All activated carbons of the invention exhibit significantly higher than the starting activated carbon beyond sorption performances both in terms of ammonia (NH3), hydrogen sulfide (H2S) and sulfur dioxide (SO2).

Overall, the sorption behavior of the activated carbons according to the invention can be classified as excellent.

[0175]

Furthermore, the figure representations illustrate accordance 6a and 6b, the significantly improved sorption behavior of an inventively equipped charcoal (final product) as compared to the starting material or the starting activated carbon used employed.

Thus, the activated carbon produced on the basis of the inventive method performed and equipped with nitrogen shows a significantly improved breakdown behavior towards the to be sorbed gases sulfur dioxide (SO2) (6a) on the one hand and hydrogen sulphide (H2S) (6b) on the other.

To determine the breakdown data the respective activated carbons were exposed under defined conditions of a constant volume flow with the enriched to be sorbed gas atmosphere for a defined period, the references cited in the figures of the concentrations to be sorbed gas were used.

[0176]

Finally, the figure diagrams show 7a and 7b according to the presence of oxygen-containing functional groups of a subsequent modification of the nitrogen or

Stickstofffunktionalisierung used oxidized activated carbon on its surface.

By oxidation with the inclusion of an oxidizing reagent ("OR") can be obtained many oxygen-containing functional groups, such as.

B. carboxyl and carbonyl groups which or as a reactant

Amino groups for subsequent modification or

Act functionalization with the Stickstoffmodifizierungsreagenz ("SMR").

[0177]

In summary, it is within the scope of the present invention for the first time succeeded through the implementation of a special process, a functionalization of activated carbon or of polymer-based spherical activated carbon (PBSAC) with nitrogen-containing functional groups or of activated carbon with integration of nitrogen in the carbon surface (N-doping) to obtain.

The resulting activated carbon or polymer-based spherical activated carbons (PBSACs) in this case have a reactivity towards different target gases.

As appropriate target gases for the activated carbons obtained on the basis of the inventive method performed gases can come into consideration, their degradation via oxidation on the carbon surface is possible, as is the case for example, for SO2, H2S, ASH3 and DMS.

[0178]

The activated carbons obtained in the context of the inventive method performed alike can have nitrogen-containing functional groups on the surface of which, or with organic gases

Steaming bonds can form, such as formaldehyde and optionally NOx compounds.

By Stickstofffunktionalisierung the basicity of the surface of the activated carbon can be (as opposed to oxidation) is increased in general.

The formation of nitrogen-containing functional groups or the doping of activated carbon with nitrogen, in the context of the present invention implemented process management in non-limiting manner by filling the pores with a nitrogen-containing organic compound (such.

B. Urea) carried out in particular from aqueous solutions and a subsequent pyrolysis.

[0179]

After the actual manufacturing process itself can be a purification step, in particular a washing with water, connect, especially to any pyrolysis or

To remove combustion residues.

The selected when Stickstofffunktionalisierung or modification temperature influences in the context of the present invention implemented procedure, the chemical constitution of the incorporated nitrogen.

In this context, lead low temperatures, especially in the range of 500 ° C, in particular to the formation of nitrogen-containing functional groups, while higher temperatures, especially in the range of 920 ° C primarily leads to the N-doped activated carbons described above.

[0180]

Submit Corrections Close

In the present invention, it has shown to be particularly advantageous, that in the context of the inventive method performed an upstream oxidation of the active carbon is carried out, since this enables the absorption of nitrogen in significant quantities.

In this connection correlates the amount of absorbed nitrogen or integrated with the volatile consituents of the oxidized activated carbon as a measure of the amount or the content of surface oxides on the activated carbon.

EMBODIMENTS:

1. Preparation of an inventively equipped with activated carbon Stickstofffunktionalisierung or modification:

[0181]

As part of the production of activated carbons according to the invention described below, a spherical activated carbon was used as the starting activated carbon as a starting material, which has been prepared on the basis of divinylbenzolvernetztem polystyrene.

Such output activated charcoal is of the firm. Blücher GmbH, Erkrath (Germany).

a) 500 g of the starting activated carbon with 1,000 g of HNO 3 solution (50%) merged to prepare the activated carbon A inventive, and the resulting mixture was stirred for 240 min.

Subsequently, the excess nitric acid was decanted off and the oxidized active carbon thus obtained was washed with distilled water and then dried.

An amount of 500 g of the oxidized activated carbon on their surface were then combined with 1,000 g of a saturated solution of urea, and the resulting mixture was stirred for 2.5 h.

The excess urea solution was decanted.

Equipped with the urea solution activated charcoal was then treated in an inert gas at 500 ° C for 240 min.

The nitrogen-modified or stickstofffunktionalisierte activated carbon was then washed with distilled water and dried to any combustion or

Remove pyrolysis residues.

b) 8 500 g of the starting activated carbon with 1000 g of HNO3 solution were combined (50%) and the resulting mixture stirred for 240 minutes to prepare the activated carbon according to the invention.

Subsequently excess HNO3 solution was decanted, and the oxidized activated carbon thus obtained was washed with distilled water and dried.

Subsequently, 500 g of the oxidized activated carbon with 1,000 g of a saturated solution of urea were combined, and the resulting mixture was stirred for 2.5 h.

The excess urea solution was decanted.

Equipped with the urea solution activated charcoal was treated in an inert gas at 920 ° C for 240 min.

The stickstofffunktionalisierte or nitrogen-modified activated carbon thus obtained was washed with distilled water and then dried to remove combustion residues.

c) 500 g of the starting activated carbon were treated in a rotary kiln in air flow at 450 ° C for 120 minutes to prepare the activated carbon C of the invention.

The oxidized activated carbon thus obtained was combined with 1,000 g of a saturated solution of urea, and the resulting mixture was stirred for 2.5 h.

The excess urea solution was decanted.

Equipped with the urea solution activated charcoal was then treated in an inert gas at 500 ° C for 240 min.

The resulting nitrogen-modified active carbon or stickstofffunktionalisierte was finally washed and dried to remove any combustion residues.

d) 50 g of the starting activated carbon were treated in a rotary kiln in air flow at 450 ° C for 120 minutes to prepare the activated carbon according to the invention D. 500 g of the thus obtained activated carbon was combined with 1,000 g of a saturated solution of urea, and the resulting mixture was stirred for 2.5 h.

The excess urea solution was decanted, and equipped with the urea solution activated charcoal was treated with inert gas at 920 ° C for 240 min.

The nitrogen-modified active carbon or stickstofffunktionalisierte thus obtained was finally washed with distilled water and then dried to remove any combustion residues.

[0182]

The activated carbons A to D according to the invention each have significantly elevated levels of nitrogen, and the chemisorptive properties are each classified as excellent.

[0183]

In this context, the respective nitrogen content of the activated carbons according to the invention was determined by methods known per se.

The total nitrogen content can be determined by means of known per se elemental analysis, while the identification of volatiles ("FB") according to the ISO 562: can be done 1981st

From the difference of certain means of elemental analysis total nitrogen content on the one hand and according to the ISO 562: 1981 certain content of volatile constituents (ie volatile nitrogen-containing functional groups), the content of immobilized or built in the carbon skeleton nitrogen can then be determined.

[0184]

Specifically result for the inventive activated carbons A to D the following nitrogen contents: Thus, the activated carbon of the invention A represents a total nitrogen content of 13% to, based on the dry weight of the nitrogen-modified or nitrogen-functionalized activated carbon, thereof about 12%, based on the total nitrogen content, is in the form of volatile constituents ("FB").

For the inventive activated carbon B results in a corresponding total nitrogen content of 18 wt .-%, based on the dry weight of the nitrogen-modified or nitrogen-functionalized activated carbon, in this respect, only 5% of nitrogen, based on the total nitrogen content in the form of volatile constituents ("FB") is present, that is, 95% of the nitrogen in the carbon matrix are integrated before.

[0185]

Furthermore, results for the inventive activated carbon C a total nitrogen content of 15 wt .-%, based on the nitrogen-modified or stickstofffunktionalisierte activated carbon.

In this case, the proportion of the volatile components in the form of ("FB") nitrogen is present, based on the total nitrogen content, 14%.

[0186]

Finally, results for the inventive activated carbon D a total nitrogen content, relative to the nitrogen-modified or activated carbon stickstofffunktionalisierte of 19.5 wt .-%, in which connection 7% of the nitrogen in the form of volatile components ("FB") is present.

[0187]

The results illustrate the high content of nitrogen in relation to the activated carbons according to the invention, which are obtained on the basis of the inventive method performed, where in this regard is guaranteed equally, that a high proportion of nitrogen present firmly integrated in the carbon skeleton.

The related integration or

Incorporation of the nitrogen in the carbon skeleton is formed stronger at higher temperatures while the nitrogen modification or functionalization, while at low temperatures is increased, the proportion of nitrogen-containing functional groups.

[0188]

With respect to the activated carbons according to the invention breakdown studies were also carried out with respect to hydrogen sulfide (H2S).

PAC ET AL. EXHIBIT 1019

In this context, a defined bed of the respective activated carbons A to D, each of which had a height of 2 cm, exposed at temperatures from 30 ° C to a constant volume flow with constant flow rate, which contained 20 ppm H2S.

Activated charcoal invention had thereby following the penetration times on: How could the inventive activated carbon A is a breakthrough time of 112 minutes and for the inventive activated carbon B a breakthrough time of 123 minutes can be determined.

Furthermore resulted for the inventive activated carbon C a breakthrough time of 112 minutes, and for the inventive activated carbon D was a breakthrough time of 119 minutes can be determined.

A used as comparative untreated starting activated carbon had a breakthrough time of only 75 min.

The above results demonstrate the significant improvement of the adsorption capacity of the activated carbon according to the invention with respect to the noxious gas to be sorbed.

[0189]

The above-described preparation examples were repeated except as Stickstoffmodifizierungsreagenz melamine ("activated carbon I"), gaseous ammonia ("activated carbon F"), ammonia water ("activated carbon G") or amino acids ("activated carbon H") were used; comparable results were obtained.

2. Further embodiments and experimental studies:

[0190]

Below is underlying to the previously described figure representations investigations or

Embodiments BEYOND received:

a) As indicated above, the figure representation is 1a a study of the influence of the performed oxidation of the starting activated carbon on certain parameters of the resultant oxidized on the surface of activated carbon based accordance.

In this regard, a low output activated charcoal with a relatively low total pore volume on the one hand and a high output activated charcoal with a relatively high total pore volume on the other hand was used as employed for the subsequent oxidation material.

The oxidation was carried out using (atmospheric) oxygen as oxidizer ("OR") is carried out within the meaning of the previously defined thermal oxidation, wherein the parameters shown in Figure 1a are determined as a function of oxidation time in this context.

It is found that for both output activated carbons with increasing oxidation time, an increase of the volatile components ("FB") is present, which corresponds to a generation of oxygen-containing functional groups at the surface of the respective activated carbon.

Similarly, the figure shows display 1a according to that with increasing oxidation time the surface pH value and the tap density of the oxidized, but not yet a nitrogen or modification

Stickstofffunktionalisierung subjected activated carbon sink.

Then walking is observed with respect to the total pore volume, a slight increase.

The dependencies discovered in this regard that at issue parameters of the underlying process operation is confirmed both by the character representation according to 1b.

For more on this subject have to be made to the above observations regarding the corresponding figure represenations.

In summary, the Court finds that by careful selection of process parameters such.

B. the oxidation time can be adjusted as required in the context of the present invention conducted processes underlying oxidation of activated carbon output, the features that the oxidised at their surface of activated carbon as an intermediate of the present invention implemented process management and tailor-made.

b) The aforementioned influence of process parameters on the textural properties of the oxidised at their surface of activated carbon is also by the figure representation according 1c to 1f underlying investigation complex which or on the influence of oxidation conditions on the basicity

PAC ET AL. EXHIBIT 1019

Acidity of the surface oxides formed turns off, confirmed.

In this context, appropriate output activated carbons were firstly a thermal oxidation using (atmospheric) oxygen as oxidizer ("OR") and on the other hand a chemical oxidation using nitric acid or

Hydrogen peroxide as oxidizer ("OR") subjected.

A subsequent analysis of the resulting oxidized on their surface active carbons shows that for thermal oxidation conditions primarily basic surface oxides are formed, whereas for chemical oxidation conditions and acidic surface oxides are formed.

Can be selectively adjusted or tailored On this basis, therefore, the chemical structure of the surface of the oxidized activated carbon.

For further details, reference may be made to avoid unnecessary repetition of the above observations regarding the corresponding figure representations.

In conclusion, therefore, the underlying studies show that by careful selection of the oxidation conditions or alkalinity

Acidity can be controlled by forming a special surface oxides.

c) In the context of another investigation complex corresponding starting materials were a part of a thermal oxidation under the influence of (atmospheric) oxygen and on the other hand a chemical oxidation using hydrogen peroxide or

Nitric subjected as respective oxidation reagents ("OR").

The resultant oxidized at its surface activated carbons (intermediate) were then in terms of adsorption or

Absorption of water vapor in comparison to an untreated starting activated carbon (starting material) were examined.

As shown in the figure in accordance with representations 2a and 2b, takes place here for the treated activated carbons marked shift towards smaller P / P0 values.

In this regard, reference can be made to the above statements to 2a and 2b.

As a result, show the 2a and 2b taken in the figural depictions in accordance regarding investigations that Wasserdampfisothermen be significantly affected by the inventively provided oxidation of activated carbon, which in particular as a measure of the presence of an increased hydrophilicity of the surface of the activated carbon as a result of the generated oxygen-containing functional groups can be used.

d) With regard to the figure representation according to Figures 3a and 3b underlying studies, so these to test parameters and analytical results for two stickstofffunktionalisierte or nitrogen modified in various ways activated carbons focus according to the invention (N-PBSAC) which, each starting from starting activated carbon based on carbonized were prepared activated polymers (PBSAC).

The oxidized Basisadsorbenz produced in the context of the present invention the method performed (intermediate) containing 13.7 wt .-% while volatiles ("FB"), based on the dry weight of the intermediate.

With respect to a first oxidized on the surface of activated carbon then the nitrogen modification or functionalization at a temperature of T = performed was 500 ° C, whereby in this respect the following process steps have been performed.

The activated charcoal was on its surface in a NH3 flow rate (5 l / h) heated to 100 ° C at a heating rate of 36 K / min, and the temperature was maintained for 30 min.

It was then heated to 400 ° C at a heating rate of 26 K / min.

The mixture was then heated in a nitrogen stream at a flow rate of 6 l / h to 36 K / min to 500 ° C, whereby the temperature was maintained for 240 min.

This was followed by cooling over night under a nitrogen atmosphere.

With regard to the second activated carbon method as described above was, but with the proviso that failure to heating to 500 ° C, but at 920 ° C under a nitrogen atmosphere.

The resulting functionalized activated carbon had the following properties:

[0191]

Nitrogen Modified or stickstofffunktionalisierte charcoal <sep> T = 500 ° C <sep> T = 920 ° C

PAC ET AL. EXHIBIT 1019 Page 2019 of 2194

N content [wt .-%] <sep> 4.11 <SEP> 6.49

volatiles ("FB") <SEP> 10.2 <SEP> 0.86

RD [g / l] <sep> 547 <SEP> 541

pH <sep> 8.5 <SEP> 9.9 [cm <3>

Vtot / g] <sep> 0.7397 <sep> 0.7166 [cm <3>

VMIC / g] <sep> 0.5846 <sep> 0.5870

Mesopores [%] <sep> 21.0 <SEP> 18,1MP-BET [m <2>

/ g] <sep> 1476 <sep> 1453

The above table shows in particular that at the higher temperatures during the modification or nitrogen

Stickstofffunktionalisierung there is a reduction in the proportion of volatiles ("FB"), which corresponds to an installation or an integration of the nitrogen in the carbon skeleton or carbon matrix thus treated activated carbon.

In contrast, it should be noted for lower temperatures that the proportion of volatile constituents will be higher, which is interpreted as evidence for the presence of nitrogen in the form of nitrogen-containing functional groups.

In addition, an analysis of the corresponding Wasserdampfisothermen (3a) that at low temperatures (T = 500 ° C), the functionalization of the treated activated carbon is higher, as compared to that at higher temperatures (T = 920 ° C) functionalized activated carbon stronger to a shift of the corresponding adsorption or

Desorptionsäste to low P / P0 values leads.

Also shows, as shown in Figure 3b, that the oxidized base and the oxidized at its surface activated carbon is present, an increase in terms of the parameters according to the total pore volume, micropore volume and the MP-BET surface area, these values being represented by the following Stickstofffunktionalisierung only be reduced slightly and still be above the output values based on the output activated carbon used.

In this regard, reference can be made to the above statements on the figural depictions in accordance with 3a and 3b.

As a result, the present studies show that higher Funktionalisierungstemperaturen to increased integration or

Incorporation of nitrogen in the carbon skeleton of the thus treated activated carbon perform, while lower temperatures in the functionalization of forming nitrogen-functional groups lead.

In addition, it can be shown that the invention implemented process management leads to no negative impact on the product parameters.

e) As indicated above, the figure diagram shows the invention according 4a a process carried out by way of example underlying reaction progress with the integration of nitrogen in the carbon skeleton.

An analysis based on an XPS spectrum is as shown in Figure 4b, that at low temperatures in the context of modification or nitrogen

Stickstofffunktionalisierung primarily nitrogen-containing functional groups on the basis of amides or

Pyrroles are present, while the temperature increases there is a shift to nitrogen-containing functional groups on the basis of quaternary nitrogen compounds.

In a further temperature increase, the corresponding XPS signals of the respective functional groups take on what shall be used as evidence of the integration of nitrogen in the carbon skeleton or in the carbon matrix of the treated activated carbon.

For further details, according to the corresponding statements to the character representations 4a and 4b are made.

f) In the context of the representation according to FIG 5 experiments underlying the breakthrough times of three different inventive activated carbons for the harmful gases NH3, H2S and SO2 compared to an untreated starting activated carbon were determined.

Regarding the breakthrough times for ammonia (NH3) results in this case for the initial activated carbon, a value of only 14 minutes, while for the inventive activated carbon with nitrogen or modification

Equipment, a respective value of 20 min, 22 min and 33 min is obtained.

In terms of the breakdown time to hydrogen sulfide (H2S), a value of 80 min is achieved, while in contrast, values of 120 minutes, 110 minutes or 120 minutes again be obtained for the activated carbon of the invention for the untreated starting material.

Finally, a value of 30 minutes was determined with respect to the breakdown time to sulfur dioxide (SO2) for the untreated raw material, while for the three inventive activated carbon values of 78 min, 47 min and min was determined 58th

In this regard, reference can be made to the above statements: 5.

As a result, show the tests carried out, that activated carbons of the invention have, compared to the starting material significantly increased the penetration times for the disputed pollutants, so that the activated carbons according to the invention compared to the starting material are greatly improved in terms of performance.

g) These findings are confirmed in accordance with 6a and 6b the referenced studies in the figure representation by the: So both in terms of sulfur dioxide (SO2) as well as with regard to hydrogen sulfide (H2S), respectively, a significant improvement of the breakdown behavior compared to a untreated starting charcoal observed.

In terms of the figure representation according 6a underlying test parameters a packed bed of the to be tested activated carbon was prepared with a bed height of 1.5 cm and a bed area of 1.3 cm <2>, wherein the packed bed at a relative humidity of 70% a SO2 -Volumenstrom with 1,000 ppm SO2 at 220 ml / min was suspended.

In the final product under investigation is a nitrogen-modified or stickstofffunktionalisierte at temperatures of 920 ° C. The activated carbon of the invention.

6b in relation to the tested activated carbon was used in the form of a packed bed with a bed height of 1 cm.

At a relative humidity of 50% the activated carbon bed was exposed to H2S flow rate with 20 ppm H 2 S at 0.2 m / s.

When the activated carbon used is equal to that already in 6a referenced activated carbon.

The underlying studies thus show that a significant improvement in results based on the Stickstofffunktionalisierung invention in terms of chemisorption of harmful gases described above, which is reflected in significantly increased penetration times.

h) As part of a further study complex structure analyzes were performed on a part of the invention, carried out according to the method for obtaining the intermediate on its surface oxidized activated carbon.

As mentioned previously, are represented by the oxidation with the inclusion of an oxidizing reagent ("OR") different oxygen-containing functional groups, or

Species generated, which subsequently or as a sort of anchor groups

Reactants for the connection with the Stickstoffmodifizierungsreagenz act ("SMR").

Equally influence the oxygen-containing functional groups prepared in this manner, the surface properties of the oxidized activated carbon, particularly with regard to the pH value; the hydrophilicity, and the like, which also leads in particular to an optimization of the subsequent interaction with the Stickstoffmodifizierungsreagenz.

In this regard, reference can be made to the above remarks to the figure representations according 7a and 7b.

i) If further activated carbons according to the invention were prepared using urea solutions, in the method described above, wherein the urea treatment followed by heat treatment at T = 900 ° C was carried out.

The above surface oxidation was carried out in the presence of atmospheric oxygen.

The activated carbon obtained were for the breakdown measurements on a packed bed (diameter: 50 mm; height: 20 mm) tested for various gases (H2S and SO2) (current with 1,000 ppm noxious gas; flow rate: 0.1 m / s; 70% relative humidity ; measuring temperature: 20 ° C; breakthrough in 10 ppm for H2S and 5 ppm for SO2).

Served as a comparison an untreated activated carbon (Comparative I) and a conventionally base-impregnated activated carbon (compare II).

For H2S or

SO2 was in the activated carbon of the invention is a breakthrough time of 122 min and 133 min are determined, while for the comparative carbon I the values of <1 min or 4 min and for comparative coal II at 57 min and 46 min were.

The activated carbon of the invention thus have two- to three-fold increase in the penetration times compared to conventionally impregnated activated carbons; for cyclohexane and chlorine very long breakthrough times are obtained.

3. Comparison of an activated carbon according to the invention with nitrogen modification to comparison activated carbons:

[0192]

In the context of investigations underlying the present invention, an activated carbon, as obtained on the basis of the embodiments to the prepared under 1) according to the invention activated carbon B was compared to Comparative activated carbons, which were equipped in different ways with nitrogen:

Thus, a first comparison coal I was obtained by mixing was carried out starting from corresponding polymers, a two-step process for the preparation of the activated carbon based on a carbonization and subsequent activation, has been the activation in the presence of carbon dioxide, water vapor and ammonia gas carried out; the nitrogen-containing agent in the form of NH3 was thus added his frame of activated carbon production during activation.

[0193]

Furthermore, it was given a second comparative activated carbon II, by a finished activated carbon (ie after carbonization and activation) subjected as such a conventional urea impregnation, was said in this regard mixed a urea solution with activated carbon and impregnated activated carbon in this way or soaked.

The activated carbon thus obtained was then dried.

Finally, a comparison of activated carbon III was obtained by an activated carbon was directly subjected to nitrogen modification without intermediate oxidation by a urea solution with activated carbon was contacted and the thus treated activated carbon a subsequent heat treatment was subjected.

The comparative activated carbon III thus differs from the activated carbon according to the invention in that an activated carbon was subjected as such and thus not oxidized on the surface of activated carbon a subsequent treatment for nitrogen modification.

The corresponding active carbon thus had with respect to the Stickstoffmodifizierungsreagenz no anchor groups.

[0194]

At the investigations thus obtained respective analyzes of the nitrogen content and further investigations with respect to the breakdown behavior of hydrogen sulfide (H2S) were performed.

Regarding the analysis of the nitrogen content and the presence of nitrogen in the activated carbon can be made to the above embodiments.

The breakthrough experiments were = 30 ° C performed on the basis of a bed of the respective activated carbon with a height of 2 cm in a constant volume flow at a temperature of T, where the run with a constant flow rate through the bed volume flow was provided with 20 ppm H2S.

The following table shows the results obtained.

Activated carbon <sep> B (Req.) <Sep> I (See.) <Sep> II (See.) <SEP> III (See.

)

Nitrogen content N content [wt .-%] <sep> 18 <SEP> 1 <SEP> 4 <sep> 8

Nitrogen content not in the form of volatile components (wt .-%) <SEP> 95 <SEP> ≤ 0.1 <sep> ≤ 0.1 <sep> ≤ 0.5

Breakthrough time against H2S [min] <sep> ≥ 100 <SEP> 54.5 <SEP> 62.5 <SEP> 81

[0195]

The table shows that with respect to the activated carbon according to the invention B, both the content is increased in the skeleton bound (ie, not present in the form of volatile components) of nitrogen in the activated carbon, wherein in contrast to the comparative activated carbon a significantly greater proportion of the nitrogen in the form of non-volatile nitrogen components present, which is to be understood as a measure for the integration of the nitrogen in the activated carbon matrix or the activated carbon scaffold.

[0196]

Similarly, the activated carbon according to the invention B significantly improved breakdown behavior with respect to hydrogen sulfide, and therefore a significantly improved performance compared to the comparison to activated carbons I to III.

[0197]

As part of a further investigation, the underlying active carbons, namely, the activated carbon of the present invention B and the comparative activated carbon I to III, to a washing operation using 1 N hydrochloric acid for a period of time were subjected to one hour.

Subsequently, the activated carbons were washed neutral and subsequently dried.

With the thus treated activated carbons breakthrough measurements were again with respect to hydrogen sulfide (H2S) as described above is performed.

While the activated carbon according to the invention B represents a breakthrough time of still more than 100 minutes could be determined, were the corresponding breakthrough times for the comparative activated carbons I to III 15 min, 18 min or 25 min.

This should be seen as evidence that was removed a significant amount of nitrogen due to the washing process with hydrochloric acid with respect to the comparative activated carbon I to III, which is not the case for the inventive activated carbon B.

This means that at least substantially does not exist with respect to the comparison active charcoal I to III of the nitrogen in immobilized form and thus can easily be removed.

In contrast, is immobilized due to the incorporation of nitrogen in the carbon skeleton according activated carbon B of nitrogen and firmly anchored, resulting in the high resistance against acids.

[0198]

As a result, the tests carried out show the high efficiency and the positive characteristics of the available on the basis of the inventive method performed nitrogen or nitrogen-functionalized modified activated carbons.

QUOTES contained in the description

[0199]

This list of references cited by the applicant has been generated automatically and is recorded exclusively to inform the reader.

The list is not part of the German Patent and

Utility model application.

The DPMA shall not be liable for any errors or omissions.

Cited patent literature

[0200]

WO 98/07655 A1 [0009]

DE 4328219 A1 [0010, 0105]

DE 4304026 A1 [0010, 0105]

DE 19600237 A1 [0010, 0105]

DE 19625069 A1 [0010]

DE 102007050971 A1 [0011]

DE 19519869 A1 [0015]

EP 1918022 A1 [0105]

US 7737038 B2 [0105]

Cited non-patent literature

[0201]

H. v.

Kienle and E. baths, "activated carbon and its industrial application", Enke Verlag Stuttgart, 1980 [0006]

European Standard EN 14387 (January 2004) [0016]

ISO 562: 1981 [0061]

ISO 562: 1981 [0086]

ISO 562: 1981 [0090]

ISO 562: 1981 [0090]

L. Gurvich (1915), J. Phys.

Chem.

Soc.

Russ. 47, 805, and on S. Lowell et al, Characterization of Porous Solids and Powders:. Surface Area Pore Size and Density, Kluwer Academic Publishers, Article Technology Series, pages 111 et seq [0093]

RW Magee, Evaluation of the External Surface Area of Carbon Black by Nitrogen adsorption, Presented at the Meeting of the Rubber Division of the American Chem.

Soc., October 1994 z.

B. gives a lecture in: Quantachrome Instruments, AUTOSORB-1, AS1 WinVersion 1.50 Operating Manual, OM, 05061, Quantachrome Instruments in 2004, Florida, USA, pages 71 et seq [0095]

ASTM D6556-04 [0098]

ASTM D6556-04 [0099]

Römpp Chemie Lexikon, 10th

Edition, Georg Thieme Verlag, Stuttgart / New York, keyword: "BET method", including the references cited therein, and to Winnacker-Kuchler (. 3

Edition), Volume 7, pages 93 ff.

[0099]

Z. Anal.

Chem.

238, pages 187-193 (1968) [0099]

ASTM D2862-97 / 04 [0106]

ISO 562: 1981 [0183]

ISO 562: 1981 [0183]

(19) Deutsches Patent- und Markenamt

(10) **DE 20 2012 003 747 U1** 2013.01.10

(12) # Gebrauchsmusterschrift

(21) Aktenzeichen: **20 2012 003 747.1**
(22) Anmeldetag: **16.04.2012**
(47) Eintragungstag: **15.11.2012**
(43) Bekanntmachungstag im Patentblatt: **10.01.2013**

(51) Int Cl.: ***C01B 31/08*** (2012.01)
A41D 13/00 (2012.01)
B01J 20/20 (2012.01)
B01J 21/18 (2012.01)

(66) Innere Priorität:
10 2011 117 715.2 **07.11.2011**
10 2011 117 822.1 **08.11.2011**

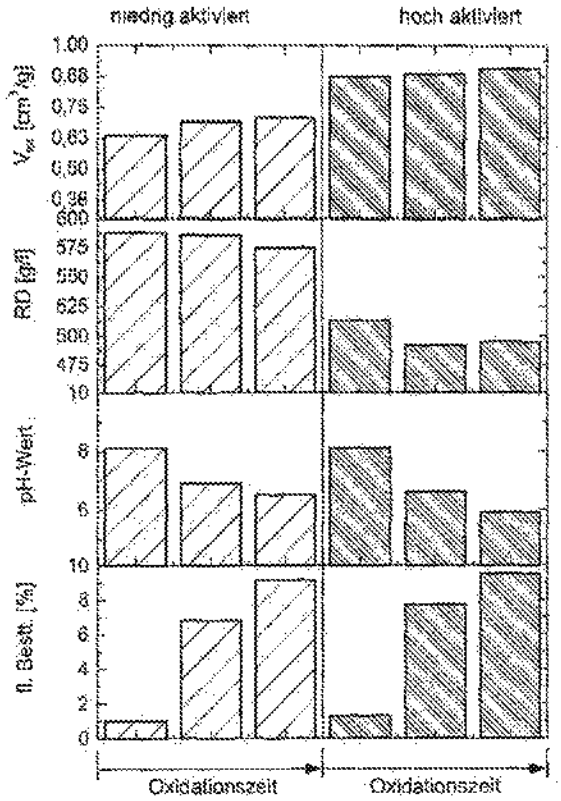
(73) Name und Wohnsitz des Inhabers:
Blücher GmbH, 40699, Erkrath, DE

(74) Name und Wohnsitz des Vertreters:
Patentanwälte Gesthuysen, von Rohr & Eggert, 45128, Essen, DE

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: **Oberflächenmodifizierte Adsorbentien**

(57) Hauptanspruch: Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle, insbesondere mit katalytischen und/oder reaktiven Eigenschaften, vorzugsweise Aktivkohle mit Stickstoff als katalytisch aktivem Heteroatom, erhältlich durch ein Verfahren, wobei bei dem Verfahren eine als Ausgangsmaterial eingesetzte Aktivkohle ("Ausgangsaktivkohle") zunächst einer Oberflächenoxidation unter Verwendung und/oder in Gegenwart mindestens eines Oxidationsreagenzes ("OR") unterzogen wird und die auf diese Weise erhaltene, an ihrer Oberfläche oxidierte Aktivkohle nachfolgend einer Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff, insbesondere mit stickstoffhaltigen funktionellen Gruppen, unter Verwendung und/oder in Gegenwart mindestens eines Stickstoffmodifizierungsreagenzes ("SMR") unterzogen wird.



Beschreibung

[0001] Die vorliegende Erfindung betrifft das technische Gebiet adsorptiver Materialien auf Basis von Aktivkohle, welche insbesondere katalytische und/oder reaktive Eigenschaften, insbesondere auf Basis einer Stickstoffmodifizierung und/oder Stickstofffunktionalisierung, vorzugsweise mit Stickstoff als katalytisch aktivem Heteroatom, aufweisen.

[0002] Insbesondere betrifft die vorliegende Erfindung eine stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle, insbesondere mit katalytischen und/oder reaktiven Eigenschaften, vorzugsweise eine Aktivkohle mit Stickstoff als katalytisch aktivem Heteroatom, welche durch ein Verfahren zu deren Herstellung erhältlich ist.

[0003] Des Weiteren betrifft die vorliegende Erfindung Schutzmaterialien, welche unter Verwendung der Aktivkohle nach der Erfindung hergestellt sind bzw. die Aktivkohle nach der Erfindung aufweisen.

[0004] Zudem betrifft die vorliegende Erfindung auch Filter bzw. Filtermaterialien, welche unter Verwendung der Aktivkohle nach der Erfindung hergestellt sind bzw. welche die erfindungsgemäße Aktivkohle aufweisen.

[0005] Aktivkohle ist aufgrund ihrer recht unspezifischen adsorptiven Eigenschaften das am meisten angewendete Adsorbens. Gesetzliche Auflagen, aber auch das steigende Bewusstsein der Verantwortung für die Umwelt, führen zu einem steigenden Bedarf an Aktivkohle.

[0006] Aktivkohle wird im Allgemeinen durch Carbonisierung (synonym auch als Schwelung, Pyrolyse, Abbrand etc. bezeichnet) und anschließende Aktivierung kohlenstoffhaltiger Ausgangsverbindungen erhalten. Die Beschaffenheit der erzeugten Aktivkohle – fein- oder grobporig, fest oder brüchig, feinteilig oder kornförmig etc. – hängt dabei insbesondere auch vom Ausgangsmaterial ab – neben den Verfahrensbedingungen für die Carbonisierung und Aktivierung. Übliche Ausgangsmaterialien sind insbesondere Kokosnussschalen, Holzkohle und Holz (z. B. Holzabfälle), Torf, Steinkohle, Peche, aber auch besondere Kunststoffe bzw. organische Polymere, die unter anderem bei der Herstellung von Aktivkohlegeweben eine gewisse Rolle spielen. Für weitergehende Einzelheiten zur Aktivkohleherstellung kann insbesondere verwiesen werden auf H. v. Kienle und E. Bäder, "Aktivkohle und ihre industrielle Anwendung", Enke Verlag Stuttgart, 1980.

[0007] Aktivkohle wird in verschiedenen Formen verwendet: Pulverkohle, Splitterkohle bzw. Kornkohle, Formkohle und seit Ende der 1970er Jahre auch kugelförmige Aktivkohle ("Kugelkohle"). Kugelförmige Aktivkohle hat gegenüber anderen Formen von Aktivkohle, wie Pulver-, Splitter-, Korn- und Formkohle und dergleichen, eine Reihe von Vorteilen, die sie für bestimmte Applikationen wertvoll oder sogar unverzichtbar macht: Sie ist rieselfähig, abriebfest bzw. staubfrei und hart. Kugelkohle ist wegen ihrer speziellen Form, aber auch wegen der hohen Abriebfestigkeit beispielsweise für besondere Einsatzgebiete sehr gefragt.

[0008] Kugelkohle wird heute noch meist durch mehrstufige und sehr aufwendige Verfahren hergestellt. Das bekannteste Verfahren besteht in der Herstellung von Kügelchen aus Steinkohlenteerpech und geeigneten asphaltartigen Rückständen der Erdölchemie, welche oxidiert – damit sie unschmelzbar werden – und nachfolgend geschwelt und aktiviert werden. Beispielsweise kann die Kugelkohle auch in einem mehrstufigen Verfahren ausgehend von Bitumen hergestellt werden. Diese mehrstufigen Verfahren sind sehr kostenintensiv, und der damit verbundene hohe Preis dieser Kugelkohle verhindert viele Anwendungen, bei denen die Kugelkohle aufgrund ihrer Eigenschaften eigentlich bevorzugt werden müsste.

[0009] In der WO 98/07655 A1 wird ein Verfahren zur Herstellung von Aktivkohlekügelchen beschrieben, bei dem zunächst eine Mischung, die einen aus der Diisocyanatherstellung stammenden Destillationsrückstand, einen kohlenstoffhaltigen Verarbeitungshilfsstoff und gegebenenfalls einen oder mehrere weitere Zusatzstoffe umfasst, zu rieselförmigen Kügelchen verarbeitet wird und anschließend die auf diese Weise erhaltenen Kügelchen carbonisiert und dann aktiviert werden.

[0010] Aus dem Stand der Technik bekannt ist ferner die Herstellung von Kugelkohle durch Schwelung und anschließende Aktivierung von neuen oder gebrauchten Ionenaustauschern, die Sulfonsäuregruppen enthalten, bzw. durch Schwelung von Ionenaustauschervorstufen in Gegenwart von Schwefelsäure und anschließende Aktivierung, wobei die Sulfonsäuregruppen bzw. die Schwefelsäure die Funktion eines Vernetzers haben. Solche Verfahren sind beispielsweise in der DE 43 28 219 A1 und in der DE 43 04 026 A1 sowie in der DE 196 00 237 A1 einschließlich der deutschen Zusatzanmeldung DE 196 25 069 A1 beschrieben.

PAC ET AL. EXHIBIT 1019
Page 2200

[0011] Weiterhin sind aus dem Stand der Technik Verfahren bekannt, bei denen die Herstellung von Aktivkohle, insbesondere Kugelkohle, durch Schwelung und anschließende Aktivierung sulfonierter divinylbenzolvernetzter Polystyrole (d. h. sulfonierte Styrol(Divinylbenzol-Copolymere) erfolgt (vgl. z. B. DE 10 2007 050 971 A1).

[0012] Bei speziellen Anwendungen ist aber nicht nur die Geometrie bzw. die äußere Gestalt der Aktivkohle von entscheidender Bedeutung, sondern auch deren Porosität, insbesondere das Gesamtporenvolumen und die Adsorptionskapazität einerseits und die Verteilung der Poren, d. h. der Anteil an Mikro-, Meso- und Makroporen in Bezug auf das Gesamtporenvolumen, andererseits; insbesondere kann die Porosität durch die Auswahl der Ausgangsmaterialien sowie die Verfahrensbedingungen gezielt gesteuert werden. Im Rahmen der vorliegenden Erfindung bezeichnet der Begriff der Mikroporen solche Poren mit Porendurchmessern von weniger als 2 nm, wohingegen der Begriff der Mesoporen solche Poren mit Porendurchmessern im Bereich von 2 nm (d. h. 2 nm einschließlich) bis 50 nm einschließlich bezeichnet und der Begriff der Makroporen solche Poren mit Porendurchmessern von mehr als 50 nm (d. h. > 50 nm) bezeichnet.

[0013] Aufgrund ihrer guten adsorptiven Eigenschaften kommt Aktivkohle für eine Vielzahl von Anwendungen zum Einsatz: So wird Aktivkohle beispielsweise in der Medizin oder Pharmazie eingesetzt, aber auch in der Lebensmittelindustrie. Auch für Filteranwendungen findet Aktivkohle weitreichende Anwendungen (z. B. Filtration von Gasen und Flüssigkeiten, Entfernung von unerwünschten oder schädlichen bzw. toxischen Gasen etc.).

[0014] Insbesondere kann Aktivkohle in Adsorptionsfiltermaterialien, insbesondere auch speziell in Schutzmaterialien gegenüber Giften, wie chemisch-biologischen Kampfstoffen, wie beispielsweise ABC-Schutzbekleidung, zum Einsatz kommen. Zu diesem Zweck sind insbesondere luft- und wasserdampfdurchlässige Schutzanzüge gegen chemische Kampfstoffe bekannt; derartige luft- und wasserdampfdurchlässige Schutzanzüge besitzen oftmals eine Adsorptionsfilterschicht mit Aktivkohle, welche die chemischen Gifte adsorbieren.

[0015] Zur Steigerung der Adsorptionsleistung wird Aktivkohle oft mit einer katalytisch aktiven oder reaktiven Komponente ausgerüstet, indem die Aktivkohle beispielsweise mit einem biozid bzw. biostatisch wirkenden Katalysator, insbesondere auf Basis von Metallen oder Metallverbindungen, imprägniert wird. Eine derartige Aktivkohle kann insbesondere in Schutzmaterialien zum Einsatz kommen, wie sie beispielsweise beschrieben sind in der DE 195 19 869 A1, welche ein mehrlagiges, textiles, gasdurchlässiges Filtermaterial mit einer Adsorptionsschicht auf Basis von Aktivkohle, insbesondere in Form von karbonisierten Fasern, enthält, die mit einem Katalysator aus der Gruppe von Kupfer, Cadmium, Platin, Palladium, Quecksilber und Zink in Mengen von 0,05 bis 12 Gew.-%, bezogen auf das Aktivkohlematerial, imprägniert ist.

[0016] Eine spezielle, in diesem Zusammenhang zum Einsatz kommende Imprägnierung ist beispielsweise eine so genannte ABEK-Imprägnierung, welche gegenüber spezifischen toxischen Substanzen eine katalytische bzw. abbauende Wirkung aufweist. In diesem Zusammenhang bezieht sich Typ A auf bestimmte organische Gase und Dämpfe mit einem Siedepunkt > 65°C, beispielsweise Cyclohexan. Typ B bezieht sich auf bestimmte anorganische Gase und Dämpfe, beispielsweise Cyanwasserstoff. Typ E bezieht sich auf eine abbauende bzw. schützende Wirkung gegenüber Schwefeldioxid und anderen sauren Gasen und Dämpfen. Typ K schließlich bezieht sich auf eine Schutzfunktion gegenüber Ammoniak und organischen Ammoniakderivaten. Für weiterführende Informationen kann auf die diesbezügliche Europäische Norm EN 14387 (Januar 2004) verwiesen werden.

[0017] Nachteilig bei herkömmlichen Imprägnierungen von Aktivkohle mit Metallen bzw. Metallsalzen ist insbesondere die Tatsache, dass durch die Imprägnierung ein Teil der Adsorptionskapazität der Aktivkohle, welche für die Adsorption und somit für die Unschädlichmachung von chemischen Schadstoffen benötigt wird, verlorengeht. Durch die aus dem Stand der Technik bekannten Imprägnierprozesse der Aktivkohle mit Metallen bzw. Metallsalzen wird somit die Leistungsfähigkeit der Aktivkohle nachteilig beeinträchtigt. Des Weiteren wird durch eine herkömmliche Imprägnierung nicht immer die gewünschte Wirksamkeit erreicht. Auch das Problem des Durchschlagens von Gift- bzw. Kampfstoffen bei hohen Konzentrationen wird durch dieses Prinzip nicht immer gelöst; andererseits wird bei sehr geringen Konzentrationen an zu entfernenden Schadstoffen oder störenden Gasen (z. B. bei der Luftaufbereitung für Reinraumbedingungen) oft nicht die gewünschte Effizienz erreicht, da eine Adsorption erst bei höheren Konzentrationen einsetzt. Schließlich benötigt der herkömmliche Imprägnierprozess mit Metallen bzw. Metallsalzen relativ große Mengen des Imprägniermaterials, da ein großer Teil des als Feststoff vorliegenden Imprägniermaterials bei der Adsorption nicht zur Verfügung steht, insbesondere dann nicht, wenn größere Schichtdicken des Imprägniermaterials im Porensystem der Aktivkohle, insbesondere in Form von Kristalliten, vorliegen.

PAC ET AL. EXHIBIT 1019
Page 2201

[0018] Ein weiterer Nachteil der Ausrüstung von Aktivkohle mit Metallen bzw. Metallsalzen besteht darin, dass herkömmliche Aktivkohle an ihrer Oberfläche unpolar bzw. hydrophob ausgebildet ist und insbesondere keine signifikante Affinität gegenüber den eingesetzten Imprägniermitteln besitzt, welche zur reaktiven bzw. katalytischen Ausrüstung der Aktivkohle eingesetzt werden. Infolgedessen muss ein großer Überschuss an Imprägniermitteln eingesetzt werden, um überhaupt eine gewisse Beladung der Aktivkohle zu gewährleisten. Die Imprägniermittel haften im Allgemeinen nur über rein physikalische Wechselwirkungen und können bei Kontakt mit Flüssigkeiten unerwünschtermaßen zumindest zu einem überwiegenden Teil wieder entfernt werden.

[0019] Darüber hinaus ist es im Stand der Technik insbesondere im Hinblick auf die Adsorption saurer Gase, wie Schwefeldioxid und dergleichen, vorgesehen, eine nachträgliche Imprägnierung der Aktivkohle mit insbesondere basischen stickstoffhaltigen Imprägnierreagenzien, insbesondere Aminen, durchzuführen. Hierbei treten gleichermaßen die zuvor geschilderten Nachteile auf, insbesondere was den Einsatz eines großen Überschusses an Imprägniermittel, die schlechte Beständigkeit der Imprägnierung und das Verstopfen des Porensystems der Aktivkohle anbelangt.

[0020] Darüber hinaus wurde im Stand der Technik auch versucht, eine Ausrüstung bzw. Imprägnierung auf Basis von stickstoffhaltigen Imprägnierreagenzien insofern zu realisieren, als das Imprägnierreagenz im Rahmen des Herstellungsprozesses der Aktivkohle, insbesondere bei der Aktivierung, dem zu behandelnden Substrat zugegeben wird. Diesbezüglich wird im Stand der Technik Ammoniak bzw. NH_3 als entsprechendes Imprägnierreagenz eingesetzt, insbesondere in Form von Ammoniakwasser. Die zugrundeliegende Vorgehensweise, wonach nämlich das Imprägnierreagenz im Rahmen des Aktivierungsprozesses und somit während der Herstellung der Aktivkohle als solche zugegeben wird, ist jedoch insbesondere dahingehend nachteilig, dass mit einem großen Überschuss an Imprägnierreagenz gearbeitet werden muss, da ein überwiegender Teil des Imprägnierreagenes nicht zur eigentlichen Imprägnierung verwendet wird, sondern vielmehr Bestandteil des Aktivierungsprozesses ist. Weiterhin ist bei dieser Vorgehensweise nachteilig, dass der eigentliche Imprägnierprozess nur schlecht kontrolliert werden kann, da die Zugabe des Imprägnierreagenzes im Rahmen der eigentlichen Aktivierung stattfindet, bei welcher nämlich gleichzeitig auch ein Abbrand der Aktivkohle erfolgt, was einer homogenen Beladung der Aktivkohle mit hohen Mengen des Imprägnierungsreagenz abträglich ist. In diesem Zusammenhang ist auch anzuführen, dass die Gegenwart des Imprägnierungsreagenzes gleichermaßen auch eine kontrollierte und exakt reproduzierbare Durchführung des Aktivierungsprozesses erschwert bzw. verhindert, insbesondere was die Ausbildung einer definierten Porenstruktur und dergleichen anbelangt. Weiterhin ist es im Hinblick auf die zuvor geschilderte Vorgehensweise mit der Zugabe des Imprägnierreagenzes bzw. -mittels während des Aktivierungsprozesses nicht möglich, eine chemische Anbindung bzw. Integration der Stickstoffkomponente an das Aktivkohlegerüst zu erreichen, insbesondere da das zugrundeliegende Aktivkohlesubstrat hinsichtlich seiner Oberflächenbeschaffenheit unpolar bzw. hydrophob ist, was einem Inkontaktbringen bzw. einer Wechselwirkung mit dem Imprägnierreagenz abträglich ist. Auf Basis dieser Vorgehensweise ist es somit im Ergebnis nicht möglich, eine effektive Imprägnierung mit einer katalytisch aktiven Komponente zu ermöglichen, da sowohl die Ausrüstung mit der zugrundeliegenden reaktiven Komponente weder dauerhaft noch in großen Mengen bzw. homogen erfolgt und darüber hinaus gleichzeitig auch der Aktivierungsprozess als solcher nachteilig beeinflusst ist.

[0021] Es ist daher eine Aufgabe der vorliegenden Erfindung, adsorptive Materialien mit reaktiven und/oder katalytischen Eigenschaften in Form von Aktivkohle bereitzustellen, wobei die zuvor geschilderten Nachteile des Standes der Technik zumindest weitgehend vermieden oder aber wenigstens abgeschwächt werden sollen.

[0022] Insbesondere soll im Rahmen der vorliegenden Erfindung eine Aktivkohle bereitgestellt werden, welche eine reaktive bzw. katalytische Ausrüstung auf Basis von Stickstoff als katalytisch aktivem Heteroatom aufweist und welche sich insbesondere zur Adsorption bzw. Unschädlichmachung von insbesondere sauren Schadstoffen bzw. Schadgasen eignet, wobei die erfindungsgemäß bereitgestellte Aktivkohle gegenüber dem Stand der Technik weiterführend verbessert sein soll und insbesondere auch chemisorptive Eigenschaften aufweisen soll. Insbesondere soll im Rahmen der vorliegenden Erfindung ein effizientes Verfahren eingesetzt werden, welches die Bereitstellung einer Aktivkohle ermöglicht, die in effizienter Weise mit einer reaktiven bzw. katalytisch aktiven Komponente in Form von Stickstoff ausgerüstet ist, wobei gleichzeitig gewährleistet sein soll, dass die zugrundeliegende Ausrüstung mit der katalytisch aktiven Komponente dauerhaft ist und zu hervorragenden reaktiven bzw. katalytischen Eigenschaften der resultierenden Aktivkohle führt.

[0023] Wie die Anmelderin nun in völlig überraschender Weise herausgefunden hat, kann die zuvor angeführte und der vorliegenden Erfindung zugrundeliegende Aufgabe in nicht erwarteter Weise dadurch gelöst werden, dass im Rahmen der vorliegenden Erfindung eine stickstoffmodifizierte bzw. stickstofffunktionalisierte

PAC ET AL. EXHIBIT 1019
Page 2202

Aktivkohle bereitgestellt wird, welche durch ein Verfahren erhältlich ist, wonach als Ausgangsmaterial Aktivkohle als solche eingesetzt wird, welche zunächst einer Oberflächenoxidation unter Einsatz mindestens eines Oxidationsreagenzes ("OR") einer Oberflächenoxidation unterzogen wird und wonach die so erhaltene, an ihre Oberfläche oxidierte Aktivkohle nachfolgend einer Ausrüstung mit Stickstoff bzw. mit stickstoffhaltigen funktionellen Gruppen unter Einsatz mindestens eines Stickstoffmodifizierungsreagenzes ("SMR") unterzogen wird.

[0024] Zur Lösung der zuvor geschilderten Aufgabe schlägt die vorliegende Erfindung somit – gemäß einem ersten Aspekt der vorliegenden Erfindung – die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle, insbesondere mit katalytischen bzw. reaktiven Eigenschaften, vorzugsweise eine Aktivkohle mit Stickstoff als katalytisch aktivem Heteroatom, welche mit einem Verfahren zu ihrer Herstellung bereitgestellt ist, gemäß Anspruch 1 vor. Weitere, insbesondere vorteilhafte Ausgestaltungen des erfindungsgemäß durchgeführten Verfahrens sind Gegenstand der diesbezüglichen Unteransprüche.

[0025] Weiterer Gegenstand der vorliegenden Erfindung – gemäß einem zweiten Aspekt der vorliegenden Erfindung – ist die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle nach der Erfindung, welche insbesondere katalytische bzw. reaktive Eigenschaften und welche vorzugsweise Stickstoff als katalytisch aktives Heteroatom aufweist, gemäß den diesbezüglich unabhängigen Ansprüchen. Weitere, insbesondere vorteilhafte Ausgestaltungen der erfindungsgemäßen Aktivkohle sind Gegenstand der entsprechenden Unteransprüche.

[0026] Darüber hinaus sind weiterer Gegenstand der vorliegenden Erfindung – gemäß einem dritten Aspekt der vorliegenden Erfindung – die erfindungsgemäßen Schutzmaterialien, insbesondere für den zivilen bzw. militärischen Bereich, insbesondere Schutzbekleidung, gemäß dem diesbezüglich unabhängigen Anspruch.

[0027] Schließlich sind weiterer Gegenstand der Erfindung – gemäß einem vierten Aspekt der vorliegenden Erfindung – Filter und Filtermaterialien, insbesondere zur Entfernung von Schad-, Geruchs- und Giftstoffen aller Art, gemäß dem betreffenden unabhängigen Anspruch.

[0028] Es versteht sich von selbst, dass bei der nachfolgenden Beschreibung der vorliegenden Erfindung solche Ausgestaltungen, Ausführungsformen, Vorteile, Beispiele oder dergleichen, welche nachfolgend – zu Zwecken der Vermeidung unnötiger Wiederholungen – nur zu einem einzelnen Erfindungsaspekt ausgeführt werden, selbstverständlich auch in Bezug auf die übrigen Erfindungsaspekte entsprechend gelten, ohne dass dies einer ausdrücklichen Erwähnung bedarf.

[0029] Weiterhin versteht es sich von selbst, dass bei nachfolgenden Angaben von Werten, Zahlen und Bereichen die diesbezüglichen Werte-, Zahlen- und Bereichsangaben nicht beschränkend zu verstehen sind; es versteht sich dabei für den Fachmann von selbst, dass einzelfallbedingt oder anwendungsbezogen von den angegebenen Bereichen bzw. Angaben abgewichen werden kann, ohne dass der Rahmen der vorliegenden Erfindung verlassen ist.

[0030] Zudem gilt, dass alle im Folgenden genannten Werte- bzw. Parameterangaben oder dergleichen grundsätzlich mit genormten bzw. standardisierten oder explizit angegebenen Bestimmungsverfahren oder aber andernfalls mit dem Fachmann auf diesem Gebiet an sich geläufigen Bestimmungs- bzw. Messmethoden ermittelt bzw. bestimmt werden können.

[0031] Im Übrigen gilt, dass bei allen nachstehend aufgeführten relativen bzw. prozentualen, insbesondere gewichtsbezogenen Mengenangaben, zu beachten ist, dass diese Angaben im Rahmen der vorliegenden Erfindung vom Fachmann derart auszuwählen bzw. zu kombinieren sind, dass in der Summe – gegebenenfalls unter Einbeziehung weiterer Komponenten bzw. Inhaltsstoffen, insbesondere wie nachfolgend definiert – stets 100% bzw. 100 Gew.-% resultieren. Dies versteht sich für den Fachmann aber von selbst.

[0032] Dies vorausgeschickt, wird im Folgenden die vorliegende Erfindung näher beschrieben:
Gemäß einem ersten Aspekt der vorliegenden Erfindung betrifft die vorliegende Erfindung eine stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle, welche durch ein Verfahren zu deren Herstellung erhältlich ist, wobei die mit dem erfindungsgemäß eingesetzten Verfahren hergestellte Aktivkohle katalytische bzw. reaktive Eigenschaften aufweist. Bei der mit dem erfindungsgemäß eingesetzten Verfahren hergestellten Aktivkohle handelt es sich insbesondere um eine Aktivkohle mit Stickstoff als katalytisch aktivem Heteroatom. Das erfindungsgemäß durchgeführte Verfahren zeichnet sich dadurch aus, dass eine als Ausgangsmaterial eingesetzte Aktivkohle ("Ausgangsaktivkohle") zunächst einer Oberflächenoxidation unter Verwendung bzw. in Gegenwart mindestens eines Oxidationsreagenzes ("OR") unterzogen wird und die auf diese Weise erhaltene, an ih-

PAC ET AL. EXHIBIT 1019
Page 2203

rer Oberfläche oxidierte Aktivkohle ("Intermediat") nachfolgend einer Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, mit Stickstoff, insbesondere mit stickstoffhaltigen funktionellen Gruppen, unter Verwendung bzw. in Gegenwart mindestens eines Stickstoffmodifizierungsreagenzes ("SMR") unterzogen wird.

[0033] Wie zuvor angeführt, besteht die grundlegende Idee der vorliegenden Erfindung somit darin, eine Aktivkohle auf Basis eines Verfahrens bereitzustellen, auf dessen Basis es möglich ist, eine Aktivkohle als Ausgangsmaterial in optimierter Weise mit Stickstoff zu modifizieren bzw. zu funktionalisieren, wobei Stickstoff als katalytisch aktives Heteroatom fungiert und wobei Stickstoff in gezielter Weise insbesondere an die Oberflächenstruktur der eingesetzten Aktivkohle gekoppelt bzw. chemisch gebunden bzw. dauerhaft immobilisiert wird, und zwar in Form von stickstoffhaltigen funktionellen Gruppen einerseits oder aber nach Art einer Dotierung mit Stickstoff bzw. einer N-Dotierung unter Integration bzw. Einbau in das Kohlenstoffgerüst der Aktivkohle (d. h. unter Immobilisierung bzw. Einbindung des Stickstoffs in bzw. an das Kohlenstoffgerüsts des Endprodukts) andererseits.

[0034] In diesem Zusammenhang ist es im Rahmen der vorliegenden Erfindung völlig überraschend, dass durch die der eigentlichen Stickstofffixierung bzw. -modifizierung vorgeschaltete Oberflächenoxidation der als Ausgangsmaterial eingesetzten Aktivkohle eine signifikante Verbesserung der Stickstoffmodifizierung bzw. Stickstofffunktionalisierung der Aktivkohle erreicht wird. Ohne sich auf diese Theorie beschränken bzw. festlegen zu wollen, wird durch die gezielte und zweckgerichtete Oxidation der Oberfläche der eingesetzten Aktivkohle unter Verwendung spezieller Oxidationsreagenzien ("OR") die Oberflächenstruktur der Aktivkohle im Hinblick auf die Modifizierung bzw. Funktionalisierung mit Stickstoff insofern optimiert, als zum einen hydrophile Strukturen geschaffen bzw. die Hydrophilität der Aktivkohle als solche gesteigert wird, was die Interaktion mit dem Stickstoffmodifizierungsreagenz ("SMR") verbessert. Zum anderen werden durch die gezielte Oxidation der Oberfläche der Aktivkohle insbesondere solche funktionellen chemischen Gruppen geschaffen, welche mit dem Stickstoffmodifizierungsreagenz ("SMR") insbesondere unter Ausbildung chemischer Bindungen zu interagieren bzw. zu reagieren imstande sind, was die chemische Bindung bzw. Integration des Stickstoffs in Bezug auf die Aktivkohle verbessert bzw. ermöglicht. Auf Basis der erfindungsgemäß durchgeführten Oxidation im Sinne einer Vorbehandlung der Aktivkohle wird die Affinität der Aktivkohle zum Stickstoffmodifizierungsreagenz ("SMR") erhöht.

[0035] Wie nachfolgend noch im Einzelnen geschildert, ist es aufgrund der speziellen Verfahrensführung möglich, die resultierende stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle bzw. die mit Stickstoff ausgerüstete Aktivkohle individuell anzupassen bzw. maßzuschneidern, was sowohl auf Ebene der Oxidation der eingesetzten (Ausgangs-)Aktivkohle als auch im Hinblick auf die nachfolgende Stickstoffmodifizierung möglich ist, so dass im Ergebnis auf Basis des erfindungsgemäß durchgeführten Verfahrens Aktivkohlen bereitgestellt werden, welche insgesamt einem breiten Einsatzspektrum zugänglich sind bzw. im Speziellen für die Adsorption bzw. Unschädlichmachung spezieller toxischer Substanzen optimiert sind.

[0036] Ein weiterer zentraler Vorteil der erfindungsgemäß durchgeführten Verfahrensführung ist darin zu sehen, dass eine Vielzahl kommerziell erhältlicher bzw. handelsüblicher Aktivkohlen als Ausgangsmaterial für die erfindungsgemäß vorgesehene Verfahrensführung bzw. Modifizierung eingesetzt werden können, so dass das erfindungsgemäß durchgeführte Verfahren gewissermaßen universell im Hinblick auf die Ausgangsmaterialien auf Basis von Aktivkohle, beispielsweise mit variabler Porosität oder dergleichen, eingesetzt werden kann. Aufgrund der sozusagen nachgeschalteten Modifizierung bzw. Ausrüstung mit Stickstoff werden im Rahmen der Aktivkohleherstellung als solche vorliegende Prozesse, wie Carbonisierung und Aktivierung, nicht beeinflusst.

[0037] Aufgrund der erfindungsgemäß realisierten Verfahrensführung mit der Funktionalisierung der Aktivkohle mit stickstoffhaltigen funktionellen Gruppen bzw. mit der gezielten Integration von Stickstoff in die Kohlenstoffoberfläche bzw. in das Gerüst der Aktivkohle werden somit spezielle stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohlen erhalten, welche eine katalytische Aktivität bzw. Reaktivität und somit chemisorptive Eigenschaften gegenüber unterschiedlichen Substanzen, insbesondere toxischen gasförmigen Substanzen, aufweisen. Diesbezüglich weisen die mit dem erfindungsgemäß durchgeführten Verfahren erhaltenen stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohlen eine hohe Eignung für den insbesondere katalytischen bzw. reaktiven Abbau verschiedener toxischer Gase auf. Hierbei kann es sich beispielsweise und in nicht beschränkender Weise um sogenannte Chemical Warfare Agents (CWAs), Toxic Industrial Materials (TIMs), wie größere Moleküle, beispielsweise Ethylenoxid oder dergleichen, um Toxic Industrial Chemicals (TICs), wie NH_3, SO_2, H_2S, Cl_2, HCl oder dergleichen, handeln. Insbesondere eignet sich die mit dem erfindungsgemäß durchgeführten Verfahren erhaltene stickstofffunktionalisierte bzw. stickstoffmodifizierte Aktivkohle bzw. die mit Stickstoff ausgerüstete Aktivkohle zur Adsorption bzw. Unschädlichmachung von insbesondere sauren toxischen Gasen, wie H_2S, SO_2 bzw. HCl.

PAC ET AL. EXHIBIT 1019
Page 2204

[0038] Ohne sich auf diese Theorie beschränken bzw. festlegen zu wollen, ist insbesondere ein Abbau auch von solchen toxischen Gasen bzw. Schadgasen über eine Oxidation an der Kohlenstoffoberfläche der modifizierten Aktivkohle möglich, wie es beispielsweise in nicht beschränkender Weise für SO_2, H_2S, AsH_3 sowie DMS, möglich ist. Dies ist insbesondere dann der Fall, wenn der Stickstoff, wie zuvor geschildert, in das Kohlenstoffgerüst der erfindungsgemäß modifizierten Aktivkohle nach Art einer N-Dotierung integriert bzw. inkorporiert ist, d. h. der Stickstoff sozusagen immobilisiert ist, insbesondere durch chemische und/oder kovalente Bindung in das Kohlenstoffgerüst der erfindungsgemäß modifizierten Aktivkohle.

[0039] Darüber hinaus weist die auf Basis des erfindungsgemäß eingesetzten Verfahrens erhältliche stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle – gleichermaßen ohne sich auf diese Theorie beschränken bzw. festlegen zu wollen – eine katalytische Aktivität bzw. reaktive Eigenschaften gegenüber solchen toxischen Substanzen bzw. Gasen auf, welche mit den ausgebildeten stickstoffhaltigen funktionellen Gruppen auf der Oberfläche der erfindungsgemäß modifizierten Aktivkohle zu reagieren imstande sind, wie beispielsweise Formaldehyd und NO_x-Verbindungen.

[0040] Auf Basis der der vorliegenden Erfindung zugrundeliegenden Konzeption mit der speziellen Ausrüstung von Aktivkohle mit Stickstoff wird somit in völlig überraschender Weise eine Aktivkohle nach der Erfindung bereitgestellt, welche über hervorragende Eigenschaften hinsichtlich der (Chemi-)Sorption bzw. des katalytischen und/oder reaktiven Abbaus von unterschiedlichen Schadstoffen bzw. toxischen Gasen, wie chemischen Gift- bzw. Kampfstoffen, verfügt. Beispielsweise eignet sich die so ausgerüstete Aktivkohle auch für den insbesondere oxidativen Abbau von insbesonders schwefelhaltigen Komponenten eignen. Gleichermaßen können die so erhaltenen Aktivkohlen durch eine zweckgerichtete Optimierung der diesbezüglichen Ausrüstungen für Breitbandanwendungen, beispielsweise im Rahmen von Atemschutzanwendungen, eingesetzt werden. In diesem Zusammenhang kommt auch ein Einsatz in ABEK-Filtern, insbesondere in Kombination mit weiteren Adsorbentien in Betracht.

[0041] Im Allgemeinen eignet sich die erfindungsgemäße Aktivkohle beispielsweise zu Gasadsorptionen und insbesondere zur Adsorption von Schwefel enthaltenden Gasen (wie Schwefeloxiden und/oder Schwefelwasserstoff), von stickstoffenthaltenden Gasen (wie Stickoxiden und/oder Stickstoffwasserstoffen, wie Ammoniak) sowie von halogenhaltigen Gasen (wie Chlorwasserstoffgas). Gleichermaßen eignet sich die erfindungsgemäße Aktivkohle auch zur Adsorption von organisch basierten schädlichen Substanzen, wie beispielsweise Formaldehyd oder dergleichen. Insbesondere weist die erfindungsgemäße Aktivkohle besonders gute Eigenschaften im Hinblick auf die Sorption, insbesondere Physisorption und/oder Chemisorption, von Schwefel- und Stickstoffoxiden, Halogenwasserstoffen, Cyangas, Cyanwasserstoff, Schwefelwasserstoff, Chlorgas, Arsenwasserstoff und/oder Ammoniak auf.

[0042] Aufgrund der erfindungsgemäßen Konzeption des erfindungsgemäß eingesetzten Verfahrens mit der sozusagen vorgeschalteten Oberflächenoxidation bzw. der der Oberflächenoxidation nachgeschalteten Ausrüstung mit Stickstoff der zu behandelnden Aktivkohle als Ausgangsmaterial wird eine besonders homogene bzw. gleichmäßige Ausrüstung bzw. Beladung der Aktivkohle – und zwar insbesondere über das gesamte Porenspektrum – mit dem zu inkorporierenden Stickstoff erreicht, da das Stickstoffmodifizierungsreagenz ("SMR") besonders gut in das Porensystem eindringen kann und dort aufgrund der vorgeschalteten Oxidation mit der hohen Affinität der Reaktionsparameter zueinander eine gleichmäßige Beladung der Aktivkohle unter Ausbildung stickstoffhaltiger funktioneller Gruppen bzw. unter Integration bzw. Immobilisierung von Stickstoff in das Kohlenstoffgerüst gewährleistet.

[0043] Das erfindungsgemäß durchgeführte Verfahren zeichnet sich dabei durch eine gewissermaßen zweistufige Verfahrensführung aus, wobei nämlich zunächst herkömmliche Aktivkohle als Ausgangsmaterial einer Oberflächenoxidation unterzogen wird und nachfolgend die so erhaltene, an ihrer Oberfläche oxidierte Aktivkohle nachfolgend in zweckgerichteter Weise unter Verwendung eines Stickstoffmodifizierungsreagenzes ("SMR") mit Stickstoff ausgerüstet wird, und zwar auf Basis von stickstoffhaltigen funktionellen Gruppen und/oder auf Basis der Inkorporation bzw. des Einbaus von Stickstoff im Sinne einer Stickstoffdotierung (N-Dotierung) in das Kohlenstoffgerüst, insbesondere in das die äußere und innere Oberfläche bildende Kohlenstoffgerüst.

[0044] In diesem Zusammenhang ist es erfindungsgemäß zudem völlig überraschend, dass das Porensystem der als Ausgangsmaterial eingesetzten Aktivkohle zumindest im Wesentlichen nicht durch die Ausrüstung mit dem Stickstoff beeinflusst wird. Mit anderen Worten ist es erfindungsgemäß gewährleistet, dass das Porensystem der Aktivkohle nicht bzw. zumindest im Wesentlichen nicht nachteilig hinsichtlich der Adsorption von Schadstoffen beeinflusst wird. Die auf Basis des erfindungsgemäß durchgeführten Verfahrens erhältliche Ak-

PAC ET AL. EXHIBIT 1019
Page 2205

tivkohle weist somit auch nach Ausrüstung bzw. Funktionalisierung mit Stickstoff z. B. eine hohe, der Adsorption von Schadstoffen zugängliche BET-Oberfläche auf, so dass die grundlegenden Eigenschaften der Aktivkohle als solche auch bei Ausrüstung mit Stickstoff erhalten bleiben, was nicht vorhersehbar war. Somit ist die erfindungsgemäße Vorgehensweise im Gegensatz zu der im Stand der Technik bekannten Imprägnierung mit dem Vorteil verbunden, dass kein Verlust an spezifischer Oberfläche bzw. Gesamtporenvolumen vorliegt und auch die Porenstruktur als solche im Hinblick auf ihre Verteilung in Form von Mikro-, Meso- und Makroporen zumindest im Wesentlichen nicht verändert wird.

[0045] Diesbezüglich war es im Rahmen der vorliegenden Erfindung völlig überraschend, dass durch die gezielte Ausrüstung der Aktivkohle mit Stickstoff – im grundlegenden Unterschied zu den Verfahren des Standes der Technik – nicht zu Verstopfungen des Porensystems führt, da die Stickstoffkomponente dauerhaft unter Ausbildung chemischer Bindungen in die Kohlenstoffstruktur der Aktivkohle integriert ist, und zwar entweder auf Basis stickstoffhaltiger funktioneller Gruppen oder unter Integration in die Kohlenstoffmatrix der behandelten bzw. modifizierten Aktivkohle. Insbesondere wird aufgrund der erfindungsgemäß realisierten Verfahrensführung eine Kristallbildung bzw. eine Auskristallisation innerhalb des Porensystems verhindert, was die Leistungsfähigkeit der erfindungsgemäßen Aktivkohle noch weiter verbessert. Auch hierin ist ein entscheidender Unterschied zu dem im Stand der Technik bekannten Imprägnierverfahren zu sehen, welche insbesondere bei mikroporöser Aktivkohle zu einem Auftreten von Verstopfungen im Hinblick auf die Porenstruktur der Aktivkohle führt.

[0046] Aufgrund der gezielten Ausrüstung der Aktivkohle mit Stickstoff als katalytisch aktives Heteroatom weist die mit dem erfindungsgemäß durchgeführten Verfahren hergestellte Aktivkohle, wie zuvor angeführt, sozusagen eine reaktive bzw. katalytische Oberfläche in Ergänzung zu den chemisorptiven und/oder physisorptiven Eigenschaften der Aktivkohle als solche auf. Die mit dem erfindungsgemäß durchgeführten Verfahren erhältliche Aktivkohle vereint folglich chemisorptive wie physisorptive Eigenschaften in einem einzigen Material und ist somit imstande, die Sorbate bzw. die zu sorbierenden Substanzen – im Unterschied zu nichtkatalytischer bzw. nichtreaktiver Aktivkohle – auch zuverlässig und irreversibel bzw. dauerhaft zu binden bzw. abzubauen.

[0047] Auch durch die besonders homogene bzw. gleichmäßige Ausrüstung der mit dem erfindungsgemäß durchgeführten Verfahren erhältlichen Aktivkohle mit der Stickstoffkomponente wird die Leistungsfähigkeit der so erhaltenen stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle im Hinblick auf die Sorption bzw. den Abbau zu entfernender Substanzen nochmals gesteigert, insbesondere da die so erhältliche Aktivkohle gewissermaßen über einen großen Teil ihrer Oberfläche über kombinierte Eigenschaften der Physisorption einerseits und der Chemisorption auf Basis reaktiver bzw. katalytischer Eigenschaften andererseits verfügt, welche sich zudem über die Summe der Einzelmaßnahmen hinaus verstärken, was als Indiz für das Vorliegen eines synergistischen Effekts gewertet werden muss.

[0048] Im Rahmen der vorliegenden Erfindung wird somit ein leistungsfähiges Verfahren eingesetzt, welches zu einem optimierten Adsorptionssystem mit kombinierten und sich ergänzenden Eigenschaften von Physisorption einerseits und Chemisorption andererseits führt.

[0049] Wie zuvor angeführt, resultiert erfindungsgemäß eine funktionalisierte Aktivkohle, welche im Unterschied zum Stand der Technik jedoch zumindest im Wesentlichen keine signifikante Beeinträchtigung anderer physikochemischer Parameter, wie beispielsweise Porosität, Porenvolumen, Porenverteilung und dergleichen, aufweist.

[0050] Im Rahmen der vorliegenden Erfindung ist es zudem völlig überraschend, dass sich Aktivkohle als solche überhaupt in effektiver Weise hinsichtlich der erfindungsgemäß vorgesehenen Stickstoffmodifizierung bzw. Stickstofffunktionalisierung eignet. Denn Aktivkohle weist also solche grundsätzlich hydrophobe Eigenschaften auf, was einer effizienten Behandlung bzw. Interaktion mit dem Stickstoffmodifizierungsreagenz ("SMR") zur Ausbildung funktioneller Gruppen bzw. zur Integration von Stickstoff grundsätzlich abträglich ist. Insbesondere ist es jedoch aufgrund der speziellen erfindungsgemäß durchgeführten Verfahrensweise mit der zweckgerichteten vorgeschalteten Oberflächenoxidation der als Ausgangsmaterial eingesetzten Aktivkohle in völlig überraschender und nicht vorhersehbarer Weise gelungen, die Kompatibilität von Aktivkohle einerseits und Stickstoffmodifizierungsreagenz ("SMR") andererseits zu erhöhen, um Aktivkohle als solche in effektiver Weise mit Stickstoff zu funktionalisieren bzw. zu modifizieren, was zu den zuvor angeführten positiven Eigenschaften hinsichtlich der Sorption von Schadstoffen führt.

[0051] Zusammenfassend zeichnet sich die erfindungsgemäß realisierte Verfahrensführung somit dadurch aus, dass eine speziell mit Stickstoff modifizierte bzw. funktionalisierte Aktivkohle erhalten wird, welche über

PAC ET AL. EXHIBIT 1019
Page 2206

hervorragende Adsorptionseigenschaften auf Basis einer Kombination von Physisorption und Chemisorption verfügt. Insbesondere tritt eine bei herkömmlicher Aktivkohle, z. B. bei Erschöpfung oder übermäßiger Beladung häufig vorkommende Freisetzung bzw. Resorption bereits sorbierter Substanzen bei der erfindungsgemäßen Aktivkohle nicht bzw. nicht in nennenswertem Maße auf. Aufgrund der erfindungsgemäßen Konzeption der Bereitstellung einer Aktivkohle, welche neben ihren inhärenten adsorptiven Eigenschaften gleichermaßen reaktive bzw. katalytische Eigenschaften aufweist, wird eine dauerhaft und im Allgemeinen irreversible Bindung bzw. ein effizienter Abbau sorbierter Substanzen gewährleistet, was gleichermaßen zu einer verringerten Desorption der in Rede stehenden Substanzen und zu einer Steigerung der Gesamtadsorptionskapazität führt. Aufgrund der festen chemischen Anbindung von Stickstoff an die Aktivkohlestruktur liegt zudem eine dauerhafte und beständige Modifizierung der Aktivkohle mit Stickstoff vor. Insbesondere kann der dauerhaft immobilisierte Stickstoff nicht durch Auswaschen oder dergleichen wieder von der Aktivkohle entfernt werden.

[0052] Erfindungsgemäß kann das eingesetzte Verfahren weiter zusammenfassend insofern charakterisiert werden, als zunächst im Rahmen der Verfahrensdurchführung eine Ausgangsaktivkohle bzw. ein Basisadsorbens einer chemischen bzw. thermischen Oxidation zum Erhalt einer an ihrer Oberfläche oxidierten Aktivkohle (oxidiertes Basisadsorbens) unterzogen wird, wobei das so erhaltene Intermediat nachfolgend bzw. in einem sich der Oxidation anschließenden Schritt bzw. in einem separaten Schritt mit Stickstoff modifiziert bzw. funktionalisiert wird. Hierzu wird zunächst das oxidative Intermediat mit dem Stickstoffmodifizierungsreagenz ("SMR") in Kontakt gebracht, beispielsweise unter Verwendung einer Harnstofflösung, wobei in einem solchen Fall das oxidative Intermediat im Rahmen einer Tauchmethode oder dergleichen mit dem Stickstoffmodifizierungsreagenz ("SMR") in Kontakt gebracht werden kann. Gleichermaßen ist ein Inkontaktbringen auch im Rahmen eines Luftstromes, beispielsweise unter Verwendung von Ammoniak (NH_3) oder dergleichen, möglich. Es schließt sich eine entsprechende thermische Behandlung zur Ausbildung von stickstoffhaltigen Funktionalisierungen bzw. zur Dotierung des Aktivkohlegerüstes mit Stickstoff (d. h. zur Immobilisierung des Stickstoffs) an.

[0053] Was den Begriff "Oberflächenoxidation", wie er erfindungsgemäß verwendet wird, anbelangt, so ist hierunter insbesondere eine Oxidation solcher Oberflächen der als Ausgangsmaterial eingesetzten Aktivkohle zu verstehen, welche in Kontakt mit der insbesondere das Oberflächenreagenz ("OR") enthaltenden Umgebung stehen, bzw. welche sozusagen von außen für das erfindungsgemäß eingesetzte Oxidationsreagenz ("OR") zugänglich sind. Hierbei handelt es sich insbesondere auch um das Porensystem der Aktivkohle auf Basis von Makro-, Meso- und Mikroporen.

[0054] Ohne sich auf diese Theorie beschränken bzw. festlegen zu wollen, resultiert auf Basis der erfindungsgemäß realisierten Verfahrensführung gewissermaßen eine oxidierte Schicht im Hinblick auf die Aktivkohle, welche im Allgemeinen über die nachfolgend noch angeführten sauerstoffhaltigen funktionellen Gruppen verfügt. Die sich der Oberflächenoxidation anschließende Ausrüstung mit dem Stickstoff erfolgt dann – gleichermaßen ohne sich auf diese Theorie beschränken bzw. festlegen zu wollen – insbesondere im Bereich der oxidierten (Grenz-)Schicht, wobei die sauerstoffhaltigen funktionellen Gruppen gewissermaßen als Eindungs- bzw. Ankerstellen bzw. Reaktionspartner für das erfindungsgemäß eingesetzte Stickstoffmodifizierungsreagenz ("SMR") fungieren.

[0055] Durch die sich der Oxidation anschließende Ausrüstung der Aktivkohle im Rahmen des durchgeführten Verfahrens mit Stickstoff als katalytisch aktivem Heteroatom werden somit Aktivkohlen mit reaktiven bzw. katalytisch aktiven Oberflächen generiert.

[0056] Was das erfindungsgemäß durchgeführte Verfahren weiterhin anbelangt, so kann es vorgesehen sein, dass die Oberflächenoxidation unter Ausbildung einer hydrophilen Oberfläche der Aktivkohle durchgeführt wird. Erfindungsgemäß ist es gleichermaßen möglich, dass die Oberflächenoxidation zu einer Ausbildung von sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle führt. In diesem Zusammenhang können die sauerstoffhaltigen funktionellen Gruppen ausgewählt werden aus sauren und basischen sauerstoffhaltigen funktionellen Gruppen sowie deren Kombinationen, insbesondere sauren und basischen Oberflächenoxiden. Insbesondere können die sauerstoffhaltigen funktionellen Gruppen ausgewählt werden aus der Gruppe von Hydroxyl-, Carboxyl-, Carbonyl-, Anhydrid-, Lacton-, Chinon-, Pyron-, Chromen- und Ethergruppen sowie deren Kombinationen. Derartige Gruppen eignen sich in besonderer Weise zur Interaktion mit dem Stickstoffmodifizierungsreagenz ("SMR").

[0057] Wie zuvor angeführt, führen die an der Oberfläche der Aktivkohle insbesondere durch Reaktion des Oxidationsreagenzes ("OR") mit der als Ausgangsmaterial eingesetzten Aktivkohle ("Ausgangsaktivkohle") entstehenden sauerstoffhaltigen funktionellen Gruppen zu einer Erhöhung der Hydrophilität bzw. der hydrophilen Eigenschaften der so behandelten Aktivkohle, was die Interaktion mit dem nachfolgend eingesetzten Stickstoff-

PAC ET AL. EXHIBIT 1019
Page 2207

modifizierungsreagenz ("SMR") verbessert und in entsprechender Weise zu einer verbesserten Funktionalisierung bzw. Modifizierung der Aktivkohle mit Stickstoff führt. Insbesondere können die auf diese Weise generierten sauerstoffhaltigen funktionellen Gruppen als Reaktionspartner für das Stickstoffmodifizierungsreagenz ("SMR") fungieren, um so die chemische Bindung bzw. den Einbau bzw. Integration von Stickstoff in die zu modifizierende Aktivkohle zu verbessern bzw. zu ermöglichen. Die erfindungsgemäß durchgeführte und vorgeschaltete Oberflächenoxidation dient somit gewissermaßen zur Vorbereitung der nachfolgenden Stickstoffmodifizierung bzw. -funktionalisierung der Aktivkohle. In diesem Zusammenhang wird durch die erfindungsgemäß realisierte Oberflächenoxidation insbesondere auch die Oberflächenhydrophilie des Kohlenstoffgerüsts der zu behandelnden Aktivkohle erhöht, was zu den vorgenannten Vorteilen führt.

[0058] Was das erfindungsgemäß durchgeführte Verfahren weiterhin anbelangt, so kann durch die zweckgerichtete Oberflächenoxidation auch der pH-Wert, insbesondere der Oberflächen-pH-Wert, der an ihrer Oberfläche oxidierten Aktivkohle eingestellt werden, und zwar im Vergleich zu der Ausgangsaktivkohle um einen Wert von mindestens 0,25, insbesondere mindestens 0,5, vorzugsweise mindestens 0,75, bevorzugt mindestens 1, besonders bevorzugt mindestens 1,5, verändert werden. Insbesondere kann es vorgesehen sein, dass die Acidität der an ihrer Oberfläche oxidierten Aktivkohle erhöht und/oder der pH-Wert, insbesondere der Oberflächen-pH-Wert, der an ihrer Oberfläche oxidierten Aktivkohle durch die vorgenommene Oxidation der Aktivkohle verringert wird, insbesondere um einen Wert von mindestens 0,25, insbesondere mindestens 0,5, vorzugsweise mindestens 0,75, bevorzugt mindestens 1, besonders bevorzugt mindestens 1,5, oder dass durch die vorgenommene Oxidation der Aktivkohle die Basizität der an ihrer Oberfläche oxidierten Aktivkohle erhöht und/oder der pH-Wert, insbesondere der Oberflächen-pH-Wert, der an ihrer Oberfläche oxidierten Aktivkohle erhöht wird, insbesondere um einen Wert von mindestens 0,25, insbesondere mindestens 0,5, vorzugsweise mindestens 0,75, bevorzugt mindestens 1, besonders bevorzugt mindestens 1,5. Durch die zweckgerichtete Einstellung des pH-Werts auf Basis der erfindungsgemäß durchzuführenden Oberflächenoxidation der Ausgangsaktivkohle kann insbesondere die Affinität zum nachfolgend eingesetzten Stickstoffmodifizierungsreagenz ("SMR") weiter optimiert werden, was zu einer noch weitergehenden Effizienzsteigerung hinsichtlich der Ausrüstung der auf Basis des erfindungsgemäß durchgeführten Verfahrens erhältlichen Aktivkohle mit Stickstoff führt. Insbesondere resultiert bei Verwendung von Ausgangsaktivkohlen mit relativ hohem pH-Wert bzw. basischen Ausgangsaktivkohlen eine durch die Oberflächenoxidation hervorgerufene Verringerung des Oberflächen-pH-Wertes.

[0059] Erfindungsgemäß kann es auch vorgesehen sein, dass die Oberflächenoxidation durchgeführt wird derart, dass die auf diese Weise erhaltene, an ihrer Oberfläche oxidierte Aktivkohle einen Gehalt an sauerstoffhaltigen funktionellen Gruppen, berechnet und/oder ausgedrückt als Gehalt an flüchtigen Bestandteilen ("fB") und bezogen auf das Trockengewicht der an ihrer Oberfläche oxidierten Aktivkohle, von mindestens 1 Gew.-%, insbesondere mindestens 2 Gew.-%, vorzugsweise mindestens 3 Gew.-%, bevorzugt mindestens 4 Gew.-%, und/oder im Bereich von 1 Gew.-% bis 30 Gew.-%, insbesondere 1,5 Gew.-% bis 25 Gew.-%, vorzugsweise 2 Gew.-% bis 20 Gew.-%, bevorzugt 3 Gew.-% bis 15 Gew.-%, aufweist.

[0060] In diesem Zusammenhang kann im Rahmen der erfindungsgemäß realisierten Verfahrensführung der Gehalt an sauerstoffhaltigen funktionellen Gruppen beispielsweise durch entsprechende Wahl der Temperatur und/oder Zeitdauer und/oder Art und/oder Konzentration an Oxidationsreagenz ("OR") eingestellt werden. Auf diese Weise kann eine Maßschneiderung des Oxidationsprozesses insbesondere im Hinblick auf die nachfolgende Stickstofffunktionalisierung bzw. -modifizierung erfolgen. Im Rahmen der erfindungsgemäß realisierten Verfahrensführung wird somit der Sauerstoffgehalt der an ihrer Oberfläche oxidierten Aktivkohle im Vergleich zu der eingesetzten Ausgangsaktivkohle – welche im Allgemeinen einen Sauerstoffgehalt von weniger als 1 Gew.-%, ausgedrückt als Gehalt an flüchtigen Bestandteilen ("fB") und bezogen auf das Trockengewicht der Ausgangsaktivkohle, aufweist – signifikant erhöht.

[0061] Der Gehalt an flüchtigen Bestandteilen ("fB") fungiert dabei im Allgemeinen als Maß für die Oxidation und bezieht sich insbesondere auf durch die Oxidation gebildete Oberflächenoxide. Insbesondere kann der Gehalt an flüchtigen Bestandteilen auf Basis der ISO 562:1981 bestimmt werden. Insbesondere kann der Gehalt an flüchtigen Bestandteilen ("fB") an der zuvor getrockneten, an ihrer Oberfläche oxidierten Aktivkohle bei einer entsprechenden Erwärmung für einen Zeitraum von 7 Minuten auf 900°C unter inerten Bedingungen bestimmt werden.

[0062] Durch die Einstellung des Gehalts an sauerstoffhaltigen funktionellen Gruppen kann auch die Menge des nachfolgend einzubauenden Stickstoffs vorgegeben bzw. beeinflusst werden, insbesondere durch eine entsprechende Vorgabe der Anzahl an Reaktionspartnern. Die aufgenommene Menge an Stickstoff der erfindungsgemäß bereitgestellten stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle korreliert somit

PAC ET AL. EXHIBIT 1019
Page 2208

mit dem Gehalt bzw. der Menge an Oberflächenoxiden bzw. mit den flüchtigen Bestandteilen der oxidierten Basis in Form der an ihrer Oberfläche oxidierten Aktivkohle.

[0063] Was das im Rahmen der Oberflächenoxidation eingesetzte Oxidationsreagenz ("OR") anbelangt, so können hierzu eine Vielzahl an Reagenzien bzw. Verbindungen eingesetzt werden. Grundsätzlich erfolgt dabei der Oxidationsvorgang, wie nachfolgend geschildert, für einen definierten Zeitraum insbesondere unter Wärme- bzw. Temperatureinfluss.

[0064] Im Allgemeinen kann das Oxidationsreagenz ("OR") ausgewählt werden aus der Gruppe von Sauerstoff, Ozon, anorganischen oder organischen Oxiden und Peroxiden sowie anorganischen oder organischen Säuren und Persäuren und deren Kombinationen. In erfindungsgemäß bevorzugter Weise wird das Oxidationsreagenz ausgewählt aus der Gruppe von Sauerstoff, Wasserstoffperoxid (H_2O_2), Salpetersäure (HNO_3) und Ammoniumperoxodisulfat ($(NH4)_2S_2O_8$) sowie deren Kombinationen. Im Rahmen der vorliegenden Erfindung wird insbesondere bei der Verwendung von Sauerstoff, welcher der zu oxidierenden Aktivkohle insbesondere in Form von atmosphärischer Luft zugeführt werden kann, auch von einer sogenannten thermischen Oxidation gesprochen, da diese in der Regel unter Erwärmung stattfindet, wohingegen bei Verwendung der weiteren Oxidationsreagenzien, insbesondere von H_2O_2 bzw. HNO_3 erfindungsgemäß im Allgemeinen auch von einer chemischen Oxidation gesprochen wird, das in diesem Fall in Abhängigkeit von dem eingesetzten Reagenz mitunter keine zusätzliche Erwärmung erforderlich ist, obwohl diese im Allgemeinen auch hier durchgeführt werden kann. Insbesondere können die zuvor genannten Oxidationsreagenzien ("OR") in gasförmiger und/oder in flüssiger Form, insbesondere in Form von vorzugsweise wässrigen Lösungen oder dergleichen eingesetzt werden, was dem Fachmann als solches grundsätzlich bekannt ist.

[0065] Im Allgemeinen kann die Oberflächenoxidation unter Erwärmen erfolgen. Hierbei kann die Oberflächenoxidation bei solchen Temperaturen erfolgen, dass eine Reaktion des Oxidationsreagenzes ("OR") mit der Aktivkohle unter Ausbildung von sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle erfolgt. Insbesondere kann in diesem Zusammenhang die Oberflächenoxidation im Temperaturbereich von –20°C bis 1.000°C, insbesondere 0°C bis 800°C, vorzugsweise 20°C bis 600°C, bevorzugt 30°C bis 500°C, durchgeführt werden. Insbesondere kann in diesem Zusammenhang die Oberflächenoxidation für eine Zeitdauer im Bereich von 1 Minute bis 600 Minuten, insbesondere 5 Minuten bis 500 Minuten, bevorzugt 10 Minuten bis 400 Minuten, durchgeführt werden. Hinreichend kann das Maß der Oberflächenoxidation, insbesondere die Anzahl bzw. der Gehalt an sauerstoffhaltigen Gruppen auf der Aktivkohleoberfläche, vorgegeben werden.

[0066] Gemäß einer ersten erfindungsgemäß besonders bevorzugten Ausführungsform kann das Oxidationsreagenz ("OR") ausgewählt werden aus der Gruppe von anorganischen oder organischen Oxiden und Peroxiden sowie anorganischen oder organischen Säuren und Persäuren und deren Kombinationen, bevorzugt aus der Gruppe von Wasserstoffperoxid (H_2O_2) und Salpetersäure (HNO_3), vorzugsweise Salpetersäure (HNO_3). Insbesondere kann dabei die Oberflächenoxidation dann im Temperaturbereich von –20°C bis 500°C, insbesondere –10°C bis 400°C, vorzugsweise 0°C bis 350°C, bevorzugt 10°C bis 300°C, besonders bevorzugt 15°C bis 250°C, ganz besonders bevorzugt 20°C bis 200°C, durchgeführt werden. Hierbei handelt es sich, wie zuvor beschrieben, sozusagen um eine chemische Oxidation, welche grundsätzlich und in Abhängigkeit des eingesetzten Oxidationsreagenzes auch bei Raumtemperatur durchgeführt werden kann.

[0067] Gemäß einer zweiten erfindungsgemäß besonders bevorzugten Ausführungsform kann das Oxidationsreagenz ("OR") ausgewählt werden aus der Gruppe von Sauerstoff und Ozon, vorzugsweise Sauerstoff. Insbesondere sollte dabei die Oberflächenoxidation dann im Temperaturbereich von 100°C bis 1.000°C, insbesondere 150°C bis 900°C, vorzugsweise 200°C bis 750°C, bevorzugt 225°C bis 600°C, besonders bevorzugt 250°C bis 500°C, ganz besonders bevorzugt 250°C bis 450°C, durchgeführt werden. Wie zuvor angeführt handelt es sich hierbei gewissermaßen um eine thermische Oxidation.

[0068] Was die erfindungsgemäß vorgesehene Oberflächenoxidation der Aktivkohle anbelangt, so handelt es sich hierbei zusammenfassend zum einen gezielt regelbaren bzw. einstellbaren Prozess, welcher auf Basis der Art und Weise des einzusetzenden Oxidationsreagenzes ("OR"), der Oxidationszeit und/oder der Temperatur gesteuert werden kann. Wie zuvor angeführt, wird durch die gezielte Oxidation die auf diese Weise an ihrer Oberfläche oxidierte Aktivkohle für die nachfolgende Funktionalisierung bzw. Modifizierung mit Stickstoff optimiert. So kann beispielsweise in Abhängigkeit von der Oxidationszeit der Gehalt an flüchtigen Bestandteilen als Maß für den Oxidationsgrad erhöht werden. Zudem kann der pH-Wert, insbesondere der Oberflächen-pH-Wert der an ihrer Oberfläche oxidierten Aktivkohle durch Wahl der Oxidationsbedingungen eingestellt bzw. maßgeschneidert werden, beispielsweise über die Dauer der Oxidation. So ist bei der zuvor beschriebenen chemischen Oxidation insbesondere die Bildung saurerer Oberflächenoxide bevorzugt, wohingegen bei

PAC ET AL. EXHIBIT 1019
Page 2209

der zuvor beschriebenen thermischen Oxidation insbesondere die Bildung basischer Oberflächenoxide bevorzugt ist. Gleichermaßen hat eine zunehmende Oxidationszeit in Bezug auf die an ihrer Oberfläche oxidierte Aktivkohle einen Einfluss auf die sogenannte Rütteldichte der Aktivkohle, welche im Allgemeinen mit zunehmender Oxidationszeit zumindest geringfügig abnimmt. Gleichermaßen hat die Oxidation auch einen Einfluss auf das Gesamtporenvolumen, insbesondere das Gesamtporenvolumen nach Gurvich, der Aktivkohle, welche beispielsweise mit zunehmender Oxidationszeit zumindest geringfügig vergrößert wird. Im Ergebnis kann somit auf Basis der Oxidation die Oberflächeneigenschaften der Aktivkohle in gezielter Weise hinsichtlich der nachfolgenden Modifizierung mit Stickstoff eingestellt bzw. maßgeschneidert werden.

[0069] Im Rahmen der erfindungsgemäß realisierten Verfahrensführung kann es zudem vorgesehen sein, dass im Anschluss an die Oberflächenoxidation und insbesondere vor der Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff eine Aufreinigung bzw. Trocknung der an ihrer Oberfläche oxidierten Aktivkohle erfolgt. In diesem Zusammenhang kann die Aufreinigung mittels mindestens eines Waschvorgangs in einer Flüssigkeit, insbesondere Wasser, erfolgen. Gleichermaßen kann die Trocknung unter Erwärmung der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere auf Temperaturen im Bereich von 40°C bis 200°C, insbesondere 50°C bis 150°C, vorzugsweise 60°C bis 120°C, erfolgen. Durch die gezielte Trocknung der an ihrer Oberfläche oxidierten Aktivkohle wird das so erhaltene Zwischenprodukt bzw. Intermediat weiterführend für die nachfolgende Modifizierung bzw. Funktionalisierung mit Stickstoff optimiert, insbesondere da die Zugänglichkeit für das Stickstoffmodifizierungsreagenz ("SMR") verbessert wird.

[0070] Was die sich der Oberflächenoxidation der Aktivkohle anschließende Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff anbelangt, so sollte diese ein Inkontaktbringen der nach der Oberflächenoxidation erhaltenen Aktivkohle mit dem Stickstoffmodifizierungsreagenz ("SMR"), insbesondere gefolgt von einer thermischen Behandlung, umfassen. Auf diese Weise wird die chemische Anbindung bzw. Integration bzw. die Ausbildung stickstoffhaltiger funktioneller Gruppen an der Oberfläche der zuvor oxidierten Aktivkohle gewährleistet. Wie zuvor angeführt, interagiert das Stickstoffmodifizierungsreagenz ("SMR") insbesondere mit den sauerstoffhaltigen Oberflächenfunktionalitäten, welche im Rahmen des vorangehenden Oxidationsschrittes in gezielter Weise auf der Aktivkohle generiert worden sind.

[0071] Durch das Inkontaktbringen der an ihrer Oberfläche oxidierten Aktivkohle mit dem Stickstoffmodifizierungsreagenz ("SMR") wird insbesondere auch das mit der Umgebung in Verbindung stehende Porensystem der Aktivkohle mit dem Stickstoffmodifizierungsreagenz gefüllt bzw. zusammengebracht, was auf diese Weise die nachfolgenden chemischen Reaktionen insbesondere mit den sauerstoffhaltigen funktionellen Gruppen der an ihrer Oberfläche oxidierten Aktivkohle ermöglicht.

[0072] Insbesondere erfolgt im Rahmen der Modifizierung bzw. Funktionalisierung mit Stickstoff eine Reaktion des Stickstoffmodifizierungsreagenzes ("SMR") mit den sauerstoffhaltigen funktionellen Gruppen, wie zuvor definiert, wobei diesbezüglich ein zentraler Vorteil darin zu sehen ist, dass das Porenvolumen der Aktivkohle nicht signifikant oder allenfalls nur geringfügig verändert wird. Erfindungsgemäß liegt gewissermaßen eine chemische Anbindung von Stickstoff an den sauerstoffhaltigen funktionellen Gruppen vor, welche gegebenenfalls weiterführend modifiziert werden kann, wie nachfolgend noch angeführt.

[0073] Was das erfindungsgemäß für die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff eingesetzte Stickstoffmodifizierungsreagenz ("SMR") anbelangt, so kann dieser erfindungsgemäß ausgewählt werden aus der Gruppe von Harnstoff, Ammoniak, Melamin und Aminosäuren sowie deren Kombinationen, insbesondere Harnstoff und Ammoniak sowie deren Kombinationen, vorzugsweise Harnstoff.

[0074] Gemäß einer erfindungsgemäß bevorzugten Ausführungsform kann als das für die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff eingesetzte Stickstoffmodifizierungsreagenz ("SMR") Harnstoff verwendet werden. In diesem Zusammenhang kann der Harnstoff in Form einer vorzugsweise wässrigen Lösung, bevorzugt in Form einer zumindest im Wesentlichen gesättigten Harnstofflösung, eingesetzt werden. Im Allgemeinen kann in Abhängigkeit von dem gewünschten Grad der Stickstofffunktionalisierung die Menge und Konzentration der Harnstofflösung entsprechend variiert werden, was im fachüblichen Können des Fachmanns liegt. In diesem Zusammenhang kann erfindungsgemäß beispielsweise derart vorgegangen werden, dass die an ihrer Oberfläche oxidierte Aktivkohle zunächst in die Harnstofflösung eingetaucht wird, die überflüssige Harnstofflösung dann abdekantiert wird und nachfolgend eine thermische Behandlung insbesondere in einem Inertgasstrom erfolgt.

PAC ET AL. EXHIBIT 1019
Page 2210

[0075] Gemäß einer weiteren erfindungsgemäßen Ausführungsform kann es auch vorgesehen sein, dass als Stickstoffmodifizierungsreagenz ("SMR") Ammoniak (NH_3) verwendet wird. In diesem Zusammenhang kann Ammoniak in Form des Gases und/oder als Ammoniakwasser, insbesondere in Form des Gases, eingesetzt werden. In diesem Zusammenhang kann die zu behandelnde und an ihrer Oberfläche oxidierte Aktivkohle einem Ammoniak- bzw. NH_3-Gasstrom bzw. einem NH_3-haltigen Gasstrom unter entsprechender Erwärmung ausgesetzt werden.

[0076] Was die Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff weiterhin anbelangt, so kann diese im Rahmen des erfindungsgemäß durchgeführten Verfahrens durch Reaktion, insbesondere chemische Reaktion, vorzugsweise unter Ausbildung kovalenter Bindungen, des Stickstoffmodifizierungsreagenzes ("SMR") mit der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere mit den sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle, erfolgen. In diesem Zusammenhang kann es erfindungsgemäß vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Ausbildung stickstoffhaltiger funktioneller Gruppen, insbesondere ausgewählt aus der Gruppe von Aminen, insbesondere primären, sekundären, tertiären und quartären Aminen, Iminen und Azinen sowie deren Kombinationen erfolgt, insbesondere können Amin-, Imin-, Azin-, Pyrrol-, Nitril-, Nitro-, Nitroso-, Pyridin-, Imid-, Amid-, Lactam- und/oder Pyridongruppen sowie deren Kombinationen, ausgebildet werden. Erfindungsgemäß kann somit zumindest zunächst eine chemische Anbindung von Stickstoff unter Ausbildung stickstoffhaltiger funktionellen Gruppen vorliegen, wobei die chemisch Anbindung insbesondere an der Oberfläche der zuvor oxidierten Aktivkohle lokalisiert ist und insbesondere aufgrund einer chemischen Reaktion unter Ausbildung kovalenter Bindungen mit den zuvor gebildeten sauerstoffhaltigen funktionellen Gruppen resultiert.

[0077] Erfindungsgemäß kann es aber auch vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Integration und/oder Einbau, insbesondere unter Ausbildung chemischer Bindungen, vorzugsweise unter Ausbildung kovalenter chemischer Bindungen, insbesondere zwischen Stickstoff einerseits und Kohlenstoff andererseits, in das Kohlenstoffgerüst und/oder in die Kohlenstoffmatrix der an ihrer Oberfläche oxidierten Aktivkohle erfolgt. Auf diese Weise wird der Stickstoff sozusagen direkt in das Kohlenstoffgerüst der Aktivkohle integriert bzw. eingebaut. Dies entspricht einer Dotierung mit Stickstoff (N-Dotierung). Die Integration von Stickstoff in das Kohlenstoffgerüst kann dabei ausgehend von der zuvor beschriebenen Anbindung des Stickstoffs bzw. des Stickstoffmodifizierungsreagenzes ("SMR") an die sauerstoffhaltigen funktionellen Gruppen erfolgen, insbesondere im Rahmen einer nachfolgend noch spezifizierten thermischen Behandlung, welche ausgehend von den resultierenden stickstoffhaltigen funktionellen Gruppen zu einer Integration des Stickstoffs in das Kohlenstoffgerüst der Aktivkohle insbesondere auf Basis einer Pyrolyse führt.

[0078] Was die erfindungsgemäß realisierte Verfahrensführung weiterhin anbelangt, so kann es im Rahmen der vorliegenden Erfindung vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen erfolgt, insbesondere auf Temperaturen oberhalb der Zersetzungstemperatur des Stickstoffmodifizierungsreagenzes ("SMR"). In diesem Zusammenhang kann die Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter solchen Temperaturen erfolgen, dass eine Reaktion des Stickstoffmodifizierungsreagenzes ("SMR") mit der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere mit den sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle, erfolgt. Insbesondere kann diesbezüglich derart vorgegangen werden, dass die Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff im Temperaturbereich von 200°C bis 1.200°C, insbesondere 300°C bis 1.000°C, vorzugsweise 500°C bis 950°C, durchgeführt wird. Was die Zeitdauer der Wärmebehandlung anbelangt, so kann es erfindungsgemäß zudem vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, insbesondere 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, durchgeführt wird. Insbesondere kann in Bezug auf die Verwendung von Harnstoff als Stickstoffmodifizierungsreagenz ("SMR") bei Temperaturen oberhalb von 180°C verfahren werden, wobei die vorgenannte Temperatur der Zersetzungstemperatur von Harnstoff entspricht.

[0079] Was die zur Anbindung des Stickstoffmodifizierungsreagenzes ("SMR") an die sauerstoffhaltigen Gruppen zur Ausbildung der stickstoffhaltigen funktionellen Gruppen bzw. zur Integration des Stickstoffs in das Kohlenstoffgerüst bzw. -gitter durchgeführte Wärmebehandlung der an ihrer Oberfläche oxidierten Aktivkohle gemäß einer weiteren bevorzugten Ausführungsform weiterhin anbelangt, so kann es erfindungsgemäß vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen in Form einer einstufigen Wärmebehandlung erfolgt.

PAC ET AL. EXHIBIT 1019
Page 2211

[0080] Diesbezüglich kann es insbesondere vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen auf einen Temperaturbereich von 300°C bis 700°C, insbesondere 400°C bis 600°C, vorzugsweise 400°C bis 550°C, durchgeführt wird, insbesondere für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, bevorzugt 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden. Auf diese Weise werden insbesondere stickstoffhaltige funktionelle Gruppen, wie sie zuvor definiert worden sind, ausgebildet.

[0081] Erfindungsgemäß kann es auch vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen auf einen Temperaturbereich von 750°C bis 1.200°C, insbesondere 800°C bis 1.100°C, vorzugsweise 850°C bis 1.050°C, durchgeführt wird. Diesbezüglich kann insbesondere für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, insbesondere 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, verfahren werden. Im Rahmen der zuvor beschriebenen Wärmebehandlung erfolgt insbesondere eine Integration bzw. ein Einbau des Stickstoffs in das Kohlenstoffgerüst bzw. die Kohlenstoffmatrix der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere wie zuvor definiert. Auf Basis dieser Verfahrensführung mit einer Wärmebehandlung unter höheren Temperaturen erfolgt somit vorrangig eine Immobilisierung des Stickstoffs aufgrund einer chemischen Anbindung bzw. Integration von Stickstoff an bzw. in das Kohlenstoffgerüst bzw. Kohlenstoffgitter der Aktivkohle, wobei auch diesbezüglich – ohne sich auf diese Theorie beschränken bzw. festlegen zu wollen – zunächst stickstoffhaltige funktionelle Gruppen gebildet werden können, welche nachfolgend zur Überführung des Stickstoffs in die Kohlenstoffstruktur gewissermaßen thermisch bzw. auf Basis von Pyrolyse zersetzt werden, so dass im Endprodukt reaktiver bzw. katalytischer Stickstoff direkt in das Kohlenstoffgerüst der so behandelten Aktivkohle eingebaut bzw. inkorporiert vorliegt.

[0082] Gemäß einer weiteren erfindungsgemäß bevorzugten Ausführungsform kann die Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff auch unter Erwärmen in Form einer mehrstufigen, insbesondere zweistufigen Wärmebehandlung erfolgen.

[0083] In diesem Zusammenhang kann es erfindungsgemäß insbesondere vorgesehen sein, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff in einer ersten Wärmebehandlung unter Erwärmen auf einen Temperaturbereich von 300°C bis 700°C, insbesondere 400°C bis 600°C, vorzugsweise 400°C bis 550°C, und einer nachfolgenden zweiten Wärmebehandlung unter Erwärmen auf einen Temperaturbereich von 750°C bis 1.200°C, insbesondere 800°C bis 1.100°C, vorzugsweise 850°C bis 1.050°C, durchgeführt wird. Insbesondere können dabei die jeweiligen Wärmebehandlungen, unabhängig voneinander, für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, insbesondere 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, durchgeführt werden. Insbesondere werden auf diese Weise im ersten Schritt die stickstoffhaltigen funktionellen Gruppen gebildet, welche dann im zweiten Schritt unter Pyrolyse zersetzt werden, wobei der Stickstoff in das Kohlenstoffgerüst überführt bzw. eingebaut wird.

[0084] Die Temperatur der Wärmebehandlung hat somit einen signifikanten Einfluss auf die chemische Konstitution des in die Aktivkohle eingebrachten Stickstoffs. Bei niedrigen Temperaturen der Wärmebehandlung, wie zuvor definiert, resultiert vorrangig die Bildung von stickstoffhaltigen funktionellen Gruppen, und bei höheren Temperaturen, wie zuvor definiert, erfolgt insbesondere bzw. vorrangig ein Einbau bzw. eine Integration des Stickstoffs in die Gerüststruktur der Aktivkohle.

[0085] In diesem Zusammenhang kann es auch vorgesehen sein, dass im Anschluss an die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff eine Aufreinigung und/oder Trocknung der erhaltenen Aktivkohle erfolgt. In diesem Zusammenhang kann die Aufreinigung mittels mindestens eines Waschvorganges in einer Flüssigkeit, insbesondere Wasser, erfolgen. Zudem kann eine Trocknung unter Erwärmung der mit Stickstoff ausgerüsteten Aktivkohle, insbesondere auf Temperaturen im Bereich von 40°C bis 200°C, insbesondere 50°C bis 150°C, vorzugsweise 60°C bis 120°C, erfolgen können. Durch den Aufreinigungs- bzw. Waschvorgang werden insbesondere auch Verbrennungsrückstände von der mit Stickstoff modifizierten Aktivkohle entfernt.

[0086] Aufgrund der erfindungsgemäß realisierten Verfahrensführung kann der Stickstoffgehalt der behandelten Aktivkohle signifikant gesteigert werden, wobei für das erhaltene und mit Stickstoff modifizierte Produkt der Gehalt an flüchtigen Bestandteile ("fB") der Aktivkohle als Maß auch für den Gehalt an Stickstoffgruppen nach erfolgter Stickstoffmodifizierung bzw. -funktionalisierung herangezogen werden kann, insbesondere im Hinblick auf die zuvor definierten stickstoffhaltigen funktionellen Gruppen. So kann die mit Stickstoff ausgerüstete Aktivkohle einen Gehalt an flüchtigen Bestandteilen ("fB"), bezogen auf das Trockengewicht der mit

PAC ET AL. EXHIBIT 1019
Page 2212

Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 20 Gew.-%, insbesondere 0,2 Gew.-% bis 15 Gew.-%, vorzugsweise 0,3 Gew.-% bis 12 Gew.-%, bevorzugt 0,5 Gew.-% bis 10 Gew.-%, besonders bevorzugt 1 Gew.-% bis 10 Gew.-%, aufweisen. Auch diesbezüglich können die flüchtigen Bestandteile ("fB") auf Basis der Norm ISO 562:1981 bzw. unter Erwärmen für 7 Minuten auf eine Temperatur von 900°C unter Inertatmosphäre bestimmt werden, wobei insbesondere von der Trockensubstanz ausgegangen wird.

[0087] Darüber hinaus kann die mit Stickstoff ausgerüstete Aktivkohle einen Stickstoffgehalt (d. h. Gesamtstickstoffgehalt), bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 30 Gew.-%, insbesondere 0,2 Gew.-% bis 25 Gew.-%, vorzugsweise 0,3 Gew.-% bis 20 Gew.-%, bevorzugt 0,5 Gew.-% bis 15 Gew.-%, besonders bevorzugt 1 Gew.-% bis 15 Gew.-%, aufweisen. In diesem Zusammenhang sollten mindestens 50%, insbesondere mindestens 60%, vorzugsweise mindestens 70%, bevorzugt mindestens 80% des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der mit Stickstoff ausgerüsteten Aktivkohle chemisch gebunden und/oder integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der mit Stickstoff ausgerüsteten Aktivkohle vorliegen. Gleichermaßen sollten in diesem Zusammenhang 50% bis 99,9%, insbesondere 60% bis 99%, vorzugsweise 70% bis 95%, bevorzugt 80% bis 90%, des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der mit Stickstoff ausgerüsteten Aktivkohle chemisch gebunden und/oder integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der mit Stickstoff ausgerüsteten Aktivkohle vorliegen. Mit anderen Worten sollte der Stickstoff auf Basis der obigen Ausführungen bzw. der obigen Mengen in das Kohlenstoffgerüst bzw. -gitter der Aktivkohle integriert vorliegen, wobei dann der restliche Anteil an Stickstoff in Form von stickstoffhaltigen funktionellen Gruppen vorliegt, insbesondere wie zuvor definiert. Hierdurch wird eine besonders gute katalytische Aktivität bzw. Reaktivität bei gleichzeitig hervorragender Beständigkeit der Ausrüstung mit Stickstoff erreicht.

[0088] In diesem Zusammenhang werden im Allgemeinen die höheren Werte für den in das Kohlenstoffgerüst bzw. -gitter der Aktivkohle integrierten Stickstoff erreicht, wenn die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen auf einen Temperaturbereich von 750°C bis 1.200°C, insbesondere wie zuvor definiert, durchgeführt wird. Der Stickstoff liegt dann allenfalls nur zu einem geringen Anteil in Form von stickstoffhaltigen funktionellen Gruppen vor. Dagegen werden im Allgemeinen geringere Werte für den in das Kohlenstoffgerüst bzw. -gitter der Aktivkohle integrierten Stickstoff erreicht, wenn die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen auf einen Temperaturbereich von 300°C bis 700°C, insbesondere wie zuvor definiert, durchgeführt wird. Wie zuvor erläutert, liegt der Stickstoff dann zu einem größeren Anteil in Form von stickstoffhaltigen funktionellen Gruppen vor. Hierdurch kann insbesondere eine verbesserte Abbauleistung gegenüber bestimmten Substanzen, wie insbesondere Formaldehyd, erreicht werden.

[0089] Weiterhin kann die mit Stickstoff ausgerüstete erfindungsgemäße Aktivkohle einen Gehalt an in das Kohlenstoffgerüst eingebautem bzw. integriertem (d. h. sozusagen immobilisiertem) Stickstoff, bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,05 Gew.-%, insbesondere mindestens 0,1 Gew.-%, vorzugsweise mindestens 0,2 Gew.-%, bevorzugt mindestens 0,3 Gew.-%, besonders bevorzugt mindestens 0,5 Gew.-%, ganz besonders bevorzugt mindestens 1 Gew.-%, bzw. im Bereich von 0,05 Gew.-% bis 30 Gew.-%, insbesondere 0,1 Gew.-% bis 25 Gew.-%, vorzugsweise 0,2 Gew.-% bis 20 Gew.-%, bevorzugt 0,5 Gew.-% bis 15 Gew.-%, aufweisen.

[0090] In diesem Zusammenhang kann der jeweilige Stickstoffgehalt der erfindungsgemäßen Aktivkohlen mit an sich bekannten Methoden bestimmt werden. Der Gesamtstickstoffgehalt kann mittels an sich bekannter Elementaranalyse bestimmt werden, während die Ermittlung der flüchtigen Bestandteile ("fB") gemäß der ISO 562:1981 erfolgen kann. Aus der Differenz von mittels Elementaranalyse bestimmtem Gesamtstickstoffgehalt einerseits und gemäß der ISO 562:1981 bestimmtem Gehalt an flüchtigen Bestandteilen (d. h. flüchtigen stickstoffhaltigen funktionellen Gruppen) kann dann der Gehalt an immobilisiertem bzw. in das Kohlenstoffgerüst eingebautem Stickstoff ermittelt werden.

[0091] Nachfolgend werden weitere charakteristische Eigenschaften bzw. Parameter der mit dem erfindungsgemäß durchgeführten Verfahren erhältlichen Aktivkohle definiert. Die nachfolgenden Parameterangaben be-

PAC ET AL. EXHIBIT 1019
Page 2213

züglich der im Rahmen des erfindungsgemäß durchgeführten Verfahrens erhältlichen stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle werden dabei mit genormten oder explizit angegebenen Bestimmungsverfahren oder mit dem Fachmann an sich geläufigen Bestimmungsmethoden bestimmt. Insbesondere die Parameterangaben betreffend die Charakterisierung der Porosität, der Porengrößenverteilung und anderer Adsorptionseigenschaften ergeben sich im Allgemeinen jeweils aus dem betreffenden Stickstoffsorptionsisothermen der betreffenden Aktivkohle bzw. der vermessenen Produkte.

[0092] Insbesondere wird im Rahmen der vorliegenden Erfindung eine mit Stickstoff ausgerüstete Aktivkohle bzw. eine stickstoffmodifizierte oder stickstofffunktionalisierte Aktivkohle erhalten, welche ein Gesamtporenvolumen, insbesondere ein Gesamtporenvolumen nach Gurvich, im Bereich von 0,4 bis 4 cm^3/g, insbesondere 0,5 bis 3,5 cm^3/g, vorzugsweise 0,6 bis 3 cm^3/g, besonders bevorzugt 0,7 bis 2,5 cm^3/g, aufweist. In diesem Zusammenhang sollten 30 bis 99%, insbesondere 40% bis 99%, vorzugsweise 50% bis 95%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der mit Stickstoff ausgerüsteten Aktivkohle, durch Poren mit Porendurchmessern von ≤ 50 nm, insbesondere durch Mikro- und/oder Mesoporen, gebildet werden. Gleichermaßen sollten in diesem Zusammenhang 10% bis 85%, insbesondere 20% bis 80%, vorzugsweise 30% bis 75%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der mit Stickstoff ausgerüsteten Aktivkohle, durch Poren mit Porendurchmessern im Bereich von 2 nm bis 50 nm, insbesondere durch Mesoporen, gebildet werden.

[0093] Was die Bestimmung des Gesamtporenvolumens nach Gurvich anbelangt, so handelt es sich um eine dem Fachmann auf diesem Gebiet an sich bekannte Mess-Bestimmungsmethode. Zu weitergehenden Einzelheiten bezüglich der Bestimmung des Gesamtporenvolumens nach Gurvich kann beispielsweise verwiesen werden auf L. Gurvich (1915), J. Phys. Chem. Soc. Russ. 47, 805, sowie auf S. Lowell et al., Characterization of Porous Solids and Powders: Surface Area Pore Size and Density, Kluwer Academic Publishers, Article Technology Series, Seiten 111 ff.

[0094] Insbesondere kann es im Rahmen der vorliegenden Erfindung vorgesehen sein, dass die mit Stickstoff ausgerüstete Aktivkohle ein durch Poren mit Porendurchmessern ≤ 2 nm gebildetes Porenvolumen, insbesondere Mikroporenvolumen nach Carbon Black, insbesondere nach Auswertung mittels t-plot, im Bereich von 0,05 bis 2 cm^3/g, insbesondere 0,1 bis 1,5 cm^3/g, vorzugsweise 0,2 bis 1,1 cm^3/g, besonders bevorzugt 0,3 bis 1 cm^3/g, aufweist. Gleichermaßen kann es vorgesehen sein, dass 10% bis 95%, insbesondere 20% bis 95%, vorzugsweise 30% bis 90%, des Gesamtporenvolumens der mit Stickstoff ausgerüsteten Aktivkohle durch Poren mit Porendurchmessern von ≤ 2 nm, insbesondere durch Mikroporen, gebildet werden.

[0095] Die Bestimmungsmethode nach Carbon Black ist dem Fachmann an sich bekannt, so dass es diesbezüglich keiner weitergehenden Einzelheiten bedarf. Zudem kann zu weitergehenden Einzelheiten der Bestimmung der Porenoberfläche und des Porenvolumens nach Carbon Black beispielsweise verwiesen werden auf R. W. Magee, Evaluation of the External Surface Area of Carbon Black by Nitrogen Adsorption, Presented at the Meeting of the Rubber Division of the American Chem. Soc., October 1994, z. B. referiert in: Quantachrome Instruments, AUTOSORB-1, AS1 WinVersion 1.50, Operating Manual, OM, 05061, Quantachrome Instruments 2004, Florida, USA, Seiten 71 ff.

[0096] Im Rahmen der vorliegenden Erfindung ist es gleichermaßen vorteilhaft, wenn die stickstoffmodifizierte bzw. stickstofffunktionalisierte mit Stickstoff ausgerüstete Aktivkohle einen mittleren Porendurchmesser im Bereich von 1 bis 60 nm, insbesondere 1 bis 55 nm, bevorzugt 1,5 bis 50 nm, besonders bevorzugt 2 bis 45 nm, aufweist.

[0097] Um die Sorptionseigenschaften der mit dem erfindungsgemäß durchgeführten Verfahren erhältlichen mit Stickstoff ausgerüsteten Aktivkohle zu erhalten bzw. zu gewährleisten, sollte die mit Stickstoff ausgerüstete Aktivkohle eine spezifische BET-Oberfläche im Bereich von 500 m^2/g bis 3.500 m^2/g, insbesondere 600 bis 3.000 m^2/g, vorzugsweise 700 bis 2.750 m^2/g, besonders bevorzugt 800 bis 2.500 m^2/g, aufweisen.

[0098] Die Bestimmung der spezifischen Oberfläche gemäß BET ist dem Fachmann grundsätzlich als solche bekannt, so dass diesbezüglich keine weitergehenden Einzelheiten ausgeführt zu werden brauchen. Sämtliche BET-Oberflächenangaben beziehen sich auf die Bestimmung gemäß ASTM D6556-04. Im Rahmen der vorliegenden Erfindung wird zur Bestimmung der BET-Oberfläche – im Allgemeinen und sofern nachfolgend nicht ausdrücklich abweichend angegeben – die so genannte MultiPoint-BET-Bestimmungsmethode (MP-BET) in einem Partialdruckbereich p/p_0 von 0,05 bis 0,1 angewendet.

PAC ET AL. EXHIBIT 1019
Page 2214

[0099] In Bezug auf weitergehende Einzelheiten zu der Bestimmung der BET-Oberfläche bzw. zu der BET-Methode kann auf die vorgenannte ASTM D6556-04 sowie auf Römpp Chemielexikon, 10. Auflage, Georg Thieme Verlag, Stuttgart/New York, Stichwort: "BET-Methode", einschließlich der dort referierten Literatur, und auf Winnacker-Küchler (3. Auflage), Band 7, Seiten 93 ff. sowie auf Z. Anal. Chem. 238, Seiten 187 bis 193 (1968), verwiesen werden.

[0100] Des Weiteren ist es von Vorteil, wenn die stickstoffmodifizierte bzw. stickstofffunktionalisierte bzw. die mit Stickstoff ausgerüstete Aktivkohle eine durch Mikroporen gebildete Oberfläche von 400 bis 2.500 m^2/g, insbesondere 500 bis 2.300 m^2/g, vorzugsweise 600 bis 2.100 m^2/g, besonders bevorzugt 700 bis 1.900 m^2/g, aufweist.

[0101] Die stickstoffmodifizierte bzw. stickstofffunktionalisierte bzw. die mit Stickstoff ausgerüstete Aktivkohle sollte zudem eine Dichte von 1,1 bis 3,5 g/ml, insbesondere von 1,5 bis 3 g/ml, vorzugsweise von 1,75 bis 2,75 g/ml, bevorzugt von 2 bis 2,5 g/ml, aufweisen.

[0102] Gleichermaßen sollte die stickstoffmodifizierte bzw. stickstofffunktionalisierte bzw. die mit Stickstoff ausgerüstete Aktivkohle eine Schüttdichte von 0,1 bis 1,5 g/ml, insbesondere von 0,15 bis 1 g/ml, vorzugsweise von 0,2 bis 0,8 g/ml, bevorzugt von 0,3 bis 0,6 g/ml, aufweisen.

[0103] Zudem ist es von Vorteil, wenn die stickstoffmodifizierte bzw. stickstofffunktionalisierte bzw. mit Stickstoff ausgerüstete Aktivkohle eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, von mindestens 5 Newton, insbesondere mindestens 10 Newton, vorzugsweise mindestens 15 Newton, bevorzugt mindestens 20 Newton, aufweist und/oder dass die Aktivkohle eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, im Bereich von 5 bis 50 Newton, insbesondere 10 bis 45 Newton, vorzugsweise 15 bis 40 Newton, aufweist.

[0104] Was darüber hinaus die im Rahmen des erfindungsgemäß durchgeführten Verfahrens eingesetzte Aktivkohle bzw. Ausgangsaktivkohle anbelangt, welche zunächst an ihrer Oberfläche oxidiert und nachfolgend mit Stickstoff modifiziert bzw. ausgerüstet wird, anbelangt, so kann diesbezüglich eine Vielzahl unterschiedlicher Aktivkohlen, beispielsweise mit unterschiedlicher Porenstruktur im Hinblick auf die Verteilung von Mikro-, Meso- und Makroporen, eingesetzt werden. Insbesondere können kommerziell erhältliche bzw. handelsübliche Aktivkohlen eingesetzt werden. Im Rahmen der vorliegenden Erfindung zum Einsatz kommende Aktivkohlen werden beispielsweise von der Blücher GmbH, Erkrath, Deutschland oder der AdsorTech GmbH, Premnitz, Deutschland, vertrieben.

[0105] Was die erfindungsgemäß eingesetzte Aktivkohle bzw. Ausgangsaktivkohle weiterhin anbelangt, so werden diesbezüglich insbesondere eine kornförmige, insbesondere kugelförmige Aktivkohle verwendet. Die eingesetzte Aktivkohle bzw. Ausgangsaktivkohle, insbesondere Kornkohle oder Kugelkohle, kann dabei nach bekannten Verfahren des Standes erhalten werden. Üblicherweise werden zu diesem Zweck korn- bzw. kugelförmig sulfonierte organische Polymere, insbesondere auf Basis von divinylbenzolvernetztem Polystyrol, carbonisiert und anschließend zu der betreffenden Aktivkohle aktiviert. Für weitergehende diesbezügliche Einzelheiten kann beispielsweise auf die Druckschriften DE 43 28 219 A1, DE 43 04 026 A1, DE 196 00 237 A1 sowie EP 1 918 022 A1 bzw. auf die parallele, zu derselben Patentfamilie gehörende US 7.737.038 B2 verwiesen werden. Gleichermaßen kann auch Aktivkohle auf Basis anderer Ausgangsmaterialien, wie Pech oder dergleichen, zum Einsatz kommen. Derartige Aktivkohlen sind dem Fachmann als solche bekannt.

[0106] Insbesondere wird im Rahmen der vorliegenden Erfindung eine Aktivkohle als Ausgangsmaterial eingesetzt, welche Partikelgrößen, insbesondere Teilchendurchmesser, im Bereich von 0,001 bis 2 mm, insbesondere 0,01 bis 1 mm, bevorzugt 0,05 bis 0,8 mm, vorzugsweise 0,1 bis 0,7 mm, besonders bevorzugt 0,15 bis 0,6 mm, aufweist. Dabei sollten, bezogen auf die Aktivkohle, mindestens 80 Gew.-%, insbesondere mindestens 90 Gew.-%, vorzugsweise mindestens 95 Gew.-% der eingesetzten Aktivkohle Partikelgrößen, insbesondere Teilchendurchmesser, in den vorgenannten Bereichen aufweisen. Weiterhin ist es erfindungsgemäß vorteilhaft, wenn die als Ausgangsmaterial eingesetzte Aktivkohle mittlere Partikelgrößen (D50), insbesondere mittlere Teilchendurchmesser (D50), im Bereich von 0,01 bis 1 mm, insbesondere 0,05 bis 0,8 mm, bevorzugt 0,1 bis 0,6 mm, vorzugsweise 0,15 bis 0,5 mm, besonders bevorzugt 0,2 bis 0,4 mm, aufweist. Die entsprechenden Teilchengrößen bzw. -durchmesser können beispielsweise auf Basis der Methode nach ASTM D2862-97/04 bestimmt werden. Zudem können die vorgenannten Größen mit Bestimmungsmethoden auf Basis einer Siebanalyse, auf Basis von Röntgenbeugung, Laserdiffraktometrie oder dergleichen bestimmt werden. Die jeweiligen Bestimmungsmethoden sind dem Fachmann als solche wohlbekannt, so dass es diesbe-

PAC ET AL. EXHIBIT 1019
Page 2215

züglich keiner weiteren Ausführungen bedarf. Die angegebenen Parameter der Ausgangaktivkohle finden sich in entsprechender Weise auch in der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle wieder.

[0107] Das erfindungsgemäß durchgeführte Verfahren ist mit einer Vielzahl von Vorteilen verbunden, wie sie bereits zuvor angeführt sind. Aufgrund der herausragenden Sorptionseigenschaften der mit dem erfindungsgemäß durchgeführten Verfahren erhaltenen bzw. erhältlichen Aktivkohle ist ein breites Einsatz- bzw. Verwendungsspektrum möglich, wie es nachfolgend noch im Detail angeführt ist.

[0108] Weiterer Gegenstand der vorliegenden Erfindung – gemäß einem zweiten Aspekt der vorliegenden Erfindung – ist die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle als solche, insbesondere mit katalytischen bzw. reaktiven Eigenschaften, vorzugsweise mit Stickstoff als katalytisch aktivem Heteroatom.

[0109] Die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle nach der Erfindung ist durch Oberflächenoxidation einer als Ausgangsmaterial eingesetzten Aktivkohle ("Ausgangsaktivkohle") unter Verwendung bzw. in Gegenwart mindestens eines Oxidationsreagenzes ("OR") und nachfolgender Ausrüstung, insbesondere Modifizierung bzw. Funktionalisierung, mit Stickstoff der auf diese Weise erhaltenen, an ihrer Oberfläche oxidierten Aktivkohle unter Verwendung bzw. in Gegenwart mindestens eines Stickstoffmodifizierungsreagenzes ("SMR") erhältlich.

[0110] Somit betrifft die vorliegende Erfindung gemäß diesem Erfindungsaspekt auch die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle als solche nach der Erfindung, insbesondere mit katalytischen bzw. reaktiven Eigenschaften, vorzugsweise mit Stickstoff als katalytisch aktivem Heteroatom. Die erfindungsgemäße Aktivkohle zeichnet sich dadurch aus, dass Stickstoff unter Ausbildung chemischer Bindungen, vorzugsweise unter Ausbildung kovalenter chemischer Bindungen, an die Aktivkohle gebunden ist.

[0111] Was die erfindungsgemäße Aktivkohle bzw. die mit Stickstoff ausgerüstete Aktivkohle nach der Erfindung als solche weiterhin anbelangt, so kann es erfindungsgemäß vorgesehen sein, dass Stickstoff in Form mindestens einer stickstoffhaltigen funktionellen Gruppe, insbesondere ausgewählt aus der Gruppe von Aminen, insbesondere primären, sekundären, tertiären und quartären Aminen, Iminen und Azinen sowie deren Kombinationen erfolgt. Insbesondere kann der Stickstoff in Form von Amin-, Imin-, Azin-, Pyrrol-, Nitril-, Nitro-, Nitroso-, Pyridin-, Imid-, Amid-, Lactam- und Pyridongruppen sowie deren Kombinationen, vorliegen. Dabei ist der Stickstoff vorzugsweise an der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle gebunden, vorzugsweise chemisch und/oder kovalent gebunden.

[0112] Gleichermaßen kann es erfindungsgemäß vorgesehen sein, dass in Bezug auf die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach der Erfindung Stickstoff in das Kohlenstoffgerüst bzw. in die Kohlenstoffmatrix der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle vorzugsweise unter Ausbildung kovalenter chemischer Bindungen, insbesondere zwischen Stickstoff einerseits und Kohlenstoff andererseits, integriert bzw. eingebaut ist.

[0113] Im Rahmen der vorliegenden Erfindung kann es vorgesehen sein, dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle einen Gehalt an flüchtigen Bestandteilen ("fB"), bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 20 Gew.-%, insbesondere 0,2 Gew.-% bis 15 Gew.-%, vorzugsweise 0,3 Gew.-% bis 12 Gew.-%, bevorzugt 0,5 Gew.-% bis 10 Gew.-%, besonders bevorzugt 1 Gew.-% bis 10 Gew.-%, aufweist. Wie zuvor angeführt, können die flüchtigen Bestandteile ("fB") als Maß für den Gehalt an Stickstoff im Hinblick auf das Vorliegen in Form von stickstoffhaltigen funktionellen Gruppen, insbesondere wie zuvor definiert, herangezogen werden. Für die diesbezüglichen Bestimmungsverfahren kann auf obige Ausführungen verwiesen werden.

[0114] Weiterhin ist es im Rahmen der vorliegenden Erfindung von Vorteil, wenn die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle einen Stickstoffgehalt, bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 30 Gew.-%, insbesondere 0,2 Gew.-% bis 25 Gew.-%, vorzugsweise 0,3 Gew.-% bis 20 Gew.-%, bevorzugt 0,5 Gew.-% bis 15 Gew.-%, besonders bevorzugt 1 Gew.-% bis 15 Gew.-%, aufweist. Diesbezüglich sollten mindestens 50%, insbesondere mindestens 60%, vorzugsweise mindestens 70%, bevorzugt mindestens 80%, des Stick-

PAC ET AL. EXHIBIT 1019
Page 2216

stoffs, bezogen auf den Gesamtstickstoffgehalt, in der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle chemisch gebunden bzw. integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle vorliegen. In diesem Zusammenhang sollten 50% bis 99,9%, insbesondere 60% bis 99%, vorzugsweise 70% bis 95%, bevorzugt 80% bis 90%, des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle chemisch gebunden bzw. integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle vorliegen.

[0115] Weiterhin kann die mit Stickstoff ausgerüstete erfindungsgemäße Aktivkohle einen Gehalt an in das Kohlenstoffgerüst eingebautem bzw. integriertem (d. h. sozusagen immobilisiertem) Stickstoff, bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von 0,05 Gew.-%, insbesondere mindestens 0,1 Gew.-%, vorzugsweise mindestens 0,2 Gew.-%, bevorzugt mindestens 0,3 Gew.-%, besonders bevorzugt mindestens 0,5 Gew.-%, ganz besonders bevorzugt mindestens 1 Gew.-%, bzw. im Bereich von 0,05 Gew.-% bis 30 Gew.-%, insbesondere 0,1 Gew.-% bis 25 Gew.-%, vorzugsweise 0,2 Gew.-% bis 20 Gew.-%, bevorzugt 0,5 Gew.-% bis 15 Gew.-%, aufweisen.

[0116] Insbesondere zeichnet sich die erfindungsgemäße Aktivkohle mit Stickstoffmodifizierung bzw. Stickstofffunktionalisierung auch durch die folgenden Parameter aus; für die diesbezüglichen Bestimmungsverfahren kann gleichermaßen auf obige Ausführungen verwiesen werden:
Erfindungsgemäß sollte die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle ein Gesamtporenvolumen, insbesondere ein Gesamtporenvolumen nach Gurvich, im Bereich von 0,4 bis 4 cm^3/g, insbesondere 0,5 bis 3,5 cm^3/g, vorzugsweise 0,6 bis 3 cm^3/g, besonders bevorzugt 0,7 bis 2,5 cm^3/g, aufweisen.

[0117] Diesbezüglich sollten mindestens 30% bis 99%, insbesondere 40% bis 99%, vorzugsweise 50% bis 95%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle, durch Poren mit Porendurchmessern von ≤ 50 nm, insbesondere durch Mikro- und/oder Mesoporen, gebildet sein. Insbesondere können dabei 10% bis 85%, insbesondere 20% bis 80%, vorzugsweise 30% bis 75%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle, durch Poren mit Porendurchmessern im Bereich von 2 nm bis 50 nm, insbesondere durch Mesoporen, gebildet sein.

[0118] Weiterhin sollte die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle erfindungsgemäß ein durch Poren mit Porendurchmessern ≤ 2 nm gebildetes Porenvolumen, insbesondere Mikroporenvolumen nach Carbon Black, insbesondere nach Auswertung mittels t-plot, im Bereich von 0,05 bis 2 cm^3/g, insbesondere 0,1 bis 1,5 cm^3/g, vorzugsweise 0,2 bis 1,1 cm^3/g, besonders bevorzugt 0,3 bis 1 cm^3/g, aufweisen. Dabei sollten 10% bis 95%, insbesondere 20% bis 95%, vorzugsweise 30% bis 90%, des Gesamtporenvolumens der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle durch Poren mit Porendurchmessern von ≤ 2 nm, insbesondere durch Mikroporen, gebildet sein.

[0119] Des Weiteren sollte die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach der Erfindung einen mittleren Porendurchmesser im Bereich von 1 bis 60 nm, insbesondere 1 bis 55 nm, bevorzugt 1,5 bis 50 nm, besonders bevorzugt 2 bis 45 nm, aufweisen.

[0120] Erfindungsgemäß sollte die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach der Erfindung zudem eine spezifische BET-Oberfläche im Bereich von 500 m^2/g bis 3.500 m^2/g, insbesondere 600 bis 3.000 m^2/g, vorzugsweise 700 bis 2.750 m^2/g, besonders bevorzugt 800 bis 2.500 m^2/g, aufweisen.

[0121] Des Weiteren sollte die mit Stickstoff ausgerüstete Aktivkohle eine durch Mikroporen gebildete Oberfläche von 400 bis 2.500 m^2/g, insbesondere 500 bis 2.300 m^2/g, vorzugsweise 600 bis 2.100 m^2/g, besonders bevorzugt 700 bis 1.900 m^2/g, aufweisen.

[0122] Darüber hinaus sollte die mit Stickstoff ausgerüstete Aktivkohle nach der Erfindung eine Dichte von 1,1 bis 3,5 g/ml, insbesondere von 1,5 bis 3 g/ml, vorzugsweise von 1,75 bis 2,75 g/ml, bevorzugt von 2 bis 2,5 g/ml, aufweisen.

[0123] Weiterhin sollte die mit Stickstoff ausgerüstete Aktivkohle nach der Erfindung eine Schüttdichte von 0,1 bis 1,5 g/ml, insbesondere von 0,15 bis 1 g/ml, vorzugsweise von 0,2 bis 0,8 g/ml, bevorzugt von 0,3 bis 0,6 g/ml, aufweisen.

PAC ET AL. EXHIBIT 1019
Page 2217

[0124] Erfindungsgemäß sollte die mit Stickstoff ausgerüstete Aktivkohle zudem eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, von mindestens 5 Newton, insbesondere mindestens 10 Newton, vorzugsweise mindestens 15 Newton, bevorzugt mindestens 20 Newton, aufweisen. Zudem sollte die Aktivkohle eine Druckund/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, im Bereich von 5 bis 50 Newton, insbesondere 10 bis 45 Newton, vorzugsweise 15 bis 40 Newton, aufweisen.

[0125] Was die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle weiterhin anbelangt, so kann diese selbsttragend sein bzw. in Form einer insbesondere losen Schüttung vorliegt.

[0126] Alternativ ist es aber auch möglich, dass die Aktivkohle auf einem Trägermaterial aufgebracht ist.

[0127] In diesem Zusammenhang kann das Trägermaterial gasdurchlässig, insbesondere luftdurchlässig, ausgebildet sein.

[0128] Was in diesem Zusammenhang das Trägermaterial als solches anbelangt, so sollte dieses eine Gasdurchlässigkeit, insbesondere Luftdurchlässigkeit, von mindestens 10 $l \cdot m^{-2} \cdot s^{-1}$, insbesondere mindestens 30 $l \cdot m^{-2} \cdot s^{-1}$, vorzugsweise mindestens 50 $l \cdot m^{-2} \cdot s^{-1}$, besonders bevorzugt mindestens 100 $l \cdot m^{-2} \cdot s^{-1}$, ganz besonders bevorzugt mindestens 500 $l \cdot m^{-2} \cdot s^{-1}$, und/oder eine Gasdurchlässigkeit, insbesondere Luftdurchlässigkeit, von bis zu 10.000 $l \cdot m^{-2} \cdot s^{-1}$, insbesondere bis zu 20.000 $l \cdot m^{-2} \cdot s^{-1}$, bei einem Strömungswiderstand von 127 Pa aufweisen.

[0129] Gemäß einer Ausführungsform der vorliegenden Erfindung kann das erfindungsgemäß eingesetzte Trägermaterial eine dreidimensionale Struktur aufweisen. Insbesondere kann das erfindungsgemäß eingesetzte Trägermaterial gemäß dieser Ausführungsform als vorzugsweise offenporiger Schaumstoff, besonders bevorzugt als Polyurethanschaumstoff, ausgebildet sein.

[0130] Gemäß einer alternativen Ausführungsform dagegen kann das erfindungsgemäß eingesetzte Trägermaterial eine zweidimensionale bzw. flächige Struktur aufweisen. Insbesondere kann bei dieser Ausführungsform das erfindungsgemäß eingesetzte Trägermaterial als vorzugsweise textiles Flächengebilde ausgebildet sein. Beispielsweise kann das Trägermaterial als ein textiles Flächengebilde, vorzugsweise ein luftdurchlässiges Textilmaterial, bevorzugt ein Gewebe, Gewirke, Gestricke, Gelege oder Textilverbundstoff, insbesondere Vlies (Nonwoven), ausgebildet sein. Gleichermaßen kann das Trägermaterial ein Flächengewicht von 5 bis 1.000 g/m^2, insbesondere 10 bis 500 g/m^2, bevorzugt 25 bis 450 g/m^2, aufweisen.

[0131] Bei dieser Ausführungsform kann das Trägermaterial ein natürliche Fasern und/oder synthetische Fasern (Chemiefasern) enthaltendes oder hieraus bestehendes textiles Flächengebilde sein. In diesem Zusammenhang können die natürlichen Fasern aus der Gruppe von Wollfasern und Baumwollfasern (CO) ausgewählt sein. Zudem können die synthetischen Fasern ausgewählt sein aus der Gruppe von Polyester (PES); Polyolefinen, insbesondere Polyethylen (PE) und/oder Polypropylen (PP); Polyvinylchloriden (CLF); Polyvinylidenchloriden (CLF); Acetaten (CA); Triacetaten (CTA); Polyacryl (PAN); Polyamiden (PA), insbesondere aromatischen, vorzugsweise flammfesten Polyamiden; Polyvinylalkoholen (PVAL); Polyurethanen; Polyvinylestern; (Meth-)Acrylaten; Polymilchsäuren (PLA); Aktivkohle; sowie deren Mischungen.

[0132] Üblicherweise ist die stickstofffunktionalisierte bzw. stickstoffmodifizierte Aktivkohle nach der Erfindung an bzw. auf dem Trägermaterial fixiert. Dies kann beispielsweise mittels Verklebung (z. B. mittels eines Klebstoffs) oder infolge von Eigenklebrigkeit oder Eigenadhäsion, insbesondere des Trägermaterials verwiesen werden.

[0133] Die erfindungsgemäße Aktivkohle mit der Stickstoffmodifizierung bzw. Stickstofffunktionalisierung ist mit einer Vielzahl von Vorteilen verbunden, wie sie bereits zuvor angeführt sind.

[0134] Die Aktivkohle nach der Erfindung kann für zahlreiche Verwendungen eingesetzt werden.

[0135] So kann die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle zur Herstellung von Filtern und Filtermaterialien aller Art, insbesondere zur Entfernung von Schad-, Geruchs- und Giftstoffen aller Art, insbesondere aus Luft- und/oder Gasströmen, wie ABC-Schutzmaskenfiltern, Geruchsfiltern, Flächenfiltern, Luftfiltern, insbesondere Filtern für die Raumluftreinigung, adsorptionsfähigen Trägerstrukturen und Filtern für den medizinischen Bereich, verwendet werden.

PAC ET AL. EXHIBIT 1019
Page 2218

[0136] Zudem kann die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle zur Herstellung von Schutzmaterialien aller Art, insbesondere von Schutzbekleidung, insbesondere für den zivilen oder militärischen Bereich, wie Schutzanzügen, Schutzhandschuhe, Schutzschuhwerk, Schutzsocken, Kopfschutzbekleidung und dergleichen, und von Schutzabdeckungen aller Art, vorzugsweise alle vorgenannten Schutzmaterialien für den ABC-Einsatz, verwendet werden.

[0137] Dabei weist die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle ausgezeichnete Sorptionseigenschaften auf, insbesondere in Bezug auf schwefelhaltige bzw. stickstoffhaltige Gase, wie Schwefelwasserstoffe, insbesondere Schwefelwasserstoff (H_2S), sowie gegenüber Ammoniak (NH_3).

[0138] Insbesondere eignet sich die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle auch zur Verwendung als Sorptionsspeicher für Gase oder Flüssigkeiten. Zudem kann die erfindungsgemäße Aktivkohle mit Stickstofffunktionalisierung bzw. Stickstoffmodifizierung als Katalysator oder Katalysatorträger Verwendung finden. Für die vorgenannten Anwendungen ist die hohe spezifische Oberfläche und die ausgezeichnete Reaktivität bzw. katalytische Aktivität der erfindungsgemäßen stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle von entscheidender Bedeutung.

[0139] Weiterhin kann die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle für die chemische Katalyse, insbesondere zur Katalyse chemischer Prozesse und Reaktionen, eingesetzt werden.

[0140] Eine weitere Anwendungsmöglichkeit der erfindungsgemäßen stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle liegt in der Verwendung in oder als Gassensoren oder in Brennstoffzellen.

[0141] Darüber hinaus liegt eine weitere Anwendungsmöglichkeit der Aktivkohle nach der Erfindung mit Stickstoffmodifizierung bzw. Stickstofffunktionalisierung in der Verwendung für sorptive, insbesondere adsorptive Anwendungen, insbesondere als vorzugsweise reaktives und/oder katalytisches Adsorbens.

[0142] Darüber hinaus eignet sich die erfindungsgemäße Aktivkohle mit Stickstoffmodifizierung bzw. Stickstofffunktionalisierung zur Verwendung für die Gasreinigung bzw. für die Gasaufbereitung.

[0143] Eine weitere Verwendung der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle nach der Erfindung ist im Rahmen der Entfernung von Schadstoffen, insbesondere gasförmigen Schadstoffen, oder von umweltschädlichen, gesundheitsschädlichen oder toxischen Substanzen oder Gasen zu sehen.

[0144] Schließlich eignet sich die erfindungsgemäße stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle auch für die Verwendung zur Aufbereitung und/oder Bereitstellung von Reinraumatmosphären, insbesondere für die Elektroindustrie, insbesondere für die Halbleiter- oder Chipherstellung.

[0145] Darüber hinaus betrifft die vorliegende Erfindung – gemäß einem dritten Aspekte der vorliegenden Erfindung – Schutzmaterialien, insbesondere für den zivilen oder militärischen Bereich, insbesondere Schutzbekleidung, wie Schutzanzüge, Schutzhandschuhe, Schutzschuhwerk, Schutzsocken Schutzbekleidung und dergleichen, sowie Schutzabdeckungen, vorzugsweise alle vorgenannten Schutzmaterialien für den ABC-Einsatz, welche unter Verwendung der zuvor definierten stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle nach der Erfindung hergestellt sind bzw. welche die zuvor definierte stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle nach der Erfindung aufweisen.

[0146] Darüber hinaus sind weiterer Gegenstand der vorliegenden Erfindung – gemäß einem vierten Aspekt der vorliegenden Erfindung – Filter und Filtermaterialien, insbesondere zur Entfernung von Schad-, Geruchs- und Giftstoffen aller Art, insbesondere aus Luft- und/oder Gasströmen, wie ABC-Schutzmaskenfilter, Geruchsfilter, Flächenfilter, Luftfilter, insbesondere Filter für die Raumluftreinigung, adsorptionsfähige Trägerstrukturen und Filter für den medizinischen Bereich, hergestellt unter Verwendung der zuvor definierten Aktivkohle nach der Erfindung mit Stickstoffmodifizierung bzw. Stickstofffunktionalisierung bzw. aufweisend die zuvor definierte stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle nach der Erfindung.

[0147] Im Folgenden wird die vorliegende Erfindung anhand von bevorzugte Ausführungsbeispiele darstellenden Zeichnungen bzw. Figurendarstellungen näher erläutert. Im Zusammenhang mit der Erläuterung dieser bevorzugten Ausführungsbeispiele der vorliegenden Erfindung, welche jedoch in Bezug auf die vorliegende Erfindung keinesfalls beschränkend sind, werden auch weitergehende Vorteile, Eigenschaften, Aspekte und Merkmale der vorliegenden Erfindung beschrieben.

PAC ET AL. EXHIBIT 1019
Page 2219

[0148] In den Figurendarstellungen zeigt:

[0149] Fig. 1a eine grafische Darstellung des Einflusses für die thermische Oxidation der als Ausgangsmaterial eingesetzten Aktivkohle gewählten Oxidationszeit auf verschiedene Parameter bzw. auf die texturellen Eigenschaften der als Intermediat erhaltenen, an ihrer Oberfläche oxidierten Aktivkohle;

[0150] Fig. 1b eine grafische Darstellung der Abhängigkeit verschiedener Parameter bzw. der texturellen Eigenschaften der an ihrer Oberfläche oxidierten Aktivkohle von dem Gehalt an flüchtigen Bestandteilen ("fB") der an ihrer Oberfläche oxidierten Aktivkohle als Maß für den Gehalt an sauerstoffhaltigen funktionellen Gruppen bzw. als Maß für den Oxidationsgrad der als Intermediat erhaltenen an ihrer Oberfläche oxidierten Aktivkohle;

[0151] Fig. 1c eine grafische Darstellung zur Analyse der chemischen Beschaffenheit der an ihrer Oberfläche oxidierten Aktivkohle im Hinblick auf Basizität und Azidität der gebildeten Oberflächenoxide, wobei die zugrundeliegende Bestimmung mittels potentiometrischer Titration durchgeführt worden ist. Die Figurendarstellung zeigt dabei die Ausbildung von Oberflächenoxiden unter Einsatz von (Luft-)Sauerstoff als Oxidationsreagenz ("OR") unter variablen Oxidationstemperaturen (thermische Oxidation). In der Figur bezeichnet der Buchstabe "a" das basische Oberflächenoxide indizierende Kurvenmaximum;

[0152] Fig. 1d eine grafische Darstellung zur weiteren Analyse der chemischen Beschaffenheit der gebildeten Oberflächenoxide bzw. der sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle nach Maßgabe der Ausführungen in Fig. 1c. Als Oxidationsreagenz ("OR") wurden jedoch unterschiedlich konzentrierte Harnstofflösungen bzw. Wasserstoffperoxid in unterschiedlichen Konzentrationen eingesetzt (chemische Oxidation). In der Figur bezeichnet der Buchstabe "b" das saure Oberflächenoxide indizierende Kurvenmaximum;

[0153] Fig. 1e eine grafische Darstellung zur Analyse der chemischen Beschaffenheit im Hinblick auf Basizität bzw. Azidität der im Rahmen der Oxidation erhaltenen sauerstoffhaltigen funktionellen Gruppen, wobei die Daten mittels TPD-MS (Temperaturprogrammierte Desorption, gekoppelt mit Massenspektroskopie) ermittelt worden sind. Die Desorption von Kohlendioxid (CO_2) indiziert dabei die während der Oxidation vorliegende Bildung saurer Oberflächenoxide, wogegen die Desorption von Kohlenmonoxid (CO) die im Rahmen der Oxidation hervorgerufene Bildung basischer Oberflächenoxide Gruppen indiziert. Die Oxidation wurde auf Basis der zuvor in Fig. 1d angeführten chemischen Oxidation durchgeführt.

[0154] Fig. 1f eine grafische Darstellung nach Maßgabe von Fig. 1e, wobei sich die erhaltenen Daten bzw. Messwerte im Gegensatz hierzu auf eine mittels thermischer Oxidation erhaltenen, an ihrer Oberfläche oxidierten Aktivkohle, wie in Fig. 1c angeführt, beziehen;

[0155] Fig. 2a eine grafische Darstellung der Wasserdampfisothermen von an ihrer Oberfläche oxidierten Aktivkohlen, welche im Rahmen von Oxidation mittels (Luft-)Sauerstoff bei variablen Temperaturen bzw. Zeitdauern gewonnen wurden (thermische Oxidation), im Vergleich zu einem nichtoxidierten Ausgangsmaterial bzw. zu einer Ausgangsaktivkohle;

[0156] Fig. 2b eine grafische Darstellung von Wasserdampfisothermen von an ihrer Oberfläche oxidierten Aktivkohlen, wobei als diesbezügliches Oxidationsreagenz ("OR") Wasserstoffperoxid bzw. Salpetersäure (HNO_3) bei jeweils variabler Oxidationsdauer eingesetzt wurde (chemische Oxidation) im Vergleich zu einer nichtoxidierten Ausgangsaktivkohle;

[0157] Fig. 3a eine grafische Darstellung der Wasserdampfisothermen von stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohlen mit dem Einfluss der bei der Stickstoffausrüstung gewählten Temperatur auf das Endprodukt, wobei der jeweils rechte Adsorptionsast der untersuchten Aktivkohle die Adsorption und der jeweils linke Adsorptionsast der untersuchten Aktivkohle die Desorption von Wasser darstellt;

[0158] Fig. 3b grafische Darstellungen des Einflusses der durchgeführten Oxidation mit der nachfolgenden Stickstofffunktionalisierung bzw. -modifizierung auf die jeweiligen Parameter bzw. texturellen Eigenschaften der resultierenden Aktivkohle und des diesbezüglichen Einflusses der bei der Funktionalisierung bzw. Modifizierung mit Stickstoff gewählten Temperatur, wobei in der grafischen Darstellung das Symbol ① die Basis- bzw. Ausgangsaktivkohle, das Symbol ② die nach Oberflächenoxidation erhaltene, an ihrer Oberfläche oxidierte Aktivkohle (Intermediat), welche somit noch nicht stickstoffmodifiziert bzw. -funktionalisiert ist, und das Symbol ③ die mit Stickstoff funktionalisierte bzw. modifizierte Aktivkohle in Form des Endprodukts darstellen;

PAC ET AL. EXHIBIT 1019
Page 2220

[0159] Fig. 4a einen dem erfindungsgemäß durchgeführten Verfahren zugrundeliegenden, das erfindungsgemäß durchgeführte Verfahren jedoch in nichtbeschränkender Weise charakterisierenden Reaktionsablauf zum Erhalt einer stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle, ausgehend von einer an ihrer Oberfläche oxidierten Aktivkohle unter Einsatz von Harnstoff als Stickstoffmodifizierungsreagenz ("SMR");

[0160] Fig. 4b ein XPS-Spektrum (X-Ray Photoelectron Spectroscopy; Röntgen-Fotoelektronenspektroskopie) zum Nachweis stickstoffhaltiger funktioneller Gruppen für verschiedene Wärmebehandlungsschritte zum Erhalt der stickstofffunktionalisierten bzw. stickstoffmodifizierten Aktivkohlen;

[0161] Fig. 5 eine grafische Darstellung in Form eines Balkendiagramms mit den für verschiedene Aktivkohlen ermittelten Durchbruchzeiten in Bezug auf verschiedene Sorptionssubstanzen (NH_3, H_2S sowie SO_2), wobei in Fig. 5 das Symbol ① eine nichtoxidierte Ausgangaktivkohle darstellt und die weiteren Aktivkohlen gemäß den Symbolen ② bis ⑥ jeweils auf Basis von Harnstoff stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohlen darstellen. In diesem Zusammenhang stellen die Symbole ② bzw. ③ stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohlen dar, welche auf Basis einer mit (Luft-)Sauerstoff bei Temperaturen von 400°C bzw. 450°C an ihrer Oberfläche oxidierten Aktivkohlen erhalten wurden (thermische Oxidation). Das Symbol ⑥ stellt zudem eine stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle dar, welche auf Basis einer mittels Salpetersäure (HNO_3) an ihrer Oberfläche oxidierten Aktivkohle erhalten wurde (chemische Oxidation);

[0162] Fig. 6a eine grafische Darstellung von Durchbruchexperimenten unter Verwendung von Schwefeldioxid (SO_2) als zu sorbierendes Gas auf Basis eines Vergleichs von Ausgangsaktivkohle ("Ausgangsmaterial") einerseits und einer stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle ("Endprodukt") andererseits;

[0163] Fig. 6b eine grafische Darstellung von Durchbruchexperimenten nach Maßgabe der Ausführungen zu Fig. 6a, wobei im Unterschied hierzu Schwefelwasserstoff (H_2S) als zu sorbierendes Gas eingesetzt wurde;

[0164] Fig. 7a ein XPS-Spektrum eines C 1 s-Bereichs-Scans einer an ihrer Oberfläche oxidierten, jedoch noch nicht stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle mit der Darstellung der erhaltenen Messwerte ("Messdaten") und der entsprechenden Datenanpassung zu Zwecken der Oberflächenanalyse bzw. der chemischen Struktur der Oberfläche der oxidierten Aktivkohle als Intermediat des erfindungsgemäß durchgeführten Verfahrens;

[0165] Fig. 7b ein weiteres XPS-Spektrum eines O 1 s-Bereichs-Scans mit den auf diese Weise ermittelten Messdaten ("Messdaten") und der entsprechenden Datenanpassung für eine an ihrer Oberfläche oxidierten, jedoch noch nicht stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle.

[0166] Die Figurendarstellung gemäß Fig. 1a veranschaulicht den Einfluss der Oxidationszeit auf verschiedene Parameter bzw. auf die texturellen Eigenschaften der auf Basis der erfindungsgemäß durchgeführten Oxidation erhaltenen, an ihrer Oberfläche oxidierten Aktivkohle, wobei (Luft-)Sauerstoff als Oxidationsreagenz ("OR") eingesetzt wurde (thermische Oxidation) und wobei als Ausgangsaktivkohle zum einen eine niedrig aktivierte Aktivkohle und zum anderen eine hoch aktivierte Aktivkohle eingesetzt worden ist. Die Figur zeigt, dass mit zunehmender Oxidationszeit der Gehalt an flüchtigen Bestandteilen ("fB") für beide Aktivkohlen signifikant ansteigt. Wie zuvor angeführt, stellt der Gehalt an flüchtigen Bestandteilen der an ihrer Oberfläche aktivierten Aktivkohle ein Maß für den Gehalt an sauerstoffhaltigen funktionellen Gruppen dar, wie sie im Rahmen der Oxidation gebildet werden. Für beide Aktivkohlen wird somit mit zunehmender Oxidationszahl ein Anstieg des Gehaltes an sauerstoffhaltigen funktionellen Gruppen beobachtet, welche im weiteren Verlauf der erfindungsgemäß realisierten Verfahrensführung als Reaktionspartner für das Stickstoffmodifizierungsreagenz ("SMR") fungieren können. Fig. 1a veranschaulicht weiterhin, dass unter den gegebenen Verfahrensbedingungen mit zunehmender Oxidationszeit der Oberflächen-pH-Wert der jeweiligen Aktivkohle von einem leicht basischen Bereich in einen leicht sauren Bereich absinkt. Schließlich zeigt die grafische Darstellung gemäß Fig. 1a, dass das Gesamtporenvolumen (V_{ges}) sowie die Rütteldichte (RD) für beide Aktivkohlen im Rahmen der thermischen Oxidation geringfügig verändert werden, wobei in Bezug auf das Gesamtporenvolumen sogar eine geringfügige Erhöhung vorliegt.

[0167] Fig. 1b zeigt zur weiteren Veranschaulichung die Abhängigkeit des Oberflächen-pH-Werts der an ihrer Oberfläche oxidierten Aktivkohle einerseits sowie der Rütteldichte und des Gesamtporenvolumens andererseits von dem Gehalt an flüchtigen Bestandteilen als Maß für den Gehalt an sauerstoffhaltigen funktionellen Gruppen der an ihrer Oberfläche oxidierten Aktivkohle als Intermediat der erfindungsgemäß umgesetzten Ver-

PAC ET AL. EXHIBIT 1019
Page 2221

fahrensführung. Fig. 1b zeigt gleichermaßen, dass mit Zunahme des Gehalts an sauerstoffhaltigen funktionellen Gruppen und damit des Oxidationsgrads der pH-Wert und die Rütteldichte der an ihrer Oberfläche oxidierten Aktivkohle leicht abnimmt, während in Bezug auf das Porenvolumen eine Zunahme zu beobachten ist.

[0168] Weiterhin verdeutlicht die Figurendarstellung gemäß Fig. 1c, dass im Rahmen der thermischen Oxidation unter Einsatz von (Luft-)Sauerstoff als Oxidationsreagenz ("OR") (chemische Oxidation) die Bildung basischer Oberflächenoxide bevorzugt ist. Demgegenüber zeigt die Figurendarstellung gemäß Fig. 1d, dass unter Verwendung von Harnstoff bzw. Wasserstoffperoxid (chemische Oxidation) gleichermaßen auch saure Oberflächenoxide gebildet werden. In diesem Zusammenhang bestätigen die Figurendarstellungen gemäß Fig. 1e und Fig. 1f die zuvor angeführten experimentellen Befunde: So zeigt Fig. 1f, dass die zuvor angeführte thermische Oxidation maßgeblich zur Desorption von Kohlenmonoxid (CO) als Maß für die Bildung basischer Oberflächenoxide führt, während die Bildung saurer Oberflächenoxide, welche durch die Desorption von Kohlendioxid (CO_2) angezeigt wird, nur in geringfügigem Maße erfolgt. In diesem Zusammenhang zeigt Fig. 1a, dass unter chemischen Oxidationsbedingungen im Rahmen der erfindungsgemäß realisierten Verfahrensführung als Intermedial eine an ihrer Oberfläche oxidierte Aktivkohle erhalten wird, welche einen erhöhten Gehalt an sauren Oberflächenoxiden aufweist.

[0169] Insgesamt verdeutlicht die Figurendarstellung gemäß Fig. 1a bis Fig. 1e somit, dass es bei der erfindungsgemäß umgesetzten Verfahrensführung mit der gezielten Auswahl bzw. Abstimmung der Oxidationsbedingungen zur Bildung der an ihrer Oberfläche oxidierten Aktivkohle um einen steuerbaren bzw. individuell einstellbaren Prozess handelt, auf dessen Basis das so erhaltene Intermedial individuell ausgebildet werden kann, insbesondere im Hinblick auf die nachfolgende Ausrüstung bzw. Modifizierung mit Stickstoff. Als diesbezüglich im Rahmen der Oxidation variable Verfahrensparameter kommen insbesondere zum einen das eingesetzte Oxidationsreagenz ("OR") sowie zum anderen Temperatur und Oxidationszeit infrage. Die im Rahmen der erfindungsgemäß realisierten Verfahrensführung vorgesehene oxidative Vorbehandlung zum Erhalt der an ihrer Oberfläche oxidierten Aktivkohle als Intermedial stellt somit einen einstellbaren bzw. individuell abstimmbaren Prozess dar, wobei insbesondere die Intensität bzw. das Maß der Oxidation durch Prozessparameter wie Oxidationszeit, Oxidationstemperatur und Konzentration des eingesetzten Oxidationsreagenzes ("OR") und die Art der gebildeten Oberflächenoxide über die Auswahl des Oxidationsmittels gesteuert bzw. maßgeschneidert werden kann.

[0170] Weiterhin zeigen die Figurendarstellungen gemäß Fig. 2a und Fig. 2b die Wasserdampfisothermen von auf verschiedene Art und Weise an ihrer Oberfläche oxidierter Aktivkohle im Vergleich zu einer nichtoxidierten Ausgangsaktivkohle, wobei Fig. 2a auf eine thermische Oxidation unter Verwendung von (Luft-)Sauerstoff als Oxidationsreagenz ("OR") unter verschiedenen Temperaturen (thermische Oxidation) und Fig. 2b auf den Einsatz von Oxidationsreagenzien ("OR") auf Basis von Wasserstoffperoxid und Salpetersäure bei unterschiedlichen Oxidationszeiten (chemische Oxidation) abstellen. Dabei ist in beiden Figuren zu erkennen, dass die durchgeführte Oxidation zu einer Verschiebung der Adsorption von Wasser in Richtung kleinerer p/p_0-Werte führt, was einer Erhöhung der Kapazität infolge der durchgeführten Oxidation unter Schaffung hydrophiler Oberflächen entspricht, was wiederum im Hinblick der nachfolgenden Anbindung des Stickstoffmodifizierungsreagenzes ("SMR") von Relevanz ist. In diesem Zusammenhang zeigt Fig. 2a, dass eine Erhöhung der Temperatur einerseits und der Oxidationszeit und -dauer andererseits zu einer höheren Kapazität bzw. zu einer vermehrten Bildung hydrophiler Oberflächen der so behandelten Aktivkohle führt. Entsprechend kann Fig. 2b entnommen werden, dass unter den vorliegenden Bedingungen Salpetersäure zu einer stärkeren Kapazitätserhöhung bzw. zu einem höheren Gehalt hydrophiler Oberflächen im Vergleich zu Wasserstoffperoxid führt, wobei auch hier eine weitere Erhöhung der entsprechenden Werte bei Zunahme der Oxidationsdauer zu beobachten ist.

[0171] Die Figurendarstellung gemäß Fig. 3a zeigt die für eine unter Verwendung von Ammoniak bei verschiedenen Temperaturen stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle erhaltenen Wasserdampfisothermen, wobei bei einer geringeren Funktionalisierungstemperatur von 500°C im Vergleich zu einer höheren Funktionalisierungstemperatur von 920°C eine größere Verschiebung der Adsorption zu kleineren p/p_0-Werten zu beobachten ist, was auf eine höhere Funktionalität, insbesondere auch im Hinblick auf die Ausbildung hydrophiler Oberflächen, der erhaltenen Aktivkohle bei niedrigeren Temperaturen bzw. eine Integration von Stickstoff in das Kohlenstoffgerüst bei höheren Temperaturen spricht. In diesem Zusammenhang zeigt die Figurendarstellung gemäß Fig. 3b, dass auf Basis der erfindungsgemäßen umgesetzten Verfahrensführung mit der Oxidation von Ausgangsaktivkohle und der nachfolgenden Stickstoffmodifizierung bzw. -funktionalisierung die zugrundeliegenden Parameter bzw. texturellen Eigenschaften der erhaltenen Aktivkohle nicht negativ beeinflusst werden. Vielmehr ist sowohl in Bezug auf das Gesamtporenvolumen nach Gurvich (V_{tot}), das Mikroporenvolumen (V_{mic}) und der MP-BET-Oberfläche zu beobachten, dass die durchgeführte Oxidati-

PAC ET AL. EXHIBIT 1019
Page 2222

on zur Ausbildung funktioneller sauerstoffhaltiger Gruppen an der Oberfläche der Aktivkohle sogar zu einem leichten Anstieg und die nachfolgende Stickstoffmodifizierung bzw. -funktionalisierung allenfalls zu einer geringfügigen Abnahme der in Rede stehenden Werte führt, welche jedoch immer noch oberhalb der Werte des entsprechenden Ausgangsmaterials liegen. Die erfindungsgemäß realisierte Verfahrensführung führt somit in keiner Weise zu einer Verschlechterung der angeführten Parameter der zugrundeliegenden Aktivkohle, wobei diesbezüglich auch keine erheblichen Unterschiede hinsichtlich der bei der Stickstofffunktionalisierung bzw. -modifizierung gewählten Temperatur vorliegen. Die in Fig. 3b untersuchten Aktivkohlen wurden gleichermaßen unter Verwendung von Ammoniak mit Stickstoff ausgerüstet.

[0172] Die Figurendarstellung gemäß Fig. 4a wiederum zeigt einen beispielhaften, dem erfindungsgemäß durchgeführten Verfahren zugrundeliegenden Reaktionsablauf, wobei Abbildung A das Kohlenstoffgerüst der an ihrer Oberfläche oxidierten Aktivkohle (Intermediat) mit den ausgebildeten sauerstoffhaltigen funktionellen Gruppen darstellt. Unter Zugabe von Harnstoff als Stickstoffmodifizierungsreagenz ("SNR") wird nachfolgend das in Abbildung B veranschaulichte Zwischenprodukt mit angebundener Harnstoffkomponente erhalten. Abbildung C zeigt das bei einer Temperaturbehandlung von 500°C erhaltene (Zwischen-)Produkt mit der Umsetzung des Harnstoffs zu den entsprechenden stickstoffhaltigen funktionellen Gruppen an der Oberfläche der Kohlenstoffmatrix, wobei diesbezüglich zyklische Harnstoffderivate, Nitrile, Amide bzw. primäre Amine ausgebildet werden. Durch eine weitere Temperaturbehandlung bei 920°C erfolgt eine Integration des Stickstoffs in das Kohlenstoffgerüst bzw. in die Kohlenstoffmatrix der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle unter Abbau der stickstoffhaltigen funktionellen Gruppe, wie in Abbildung D dargestellt.

[0173] In diesem Zusammenhang veranschaulicht die Figurendarstellung gemäß Fig. 4b auf Basis eines XPS-Spektrums das Vorhandensein verschiedener Spezies von stickstoffhaltigen funktionellen Gruppen zu verschiedenen Zeitpunkten bzw. bei verschiedenen Temperaturen während des Vorgangs der Stickstoffmodifizierung bzw. -funktionalisierung. Während bei niedrigen Temperaturen insbesondere stickstoffhaltige funktionelle Gruppen auf Basis von Amiden bzw. Pyrrolen vorliegen, erfolgt bei höheren Temperaturen von 500°C eine Umwandlung bzw. eine Verlagerung zu insbesondere quaternären stickstoffhaltigen Gruppen, während bei noch höheren Temperaturen von 920°C der Gehalt an den vorgenannten Gruppen signifikant zurückgeht, was auf eine Integration von Stickstoff in das Kohlenstoffgerüst bzw. in die Kohlenstoffmatrix der so behandelten Aktivkohle hindeutet.

[0174] Was die Figurendarstellung gemäß Fig. 5 anbelangt, so zeigt diese einen Vergleich der Durchbruchzeiten von drei verschiedenen erfindungsgemäßen Aktivkohlen in Bezug auf die Sorption von Ammoniak (NH_3), Schwefelwasserstoff (H_2S) und Schwefeldioxid (SO_2) im Vergleich zu einer Ausgangsaktivkohle. Hierzu wurden die entsprechenden Aktivkohlen unter definierten Bedingungen für einen bestimmten Zeitraum einem konfinuierlichen Volumenstrom einer mit dem jeweiligen Schadgas angereicherten Atmosphäre ausgesetzt und die jeweiligen Durchbruchzeiten bestimmt. Sämtliche erfindungsgemäßen Aktivkohlen zeigen deutlich über die Ausgangsaktivkohle hinausgehende Sorptionsleistungen sowohl in Bezug auf Ammoniak (NH_3), Schwefelwasserstoff (H_2S) als auch Schwefeldioxid (SO_2). Insgesamt ist das Sorptionsverhalten der erfindungsgemäßen Aktivkohlen als hervorragend einzustufen.

[0175] Weiterhin verdeutlichen die Figurendarstellungen gemäß Fig. 6a und Fig. 6b das signifikant verbesserte Sorptionsverhalten einer erfindungsgemäß ausgerüsteten Aktivkohle (Endprodukt) im Vergleich zu dem eingesetzten Ausgangsmaterial bzw. der eingesetzten Ausgangsaktivkohle. So zeigt die auf Basis des erfindungsgemäß durchgeführten Verfahrens hergestellte und mit Stickstoff ausgerüstete Aktivkohle ein signifikant verbessertes Durchbruchverhalten gegenüber den zu sorbierenden Gasen Schwefeldioxid (SO_2) (Fig. 6a) einerseits und Schwefelwasserstoff (H_2S) (Fig. 6b) andererseits. Zur Ermittlung der Durchbruchdaten wurden die jeweiligen Aktivkohlen unter definierten Bedingungen einem konstanten Volumenstrom einer mit dem zu sorbierenden Gas angereicherten Atmosphäre für einen definierten Zeitraum ausgesetzt, wobei die in den jeweiligen Figuren angegebenen Konzentrationen des zu sorbierenden Gases eingesetzt wurden.

[0176] Schließlich zeigen die Figurendarstellungen gemäß Fig. 7a und Fig. 7b das Vorhandensein von sauerstoffhaltigen funktionellen Gruppen einer für die nachfolgende Stickstoffmodifizierung bzw. Stickstofffunktionalisierung eingesetzten an ihrer Oberfläche oxidierten Aktivkohle. Durch Oxidation unter Einbezug eines Oxidationsreagenzes ("OR") werden zahlreiche sauerstoffhaltige funktionelle Gruppen erhalten, wie z. B. Carboxyl- und Carbonylgruppen, welche als Reaktionspartner bzw. Aminogruppen für die nachfolgende Modifizierung bzw. Funktionalisierung mit dem Stickstoffmodifizierungsreagenz ("SMR") fungieren.

[0177] Zusammenfassend ist es im Rahmen der vorliegenden Erfindung durch die Umsetzung eines speziellen Verfahrens erstmalig gelungen, eine Funktionalisierung von Aktivkohle bzw. von polymerbasierter sphä-

PAC ET AL. EXHIBIT 1019
Page 2223

rischer Aktivkohle (PBSAC) mit stickstoffhaltigen funktionellen Gruppen bzw. von Aktivkohle mit Integration von Stickstoff in die Kohlenstoffoberfläche (N-Dotierung) zu erhalten. Die so erhaltenen Aktivkohlen bzw. polymerbasierten sphärischen Aktivkohlen (PBSACs) weisen dabei eine Reaktivität gegenüber unterschiedlichen Zielgasen auf. Als entsprechende Zielgase für die auf Basis des erfindungsgemäß durchgeführten Verfahrens erhaltenen Aktivkohlen können Gase in Betracht kommen, deren Abbau über eine Oxidation an der Kohlenstoffoberfläche möglich ist, wie es beispielsweise für SO_2, H_2S, ASH_3 sowie DMS der Fall ist.

[0178] Die im Rahmen des erfindungsgemäß durchgeführten Verfahrens erhaltenen Aktivkohlen können gleichermaßen stickstoffhaltige funktionelle Gruppen auf der Oberfläche aufweisen, welche mit organischen Gasen bzw. Dämpfen Bindungen eingehen können, wie Formaldehyd und gegebenenfalls NO_x-Verbindungen. Durch die Stickstofffunktionalisierung kann im Allgemeinen die Basizität der Oberfläche der Aktivkohle (im Gegensatz zur Oxidation) erhöht werden. Die Ausbildung von stickstoffhaltigen funktionellen Gruppen bzw. die Dotierung der Aktivkohle mit Stickstoff kann im Rahmen der erfindungsgemäß realisierten Verfahrensführung in nicht beschränkender Weise durch das Füllen der Poren mit einer stickstoffhaltigen organischen Verbindung (wie z. B. Harnstoff) insbesondere aus wässrigen Lösungen und einem sich anschließenden Pyrolyseprozess erfolgen.

[0179] Nach dem eigentlichen Herstellungsprozess kann sich ein Aufreinigungsschritt, insbesondere ein Waschen mit Wasser, anschließen, insbesondere um etwaige Pyrolyse- bzw. Verbrennungsrückstände zu entfernen. Die bei der Stickstofffunktionalisierung bzw. -modifizierung gewählte Temperatur beeinflusst im Rahmen der erfindungsgemäß umgesetzten Verfahrensführung die chemische Konstitution des eingebrachten Stickstoffs. In diesem Zusammenhang führen niedrige Temperaturen, insbesondere im Bereich von 500°C, insbesondere zur Ausbildung von stickstoffhaltigen funktionellen Gruppen, während höhere Temperaturen, insbesondere im Bereich von 920°C vorrangig zu den zuvor beschriebenen N-dotierten Aktivkohlen führt.

[0180] Im Rahmen der vorliegenden Erfindung hat es sich als besonders vorteilhaft gezeigt, dass im Rahmen des erfindungsgemäß durchgeführten Verfahrens eine vorgeschaltete Oxidation der Aktivkohle durchgeführt wird, da diese die Aufnahme von Stickstoff in signifikanten Mengen ermöglicht. In diesem Zusammenhang korreliert die Menge an aufgenommenem bzw. integriertem Stickstoff mit den flüchtigen Bestandteilen der oxidierten Aktivkohle als Maß für die Menge bzw. den Gehalt an Oberflächenoxiden auf der Aktivkohle.

AUSFÜHRUNGSBEISPIELE:

1. Herstellung einer erfindungsgemäß ausgerüsteten Aktivkohle mit Stickstofffunktionalisierung bzw. -modifizierung:

[0181] Im Rahmen der im Folgenden beschriebenen Herstellung von erfindungsgemäßen Aktivkohlen wurde als Ausgangsmaterial eine kugelförmige Aktivkohle als Ausgangsaktivkohle eingesetzt, welche auf Basis von divinylbenzolvernetztem Polystyrol hergestellt worden ist. Eine derartige Ausgangsaktivkohle ist von der Fa. Blücher GmbH, Erkrath (Deutschland) erhältlich.

a) Zur Herstellung der erfindungsgemäßen Aktivkohle A wurden 500 g der Ausgangsaktivkohle mit 1.000 g einer HNO_3-Lösung (50%) zusammengeführt, und die resultierende Mischung wurde für 240 min gerührt. Anschließend wurde die überschüssige Salpetersäure abdekantiert, und die auf diese Weise erhaltene oxidierte Aktivkohle wurde mit destilliertem Wasser gewaschen und anschließend getrocknet. Eine Menge von 500 g der an ihrer Oberfläche oxidierten Aktivkohle wurden dann mit 1.000 g einer gesättigten Harnstofflösung zusammengeführt, und die resultierende Mischung wurde für 2,5 h gerührt. Anschließend wurde die überschüssige Harnstofflösung abdekantiert. Die mit der Harnstofflösung ausgerüstete Aktivkohle wurde anschließend im Inertgasstrom bei 500°C für 240 min behandelt. Die erhaltene stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle wurde dann mit destilliertem Wasser gewaschen und getrocknet, um etwaige Verbrennungs- bzw. Pyrolyserückstände zu entfernen.

b) Zur Herstellung der erfindungsgemäßen Aktivkohle B wurden 500 g der Ausgangsaktivkohle mit 1.000 g einer HNO_3-Lösung (50%) zusammengeführt und die resultierende Mischung für 240 min gerührt. Anschließend wurde überschüssige HNO_3-Lösung abdekantiert, und die so erhaltene oxidierte Aktivkohle wurde mit destilliertem Wasser gewaschen und getrocknet. Anschließend wurden 500 g der oxidierten Aktivkohle mit 1.000 g einer gesättigten Harnstofflösung zusammengeführt, und die resultierende Mischung wurde für 2,5 h gerührt. Die überschüssige Harnstofflösung wurde abdekantiert. Die mit der Harnstofflösung ausgerüstete Aktivkohle wurde im Inertgasstrom bei 920°C für 240 min behandelt. Die so erhaltene stickstofffunktionalisierte bzw. stickstoffmodifizierte Aktivkohle wurde mit destilliertem Wasser gewaschen und anschließend getrocknet, um Verbrennungsrückstände zu entfernen.

PAC ET AL. EXHIBIT 1019
Page 2224

c) Zur Herstellung der erfindungsgemäßen Aktivkohle C wurden 500 g der Ausgangsaktivkohle im Drehrohrofen im Luftstrom bei 450°C für 120 min behandelt. Die so erhaltene oxidierte Aktivkohle wurde mit 1.000 g einer gesättigten Harnstofflösung zusammengeführt, und die resultierende Mischung wurde für 2,5 h gerührt. Anschließend wurde die überschüssige Harnstofflösung abdekantiert. Die mit der Harnstofflösung ausgerüstete Aktivkohle wurde anschließend im Inertgasstrom bei 500°C für 240 min behandelt. Die resultierende stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle wurde schließlich gewaschen und getrocknet, um etwaige Verbrennungsrückstände zu entfernen.
d) Zur Herstellung der erfindungsgemäßen Aktivkohle D wurden 50 g der Ausgangsaktivkohle im Drehrohrofen im Luftstrom bei 450°C für 120 min behandelt. 500 g der so erhaltenen Aktivkohle wurden mit 1.000 g einer gesättigten Harnstofflösung zusammengeführt, und die resultierende Mischung wurde für 2,5 h gerührt. Anschließend wurde die überschüssige Harnstofflösung abdekantiert, und die mit der Harnstofflösung ausgerüstete Aktivkohle wurde mit Inertgasstrom bei 920°C für 240 min behandelt. Die auf diese Weise erhaltene stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle wurde schließlich mit destilliertem Wasser gewaschen und anschließend getrocknet, um etwaige Verbrennungsrückstände zu entfernen.

[0182] Die erfindungsgemäßen Aktivkohlen A bis D weisen jeweils signifikant erhöhte Stickstoffgehalte auf, und die chemisorptiven Eigenschaften sind jeweils als hervorragend einzustufen.

[0183] In diesem Zusammenhang wurde der jeweilige Stickstoffgehalt der erfindungsgemäßen Aktivkohlen mit an sich bekannten Methoden bestimmt. Der Gesamtstickstoffgehalt kann mittels an sich bekannter Elementaranalyse bestimmt werden, während die Ermittlung der flüchtigen Bestandteile ("fB") gemäß der ISO 562:1981 erfolgen kann. Aus der Differenz von mittels Elementaranalyse bestimmtem Gesamtstickstoffgehalt einerseits und gemäß der ISO 562:1981 bestimmtem Gehalt an flüchtigen Bestandteilen (d. h. flüchtigen stickstoffhaltigen funktionellen Gruppen) kann dann der Gehalt an immobilisiertem bzw. in das Kohlenstoffgerüst eingebautem Stickstoff ermittelt werden.

[0184] Im Einzelnen ergeben sich für die erfindungsgemäßen Aktivkohlen A bis D die folgenden Stickstoffgehalte: So weist die erfindungsgemäße Aktivkohle A einen Gesamtstickstoffgehalt von 13% auf, bezogen auf das Trockengewicht der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle, wobei hiervon etwa 12%, bezogen auf den Gesamtstickstoffgehalt, in Form von flüchtigen Bestandteilen ("fB") vorliegt. Für die erfindungsgemäße Aktivkohle B ergibt sich ein entsprechender Gesamtstickstoffgehalt von 18 Gew.-%, bezogen auf das Trockengewicht der stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohle, wobei diesbezüglich lediglich 5% des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in Form von flüchtigen Bestandteilen ("fB") vorliegt, d. h. 95% des Stickstoffs liegen in der Kohlenstoffmatrix integriert vor.

[0185] Weiterhin ergibt sich für die erfindungsgemäße Aktivkohle C ein Gesamtstickstoffgehalt von 16 Gew.-%, bezogen auf die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle. In diesem Fall beträgt der Anteil des in Form von flüchtigen Bestandteilen ("fB") vorliegenden Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, 14%.

[0186] Schließlich ergibt sich für die erfindungsgemäße Aktivkohle D ein Gesamtstickstoffgehalt, bezogen auf die stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle von 19,5 Gew.-%, wobei in diesem Zusammenhang 7% des Stickstoffs in Form von flüchtigen Bestandteilen ("fB") vorliegt.

[0187] Die Ergebnisse veranschaulichen den hohen Gehalt an Stickstoff in Bezug auf die erfindungsgemäßen Aktivkohlen, welche auf Basis des erfindungsgemäß durchgeführten Verfahrens erhalten werden, wobei diesbezüglich gleichermaßen gewährleistet ist, dass ein hoher Anteil des Stickstoffs fest in das Kohlenstoffgerüst integriert vorliegt. Die diesbezügliche Integration bzw. Inkorporierung des Stickstoffs in das Kohlenstoffgerüst ist bei höheren Temperaturen während der Stickstoffmodifizierung bzw. -funktionalisierung stärker ausgebildet, während bei niedrigen Temperaturen der Anteil an stickstoffhaltigen funktionellen Gruppen erhöht ist.

[0188] In Bezug auf die erfindungsgemäßen Aktivkohlen wurden zudem Durchbruchuntersuchungen gegenüber Schwefelwasserstoff (H_2S) durchgeführt. In diesem Zusammenhang wurde eine definierte Schüttung der jeweiligen Aktivkohlen A bis D, welche jeweils eine Höhe von 2 cm aufwies, bei Temperaturen von 30°C einem konstanten Volumenstrom mit konstanter Strömungsgeschwindigkeit ausgesetzt, welcher 20 ppm H_2S enthielt. Die erfindungsgemäßen Aktivkohlen wiesen dabei folgende Durchbruchzeiten auf: So konnte für die erfindungsgemäße Aktivkohle A eine Durchbruchzeit von 112 min und für die erfindungsgemäße Aktivkohle B eine Durchbruchszeit von 123 min ermittelt werden. Weiterhin ergab sich für die erfindungsgemäße Aktivkohle C eine Durchbruchzeit von 112 min, und für die erfindungsgemäße Aktivkohle D konnte eine Durchbruchzeit von 119 min ermittelt werden. Eine als Vergleich eingesetzte unbehandelte Ausgangsaktivkohle wies eine

PAC ET AL. EXHIBIT 1019
Page 2225

Durchbruchzeit von lediglich 75 min auf. Die vorgenannten Ergebnisse belegen die signifikante Verbesserung der Adsorptionsleistung der erfindungsgemäßen Aktivkohle in Bezug auf das zu sorbierende Schadgas.

[0189] Die zuvor geschilderten Herstellungsbeispiele wurden wiederholt, wobei jedoch als Stickstoffmodifizierungsreagenz Melamin ("Aktivkohle E"), gasförmiges Ammoniak ("Aktivkohle F"), Ammoniakwasser ("Aktivkohle G") oder Aminosäuren ("Aktivkohle H") eingesetzt wurden; es wurden vergleichbare Ergebnisse erhalten.

2. Weitere Ausführungsbeispiele und experimentelle Untersuchungen:

[0190] Im Folgenden wird auf die den bereits zuvor beschriebenen Figurendarstellungen zugrundeliegenden Untersuchungen bzw. Ausführungsbeispiele weiterführend eingegangen:

a) Wie zuvor angeführt, liegt der Figurendarstellung gemäß Fig. 1a eine Untersuchung des Einflusses der durchgeführten Oxidation der Ausgangsaktivkohle auf bestimmte Parameter der erhaltenen, an ihrer Oberfläche oxidierten Aktivkohle zugrunde. Diesbezüglich wurde eine niedrig aktivierte Ausgangsaktivkohle mit relativ geringem Gesamtporenvolumen einerseits und eine hoch aktivierte Ausgangsaktivkohle mit relativ hohem Gesamtporenvolumen andererseits als für die nachfolgende Oxidation eingesetztes Material verwendet. Die Oxidation wurde unter Verwendung von (Luft-)Sauerstoff als Oxidationsreagenz ("OR") im Sinne der zuvor definierten thermischen Oxidation durchgeführt, wobei in diesem Zusammenhang die in Fig. 1a dargestellten Parameter in Abhängigkeit von der Oxidationszeit bestimmt wurden. Dabei zeigt sich, dass für beide Ausgangsaktivkohlen mit zunehmender Oxidationszeit eine Erhöhung der flüchtigen Bestandteile ("fB") vorliegt, was einer Generierung von sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der jeweiligen Aktivkohle entspricht.
Gleichermaßen zeigt die Figurendarstellung gemäß Fig. 1a, dass mit zunehmender Oxidationszeit der Oberflächen-pH-Wert und die Rütteldichte der oxidierten, jedoch noch nicht einer Stickstoffmodifizierung bzw. Stickstofffunktionalisierung unterzogenen Aktivkohle sinken. Dahingehen ist in Bezug auf das Gesamtporenvolumen eine leichte Erhöhung zu beobachten. Die diesbezüglich aufgefundenen Abhängigkeiten der in Rede stehenden Parameter von der zugrundeliegenden Verfahrensdurchführung wird gleichermaßen durch die Figurendarstellung gemäß Fig. 1b bestätigt. Für weitere diesbezügliche Ausführungen kann auf obige Ausführungen zu den entsprechenden Figurendarstellungen verwiesen werden.
Zusammenfassend ist somit festzustellen, dass durch die gezielte Auswahl von Prozessparametern, wie z. B. der Oxidationszeit, im Rahmen der dem erfindungsgemäß durchgeführten Verfahren zugrundeliegenden Oxidation von Ausgangsaktivkohle, die entsprechenden Eigenschaften der an ihrer Oberfläche oxidierten Aktivkohle als Intermediat der erfindungsgemäß umgesetzten Verfahrensführung gezielt eingestellt bzw. maßgeschneidert werden können.
b) Die zuvor aufgezeigte Einflussnahme von Prozessparametern auf die texturellen Eigenschaften der an ihrer Oberfläche oxidierten Aktivkohle wird auch durch den der Figurendarstellung gemäß Fig. 1c bis Fig. 1l zugrundeliegenden Untersuchungskomplex, welcher auf die Einflussnahme der Oxidationsbedingungen auf die Basizität bzw. Azidität der ausgebildeten Oberflächenoxide abstellt, bestätigt. In diesem Zusammenhang wurden entsprechende Ausgangsaktivkohlen zum einen einer thermischen Oxidation unter Einsatz von (Luft-)Sauerstoff als Oxidationsreagenz ("OR") und andererseits einer chemischen Oxidation unter Einsatz von Salpetersäure bzw. Wasserstoffperoxid als Oxidationsreagenz ("OR") unterzogen. Eine nachfolgende Analyse der so erhaltenen an ihrer Oberfläche oxidierten Aktivkohlen zeigt dabei, dass für thermische Oxidationsbedingungen vorrangig basische Oberflächenoxide gebildet werden, wogegen für chemische Oxidationsbedingungen auch saure Oberflächenoxide gebildet werden. Auf dieser Basis kann somit die chemische Struktur der Oberfläche der oxidierten Aktivkohle gezielt eingestellt bzw. maßgeschneidert werden.
Für weitere Ausführungen kann zur Vermeidung unnötiger Wiederholungen auf die obigen Ausführungen zu den entsprechenden Figurendarstellungen verwiesen werden.
Im Ergebnis zeigen die zugrundeliegenden Untersuchungen somit, dass durch die gezielte Auswahl der Oxidationsbedingungen die Basizität bzw. Azidität durch Bildung spezieller Oberflächenoxide gesteuert werden kann.
c) Im Rahmen eines weiteren Untersuchungskomplexes wurden entsprechende Ausgangsmaterialien einerseits einer thermischen Oxidation unter Einfluss von (Luft-)Sauerstoff und andererseits einer chemischen Oxidation unter Einsatz von Wasserstoffperoxid bzw. Salpetersäure als jeweilige Oxidationsreagenzien ("OR") unterzogen. Die so erhaltenen an ihrer Oberfläche oxidierten Aktivkohlen (Intermediat) wurden anschließend hinsichtlich der Adsorption bzw. Resorption von Wasserdampf im Vergleich zu einer nichtbehandelten Ausgangsaktivkohle (Ausgangsmaterial) untersucht. Wie in den Figurendarstellungen gemäß Fig. 2a und Fig. 2b dargestellt, erfolgt hierbei für die behandelten Aktivkohlen deutliche Verschiebung zu kleineren p/p_0-Werten. Diesbezüglich kann auch auf die obigen Ausführungen zu Fig. 2a und Fig. 2b verwiesen werden.

PAC ET AL. EXHIBIT 1019
Page 2226

Im Ergebnis zeigen die in den Figurendarstellungen gemäß Fig. 2a und Fig. 2b in Bezug genommenen Untersuchungen, dass die Wasserdampfisothermen durch die erfindungsgemäß vorgesehene Oxidation der Aktivkohle signifikant beeinflusst werden, was insbesondere als Maß für das Vorliegen einer erhöhten Hydrophilie der Oberfläche der Aktivkohle infolge der generierten sauerstoffhaltigen funktionellen Gruppen herangezogen werden kann.

d) Was die der Figurendarstellung gemäß Fig. 3a und Fig. 3b zugrundeliegenden Untersuchungen anbelangt, so fokussieren diese auf Versuchsparameter und Analyseergebnisse für zwei auf verschiedene Weise stickstofffunktionalisierte bzw. stickstoffmodifizierte Aktivkohlen nach der Erfindung (N-PBSAC), welche jeweils ausgehend von Ausgangsaktivkohle auf Basis von karbonisierten und aktivierten Polymeren hergestellt wurden (PBSAC). Das im Rahmen des erfindungsgemäß durchgeführten Verfahrens hergestellte oxidierte Basisadsorbenz (Intermediat) enthielt dabei 13,7 Gew.-% flüchtige Bestandteile ("fB"), bezogen auf das Trockengewicht des Intermediats.

In Bezug auf eine erste an ihrer Oberfläche oxidierten Aktivkohle wurde anschließend die Stickstoffmodifizierung bzw. -funktionalisierung bei einer Temperatur von T = 500°C durchgeführt, wobei diesbezüglich die folgenden Verfahrensschritte durchgeführt worden sind. Die an ihrer Oberfläche aktivierte Aktivkohle wurde in einem NH_3-Volumenstrom (5 l/h) mit einer Aufheizrate von 36 K/min auf 100°C erwärmt, und die Temperatur wurde für 30 min gehalten. Anschließend wurde mit einer Aufheizrate von 26 K/min auf 400°C erwärmt. Anschließend wurde im Stickstoffstrom mit einem Volumenstrom von 6 l/h mit 36 K/min auf 500°C aufgeheizt, wobei die Temperatur für 240 min gehalten wurde. Anschließend erfolgte eine Abkühlung über Nacht unter Stickstoffatmosphäre.

In Bezug auf die zweite Aktivkohle wurde wie zuvor beschrieben verfahren, jedoch mit der Maßgabe dass unter Stickstoffatmosphäre nicht eine Aufheizung auf 500°C, sondern auf 920°C erfolgte.

Die so erhaltenen funktionalisierten Aktivkohlen wiesen die folgenden Eigenschaften auf:

[0191]

Stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle	T = 500°C	T = 920°C
N-Gehalt [Gew.-%]	4,11	6,49
flüchtige Bestandteile ("fB")	10,2	0,86
RD [g/l]	547	541
pH-Wert	8,5	9,9
V_{tot} [cm³/g]	0,7397	0,7166
V_{mic} [cm³/g]	0,5846	0,5870
Mesoporenanteil [%]	21,0	18,1
MP-BET [m²/g]	1476	1453

Die obige Tabelle zeigt insbesondere, dass bei der höheren Temperaturen während der Stickstoffmodifizierung bzw. Stickstofffunktionalisierung eine Verringerung des Anteils an flüchtigen Bestandteilen ("fB") vorliegt, was einem Einbau bzw. einer Integration des Stickstoffs in das Kohlenstoffgerüst bzw. die Kohlenstoffmatrix der so behandelten Aktivkohle entspricht. Demgegenüber ist für niedrigere Temperaturen festzustellen, dass der Anteil an flüchtigen Bestandteilen höher ausfällt, was als Beleg für das Vorliegen des Stickstoffs in Form von stickstoffhaltigen funktionellen Gruppen zu werten ist.

Zudem zeigt eine Analyse der entsprechenden Wasserdampfisothermen (Fig. 3a), dass bei niedrigen Temperaturen (T = 500°C) die Funktionalisierung der behandelten Aktivkohle höher ist, was im Vergleich zu der bei höheren Temperaturen (T = 920°C) funktionalisierten Aktivkohle zu einer stärkeren Verschiebung der entsprechenden Adsorptions- bzw. Desorptionsäste zu geringen p/p_0-Werten führt. Zudem zeigt sich, wie in Fig. 3b dargestellt, dass die oxidierte Basis bzw. die an ihrer Oberfläche oxidierten Aktivkohlen im Hinblick auf die Parameter gemäß dem Gesamtporenvolumen, Mikroporenvolumen und der MP-BET-Oberfläche eine Erhöhung vorliegt, wobei diese Werte durch die nachfolgende Stickstofffunktionalisierung nur geringfügig verringert werden und immer noch oberhalb der Ausgangswerte auf Basis der eingesetzten Ausgangsaktivkohle liegen. Diesbezüglich kann auch auf obige Ausführungen zu den Figurendarstellungen gemäß Fig. 3a und Fig. 3b verwiesen werden.

Im Ergebnis zeigen die vorliegenden Untersuchungen, dass höhere Funktionalisierungstemperaturen zu einer vermehrten Integration bzw. Inkorporation von Stickstoff in das Kohlenstoffgerüst der so ausgerüsteten Aktivkohle führen, während niedrigere Temperaturen bei der Funktionalisierung zur Ausbildung stickstoff-

PAC ET AL. EXHIBIT 1019
Page 2227

halliger funktioneller Gruppen führen. Zudem kann gezeigt werden, dass die erfindungsgemäße realisierte Verfahrensführung zu keinerlei negativen Beeinträchtigung der Produktparameter führt.

e) Wie zuvor angeführt, zeigt die Figurendarstellung gemäß Fig. 4a einen dem erfindungsgemäß durchgeführten Verfahren beispielhaft zugrundeliegenden Reaktionsablauf mit der Integration von Stickstoff in das Kohlenstoffgerüst. Eine Analyse auf Basis eines XPS-Spektrums zeigt, wie in Fig. 4b dargestellt, dass bei niedrigen Temperaturen im Rahmen der Stickstoffmodifizierung bzw. Stickstofffunktionalisierung vorrangig stickstoffhaltige funktionelle Gruppen auf Basis von Amiden bzw. Pyrrolen vorliegen, während mit zunehmender Temperatur eine Verschiebung zu stickstoffhaltigen funktionellen Gruppen auf Basis von quaternären Stickstoffverbindungen vorliegt. Bei einer weiterführenden Temperaturerhöhung nehmen die entsprechenden XPS-Signale der jeweiligen funktionellen Gruppen ab, was als Beleg für die Integration von Stickstoff in das Kohlenstoffgerüst bzw. in die Kohlenstoffmatrix der so behandelten Aktivkohle heranzuziehen ist. Für weitere Ausführungen kann auf die entsprechenden Ausführungen zu den Figurendarstellungen gemäß Fig. 4a und Fig. 4b verwiesen werden.

f) Im Rahmen der der Figurendarstellung gemäß Fig. 5 zugrundeliegenden Untersuchungen wurden die Durchbruchzeiten von drei verschiedenen erfindungsgemäßen Aktivkohlen für die Schadgase NH_3, H_2S und SO_2 im Vergleich zu einer unbehandelten Ausgangsaktivkohle ermittelt. In Bezug auf die Durchbruchzeiten für Ammoniak (NH_3) ergibt sich hierbei für die Ausgangsaktivkohle ein Wert von lediglich 14 min, während für die erfindungsgemäßen Aktivkohlen mit der Stickstoffmodifizierung bzw. Ausrüstung ein jeweiliger Wert von 20 min, 22 min und 33 min erhalten wird. In Bezug auf die Durchbruchzeit gegenüber Schwefelwasserstoff (H_2S) wird für das unbehandelte Ausgangsmaterial ein Wert von 60 min erreicht, während demgegenüber für die erfindungsgemäßen Aktivkohlen Werte von 120 min, 110 min bzw. nochmals 120 min erhalten werden. Schließlich wurde in Bezug auf die Durchbruchzeit gegenüber Schwefeldioxid (SO_2) für das unbehandelte Ausgangsmaterial ein Wert von 30 min ermittelt, während für die drei erfindungsgemäßen Aktivkohlen Werte von 78 min, 47 min sowie 58 min ermittelt wurde. Diesbezüglich kann auch auf obige Ausführungen zu Fig. 5 verwiesen werden.

Im Ergebnis zeigen die durchgeführten Untersuchungen, dass die erfindungsgemäßen Aktivkohlen im Vergleich zu dem Ausgangsmaterial signifikant erhöhte Durchbruchzeiten für die in Rede stehenden Schadstoffen aufweisen, so dass die erfindungsgemäßen Aktivkohlen gegenüber dem Ausgangsmaterial hinsichtlich ihrer Leistungsfähigkeit erheblich verbessert sind.

g) Diese Befunde werden auch durch die in der Figurendarstellung gemäß Fig. 6a und Fig. 6b in Bezug genommenen Untersuchungen bestätigt: So ist sowohl in Bezug auf Schwefeldioxid (SO_2) als auch in Bezug auf Schwefelwasserstoff (H_2S) jeweils eine signifikante Verbesserung des Durchbruchverhaltens im Vergleich zu einer unbehandelten Ausgangsaktivkohle zu beobachten. In Bezug auf die der Figurendarstellung gemäß Fig. 6a zugrundeliegenden Versuchsparameter wurde ein Schüttbett der zu untersuchenden Aktivkohle mit einer Betthöhe von 1,5 cm und einer Bettfläche von 1,3 cm^2 hergestellt, wobei das Schüttbett bei einer relativen Feuchte von 70% einem SO_2-Volumenstrom mit 1.000 ppm SO_2 bei 220 ml/min ausgesetzt wurde. Bei dem untersuchten Endprodukt handelt es sich um eine bei Temperaturen von 920°C stickstoffmodifizierte bzw. stickstofffunktionalisierte Aktivkohle nach der Erfindung. In Bezug auf Fig. 6b wurde die untersuchte Aktivkohle in Form eines Schüttbetts mit einer Betthöhe von 1 cm eingesetzt. Bei einer relativen Feuchtigkeit von 50% wurde das Aktivkohlebett einem H_2S-Volumenstrom mit 20 ppm H_2S bei 0,2 m/s ausgesetzt. Bei der eingesetzten Aktivkohle handelt es sich gleichermaßen um die bereits in Fig. 6a in Bezug genommene Aktivkohle.

Die zugrundeliegenden Untersuchungen zeigen somit, dass auf Basis der erfindungsgemäßen Stickstofffunktionalisierung eine signifikante Verbesserung hinsichtlich der Chemisorption der zuvor beschriebenen Schadgase resultiert, was sich in deutlich vergrößerten Durchbruchzeiten widerspiegelt.

h) Im Rahmen eines weiteren Untersuchungskomplexes wurden Strukturanalysen an einer im Rahmen des erfindungsgemäß durchgeführten Verfahrens zum Erhalt des Intermediats an ihrer Oberfläche oxidierten Aktivkohle durchgeführt. Wie bereits zuvor angeführt, werden durch die Oxidation unter Einbezug eines Oxidationsreagenzes ("OR") verschiedene sauerstoffhaltige funktionelle Gruppen bzw. Spezies generiert, welche nachfolgend gewissermaßen als Ankergruppen bzw. Reaktionspartner für die Anbindung mit dem Stickstoffmodifizierungsreagenz ("SMR") fungieren. Gleichermaßen beeinflussen die auf diese Weise hergestellten sauerstoffhaltigen funktionellen Gruppen die Oberflächeneigenschaften der so oxidierten Aktivkohle, insbesondere im Hinblick auf den pH-Wert, die Hydrophilie und dergleichen, was insbesondere auch zu einer Optimierung der nachfolgenden Interaktion mit dem Stickstoffmodifizierungsreagenz führt. Diesbezüglich kann auch auf obige Ausführungen zu den Figurendarstellungen gemäß Fig. 7a und Fig. 7b verwiesen werden.

i) Es wurden weiteren erfindungsgemäße Aktivkohlen unter Verwendung von Harnstofflösungen in der oben beschriebenen Verfahrensweise hergestellt, wobei die Harnstoffbehandlung mit nachfolgender Wärmebehandlung bei T = 900°C erfolgte. Die vorangehende Oberflächenoxidation erfolgte in Gegenwart von Luftsauerstoff. Die erhaltenen Aktivkohle wurden für Durchbruchmessungen an einem Schüttbett (Durchmes-

PAC ET AL. EXHIBIT 1019
Page 2228

ser: 50 mm; Höhe: 20 mm) für verschiedene Gase (H_2S und SO_2) getestet (Strom mit jeweils 1.000 ppm Schadgas; Strömungsgeschwindigkeit: 0,1 m/s; 70% relative Feuchte; Messtemperatur: 20°C; Durchbruch bei 10 ppm für H_2S und 5 ppm für SO_2). Als Vergleich dienten eine unbehandelte Aktivkohle (Vergleich I) und eine herkömmlich basisch imprägnierte Aktivkohle (Vergleich II). Für H_2S bzw. SO_2 konnte bei der erfindungsgemäßen Aktivkohle eine Durchbruchzeit von 122 min bzw. 133 min ermittelt werden, während für die Vergleichskohle I die Werte bei < 1 min bzw. 4 min und für die Vergleichskohle II bei 57 min bzw. 46 min lagen. Die erfindungsgemäßen Aktivkohlen weisen somit zwei- bis dreifach erhöhte Durchbruchzeiten im Vergleich zu herkömmlich imprägnierten Aktivkohlen auf; auch für Cyclohexan und Chlor werden sehr lange Durchbruchzeiten erhalten.

3. Vergleich einer erfindungsgemäßen Aktivkohle mit Stickstoffmodifizierung zu Vergleichsaktivkohlen:

[0192] Im Rahmen der zugrundeliegenden Untersuchungen wurde eine erfindungsgemäße Aktivkohle, wie sie auf Basis der Ausführungen zu der unter 1.) hergestellten erfindungsgemäßen Aktivkohle B erhalten wurde, mit Vergleichsaktivkohlen verglichen, welche auf unterschiedliche Art und Weise mit Stickstoff ausgerüstet wurden: So wurde eine erste Vergleichskohle I erhalten, indem ausgehend von entsprechenden Polymeren ein zweistufiger Prozess zur Herstellung der Aktivkohle auf Basis einer Carbonisierung mit nachfolgender Aktivierung durchgeführt wurde, wobei die Aktivierung in Gegenwart von Kohlendioxid, Wasserdampf und Ammoniakgas durchgeführt wurde; das stickstoffhaltige Mittel in Form von NH_3 wurde somit ihm Rahmen der Aktivkohleherstellung bei der Aktivierung zugegeben.

[0193] Des Weiteren wurde eine zweite Vergleichsaktivkohle II erhalten, indem eine fertige Aktivkohle (d. h. nach Carbonisierung und Aktivierung) als solche einer herkömmlichen Harnstoffimprägnierung unterzogen wurde, wobei diesbezüglich eine Harnstofflösung mit der Aktivkohle gemischt und die Aktivkohle auf diese Weise imprägniert bzw. getränkt wurde. Die so erhaltene Aktivkohle wurde anschließend getrocknet. Schließlich wurde eine Vergleichsaktivkohle III erhalten, indem eine Aktivkohle ohne zwischengeschaltete Oxidation direkt einer Stickstoffmodifizierung unterzogen wurde, indem eine Harnstofflösung mit der Aktivkohle in Kontakt gebracht wurde und die auf diese Weise behandelte Aktivkohle einer nachfolgenden Wärmebehandlung unterzogen wurde. Die Vergleichsaktivkohle III unterscheidet sich somit von der erfindungsgemäßen Aktivkohle dadurch, dass eine Aktivkohle als solche und somit keine an ihrer Oberfläche oxidierte Aktivkohle einer nachfolgenden Behandlung zur Stickstoffmodifizierung unterzogen wurde. Die entsprechende Aktivkohle wies somit in Bezug auf das Stickstoffmodifizierungsreagenz keine Ankergruppen auf.

[0194] An den so erhaltenen Untersuchungen wurden entsprechende Analysen des Stickstoffgehalts und weiterführende Untersuchungen in Bezug auf das Durchbruchverhalten von Schwefelwasserstoff (H_2S) durchgeführt. Bezüglich der Analyse des Stickstoffgehalts und des Vorliegens von Stickstoff in der Aktivkohle kann auf obige Ausführungen verwiesen werden. Die Durchbruchexperimente wurden auf Basis einer Schüttung der jeweiligen Aktivkohle mit einer Höhe von 2 cm in einem konstanten Volumenstrom bei einer Temperatur von T = 30°C durchgeführt, wobei der mit einer konstanten Strömungsgeschwindigkeit durch die Schüttung geführte Volumenstrom mit 20 ppm H_2S versehen wurde. Die nachfolgende Tabelle zeigt die erhaltenen Ergebnisse.

Aktivkohle	B (Erf.)	I (Vgl.)	II (Vgl.)	III (Vgl.)
Stickstoffgehalt N-Gehalt [Gew.-%]	18	1	4	8
Gehalt an Stickstoff nicht in Form von flüchtigen Bestandteilen (Gew.-%)	95	≤ 0,1	≤ 0,1	≤ 0,5
Durchbruchszeit gegenüber H_2S [min]	≥ 100	54,5	62,5	81

[0195] Die Tabelle zeigt, dass in Bezug auf die erfindungsgemäße Aktivkohle B sowohl der Gehalt an in das Gerüst gebundenem (d. h. nicht in Form von flüchtigen Bestandteilen vorliegendem) Stickstoff in der Aktivkohle erhöht ist, wobei im Gegensatz zu den Vergleichsaktivkohlen ein erheblich größerer Anteil des Stickstoffs in Form von nichtflüchtigen Stickstoffbestandteilen vorliegt, was als Maß für die Integration des Stickstoffs in die Aktivkohlematrix bzw. das Aktivkohlegerüst zu verstehen ist.

PAC ET AL. EXHIBIT 1019
Page 2229

[0196] Gleichermaßen weist die erfindungsgemäße Aktivkohle B ein deutlich verbessertes Durchbruchverhalten gegenüber Schwefelwasserstoff und somit eine signifikant verbesserte Leistungsfähigkeit im Vergleich zu den Vergleichsaktivkohlen I bis III auf.

[0197] Im Rahmen einer weiterführenden Untersuchung wurden die zugrundeliegenden Aktivkohlen, nämlich die erfindungsgemäße Aktivkohle B und die Vergleichsaktivkohlen I bis III, einem Waschvorgang unter Verwendung von 1 N Salzsäure für eine Zeitdauer von einer Stunde unterzogen. Anschließend wurden die Aktivkohlen neutralgewaschen und nachfolgend getrocknet. Mit den so behandelten Aktivkohlen wurden erneut Durchbruchmessungen in Bezug auf Schwefelwasserstoff (H_2S), wie zuvor beschrieben, durchgeführt. Während für die erfindungsgemäße Aktivkohle B eine Durchbruchzeit von weiterhin mehr als 100 min ermittelt werden konnte, betrugen die entsprechenden Durchbruchzeiten für die Vergleichsaktivkohlen I bis III 15 min, 18 min bzw. 26 min. Dies ist als Beleg dafür zu werten, dass aufgrund des Waschvorgangs mit Salzsäure hinsichtlich der Vergleichsaktivkohle I bis III eine erhebliche Menge an Stickstoff entfernt wurde, was für die erfindungsgemäße Aktivkohle B nicht der Fall ist. Dies bedeutet, dass in Bezug auf die Vergleichsaktivkohlen I bis III der Stickstoff zumindest im Wesentlichen nicht in immobilisierter Form vorliegt und somit leicht entfernt werden kann. Im Gegensatz hierzu ist aufgrund der Inkorporation des Stickstoffs in das Kohlenstoffgerüst gemäß Aktivkohle B der Stickstoff immobilisiert bzw. fest verankert, was zu der hohen Beständigkeit auch gegenüber Säuren führt.

[0198] Im Ergebnis zeigen die durchgeführten Untersuchungen die hohe Leistungsfähigkeit und die positiven Eigenschaften der auf Basis des erfindungsgemäß durchgeführten Verfahrens erhältlichen stickstoffmodifizierten bzw. stickstofffunktionalisierten Aktivkohlen.

PAC ET AL. EXHIBIT 1019
Page 2230

ZITATE ENTHALTEN IN DER BESCHREIBUNG

Diese Liste der vom Anmelder aufgeführten Dokumente wurde automatisiert erzeugt und ist ausschließlich zur besseren Information des Lesers aufgenommen. Die Liste ist nicht Bestandteil der deutschen Patent- bzw. Gebrauchsmusteranmeldung. Das DPMA übernimmt keinerlei Haftung für etwaige Fehler oder Auslassungen.

Zitierte Patentliteratur

- WO 98/07655 A1 [0008]
- DE 4328219 A1 [0010, 0105]
- DE 4304026 A1 [0010, 0105]
- DE 19600237 A1 [0010, 0105]
- DE 19625069 A1 [0010]
- DE 102007050971 A1 [0011]
- DE 19519869 A1 [0015]
- EP 1918022 A1 [0105]
- US 7737038 B2 [0105]

Zitierte Nicht-Patentliteratur

- H. v. Kienle und E. Bäder, "Aktivkohle und ihre industrielle Anwendung", Enke Verlag Stuttgart, 1980 [0006]
- Europäische Norm EN 14387 (Januar 2004) [0016]
- ISO 562:1981 [0081]
- Norm ISO 562:1981 [0088]
- ISO 562:1981 [0089]
- ISO 562:1981 [0090]
- L. Gurvich (1915), J. Phys. Chem. Soc. Russ. 47, 805, sowie auf S. Lowell et al., Characterization of Porous Solids and Powders: Surface Area Pore Size and Density, Kluwer Academic Publishers, Article Technology Series, Seiten 111 ff [0093]
- R. W. Magee, Evaluation of the External Surface Area of Carbon Black by Nitrogen Adsorption, Presented at the Meeting of the Rubber Division of the American Chem. Soc., October 1994, z. B. referiert in: Quantachrome Instruments, AUTOSORB-1, AS1 Win-Version 1.50, Operating Manual, OM, 05061, Quantachrome Instruments 2004, Florida, USA, Seiten 71 ff [0095]
- ASTM D6556-04 [0098]
- ASTM D6556-04 [0099]
- Römpp Chemielexikon, 10. Auflage, Georg Thieme Verlag, Stuttgart/New York, Stichwort: "BET-Methode", einschließlich der dort referierten Literatur, und auf Winnacker-Küchler (3. Auflage), Band 7, Seiten 93 ff. [0099]
- Z. Anal. Chem. 238, Seiten 187 bis 193 (1968) [0099]
- ASTM D2862-97/04 [0106]
- ISO 562:1981 [0183]
- ISO 562:1981 [0183]

PAC ET AL. EXHIBIT 1019
Page 2231

Schutzansprüche

1. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle, insbesondere mit katalytischen und/oder reaktiven Eigenschaften, vorzugsweise Aktivkohle mit Stickstoff als katalytisch aktivem Heteroatom, erhältlich durch ein Verfahren, wobei bei dem Verfahren eine als Ausgangsmaterial eingesetzte Aktivkohle ("Ausgangsaktivkohle") zunächst einer Oberflächenoxidation unter Verwendung und/oder in Gegenwart mindestens eines Oxidationsreagenzes ("OR") unterzogen wird und die auf diese Weise erhaltene, an ihrer Oberfläche oxidierte Aktivkohle nachfolgend einer Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff, insbesondere mit stickstoffhaltigen funktionellen Gruppen, unter Verwendung und/oder in Gegenwart mindestens eines Stickstoffmodifizierungsreagenzes ("SMR") unterzogen wird.

2. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 1, dadurch gekennzeichnet, dass die Oberflächenoxidation unter Ausbildung einer hydrophilen Oberfläche der Aktivkohle durchgeführt wird und/oder dass die Oberflächenoxidation unter Ausbildung von sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle durchgeführt wird und/oder dass die Oberflächenoxidation zu einer Ausbildung von sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle führt, insbesondere wobei die sauerstoffhaltigen funktionellen Gruppen ausgewählt werden aus sauren und basischen sauerstoffhaltigen funktionellen Gruppen sowie deren Kombinationen, insbesondere sauren und basischen Oberflächenoxiden, und/oder insbesondere wobei die sauerstoffhaltigen funktionellen Gruppen ausgewählt werden aus Hydroxyl-, Carboxyl-, Carbonyl-, Anhydrid-, Lacton-, Chinon-, Pyron-, Chromen- und Ethergruppen sowie deren Kombinationen.

3. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 1 oder 2, dadurch gekennzeichnet,
dass durch die Oberflächenoxidation der pH-Wert, insbesondere der Oberflächen-pH-Wert, der an ihrer Oberfläche oxidierten Aktivkohle im Vergleich zu der Ausgangsaktivkohle um einen Wert von mindestens 0,25, insbesondere mindestens 0,5, vorzugsweise mindestens 0,75, bevorzugt mindestens 1, besonders bevorzugt mindestens 1,5, verändert wird; und/oder
dass die Acidität der an ihrer Oberfläche oxidierten Aktivkohle erhöht und/oder der pH-Wert, insbesondere der Oberflächen-pH-Wert, der an ihrer Oberfläche oxidierten Aktivkohle verringert wird, insbesondere um einen Wert von mindestens 0,25, insbesondere mindestens 0,5, vorzugsweise mindestens 0,75, bevorzugt mindestens 1, besonders bevorzugt mindestens 1,5, oder aber dass die Basizität der an ihrer Oberfläche oxidierten Aktivkohle erhöht und/oder der pH-Wert, insbesondere der Oberflächen-pH-Wert, der an ihrer Oberfläche oxidierten Aktivkohle erhöht wird, insbesondere um einen Wert von mindestens 0,25, insbesondere mindestens 0,5, vorzugsweise mindestens 0,75, bevorzugt mindestens 1, besonders bevorzugt mindestens 1,5.

4. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Oberflächenoxidation durchgeführt wird derart, dass die auf diese Weise erhaltene, an ihrer Oberfläche oxidierte Aktivkohle einen Gehalt an sauerstoffhaltigen funktionellen Gruppen, berechnet und/oder ausgedrückt als Gehalt an flüchtigen Bestandteilen ("fB") und bezogen auf das Trockengewicht der an ihrer Oberfläche oxidierten Aktivkohle, von mindestens 1 Gew.-%, insbesondere mindestens 2 Gew.-%, vorzugsweise mindestens 3 Gew.-%, bevorzugt mindestens 4 Gew.-%, und/oder im Bereich von 1 Gew.-% bis 30 Gew.-%, insbesondere 1,5 Gew.-% bis 25 Gew.-%, vorzugsweise 2 Gew.-% bis 20 Gew.-%, bevorzugt 3 Gew.-% bis 15 Gew.-%, aufweist, insbesondere wobei der Gehalt an sauerstoffhaltigen funktionellen Gruppen durch Temperatur und/oder Zeitdauer und/oder Art und/oder Konzentration an Oxidationsreagenz ("OR") eingestellt wird.

5. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das Oxidationsreagenz ("OR") ausgewählt wird aus der Gruppe von Sauerstoff, Ozon, anorganischen oder organischen Oxiden und Peroxiden sowie anorganischen oder organischen Säuren und Persäuren und deren Kombinationen, bevorzugt aus der Gruppe von Sauerstoff, Wasserstoffperoxid (H_2O_2), Salpetersäure (HNO_3) und Ammoniumperoxodisulfat ($(NH_4)_2S_2O_8$) sowie deren Kombinationen.

6. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Oberflächenoxidation unter Erwärmen erfolgt, insbesondere wobei die Oberflächenoxidation unter solchen Temperaturen erfolgt, dass eine Reaktion des Oxidationsreagenzes ("OR") mit der Aktivkohle unter Ausbildung von sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle erfolgt, und/oder insbesondere wobei die Oberflächenoxidation im Temperaturbereich von –20°C bis 1.000°C, insbesondere 0°C bis 800°C, vorzugsweise 20°C bis 600°C, bevorzugt 30°C bis 500°C,

PAC ET AL. EXHIBIT 1019
Page 2232

durchgeführt wird und/oder insbesondere wobei die Oberflächenoxidation für eine Zeitdauer im Bereich von 1 Minute bis 600 Minuten, insbesondere 5 Minuten bis 500 Minuten, bevorzugt 10 Minuten bis 400 Minuten, durchgeführt wird.

7. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das Oxidationsreagenz ("OR") ausgewählt wird aus der Gruppe von anorganischen oder organischen Oxiden und Peroxiden sowie anorganischen oder organischen Säuren und Persäuren und deren Kombinationen, bevorzugt aus der Gruppe von Wasserstoffperoxid (H_2O_2) und Salpetersäure (HNO_3), vorzugsweise Salpetersäure (HNO_3), insbesondere wobei die Oberflächenoxidation im Temperaturbereich von –20°C bis 500°C, insbesondere –10°C bis 400°C, vorzugsweise 0°C bis 350°C, bevorzugt 10°C bis 300°C, besonders bevorzugt 15°C bis 250°C, ganz besonders bevorzugt 20°C bis 200°C durchgeführt wird.

8. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das Oxidationsreagenz ("OR") ausgewählt wird aus der Gruppe von Sauerstoff und Ozon, vorzugsweise Sauerstoff, insbesondere wobei die Oberflächenoxidation im Temperaturbereich von 100°C bis 1.000°C, insbesondere 150°C bis 900°C, vorzugsweise 200°C bis 750°C, bevorzugt 225°C bis 600°C, besonders bevorzugt 250°C bis 500°C, ganz besonders bevorzugt 250°C bis 450°C, durchgeführt wird.

9. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass im Anschluss an die Oberflächenoxidation und insbesondere vor der Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff eine Aufreinigung und/oder Trocknung der an ihrer Oberfläche oxidierten Aktivkohle erfolgt, insbesondere wobei die Aufreinigung mittels mindestens eines Waschvorgangs in einer Flüssigkeit, insbesondere Wasser, erfolgt und/oder insbesondere wobei die Trocknung unter Erwärmung der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere auf Temperaturen im Bereich von 40°C bis 200°C, insbesondere 50°C bis 150°C, vorzugsweise 60°C bis 120°C, erfolgt.

10. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff ein Inkontaktbringen der nach der Oberflächenoxidation erhaltenen Aktivkohle und/oder der an ihrer Oberfläche oxidierten Aktivkohle mit dem Stickstoffmodifizierungreagenz ("SMR"), gefolgt von einer thermischen Behandlung, umfasst.

11. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass das für die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff eingesetzte Stickstoffmodifizierungsreagenz ("SMR") ausgewählt wird aus der Gruppe von Harnstoff, Ammoniak, Melamin und Aminosäuren sowie deren Kombinationen, insbesondere Harnstoff und Ammoniak sowie deren Kombinationen, vorzugsweise Harnstoff.

12. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass als das für die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff eingesetzte Stickstoffmodifizierungsreagenz ("SMR") Harnstoff verwendet wird, insbesondere wobei der Harnstoff in Form einer vorzugsweise wässrigen Lösung, bevorzugt in Form einer zumindest im Wesentlichen gesättigten Harnstofflösung, eingesetzt wird.

13. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass als das für die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff eingesetzte Stickstoffmodifizierungsreagenz ("SMR") Ammoniak verwendet wird, insbesondere wobei das Ammoniak in Form des Gases und/oder als Ammoniakwasser, insbesondere in Form des Gases, eingesetzt wird.

14. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff durch Reaktion, insbesondere chemische Reaktion, vorzugsweise unter Ausbildung kovalenter Bindungen, des Stickstoffmodifizierungsreagenzes ("SMR") mit der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere mit den sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle, erfolgt.

PAC ET AL. EXHIBIT 1019
Page 2233

15. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Ausbildung stickstoffhaltiger funktioneller Gruppen, insbesondere ausgewählt aus der Gruppe von Aminen, insbesondere primären, sekundären, tertiären und quartären Aminen, Iminen und Azinen sowie deren Kombinationen und/oder insbesondere ausgewählt aus der Gruppe von Amin-, Imin-, Azin-, Pyrrol-, Nitril-, Nitro-, Nitroso-, Pyridin-, Imid-, Amid-, Lactam- und Pyridongruppen sowie deren Kombinationen, erfolgt.

16. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Integration und/oder Einbau, insbesondere unter Ausbildung chemischer Bindungen, vorzugsweise unter Ausbildung kovalenter chemischer Bindungen, insbesondere zwischen Stickstoff einerseits und Kohlenstoff andererseits, in das Kohlenstoffgerüst und/oder die Kohlenstoffmatrix der an ihrer Oberfläche oxidierten Aktivkohle erfolgt.

17. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen erfolgt, insbesondere auf Temperaturen oberhalb der Zersetzungstemperatur des Stickstoffmodifizierungsreagenzes ("SMR"), insbesondere wobei die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter solchen Temperaturen erfolgt, dass eine Reaktion des Stickstoffmodifizierungsreagenzes ("SMR") mit der an ihrer Oberfläche oxidierten Aktivkohle, insbesondere mit den sauerstoffhaltigen funktionellen Gruppen an der Oberfläche der Aktivkohle, erfolgt, und/oder insbesondere wobei die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff im Temperaturbereich von 200°C bis 1.200°C, insbesondere 300°C bis 1.000°C, vorzugsweise 500°C bis 950°C, durchgeführt wird und/oder insbesondere wobei die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, insbesondere 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, durchgeführt wird.

18. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen in Form einer einstufigen Wärmebehandlung erfolgt.

19. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen auf einen Temperaturbereich von 300°C bis 700°C, insbesondere 400°C bis 600°C, vorzugsweise 400°C bis 550°C, durchgeführt wird, insbesondere für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, bevorzugt 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, insbesondere wobei stickstoffhaltige funktionelle Gruppen, wie in Anspruch 15 definiert, ausgebildet werden.

20. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen auf einen Temperaturbereich von 750°C bis 1.200°C, insbesondere 800°C bis 1.100°C, vorzugsweise 850°C bis 1.050°C, durchgeführt wird, insbesondere für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, bevorzugt 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, insbesondere wobei eine Integration und/oder ein Einbau des Stickstoffs in das Kohlenstoffgerüst und/oder die Kohlenstoffmatrix der an ihrer Oberfläche oxidierten Aktivkohle erfolgt, insbesondere wie in Anspruch 16 definiert.

21. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff unter Erwärmen in Form einer mehrstufigen, insbesondere zweistufigen Wärmebehandlung, erfolgt.

22. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, der an ihrer Oberfläche oxidierten Aktivkohle mit Stickstoff in einer ersten Wärmebehandlung unter Er-

PAC ET AL. EXHIBIT 1019
Page 2234

wärmen auf einen Temperaturbereich von 300°C bis 700°C, insbesondere 400°C bis 600°C, vorzugsweise 400°C bis 550°C, und einer nachfolgenden zweiten Wärmebehandlung unter Erwärmen auf einen Temperaturbereich von 750°C bis 1.200°C, insbesondere 800°C bis 1.100°C, vorzugsweise 850°C bis 1.050°C, durchgeführt wird, insbesondere wobei die jeweiligen Wärmebehandlungen, unabhängig voneinander, für eine Zeitdauer im Bereich von 0,1 Stunden bis 15 Stunden, insbesondere 0,2 Stunden bis 10 Stunden, vorzugsweise 0,5 Stunden bis 8 Stunden, durchgeführt werden.

23. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass im Anschluss an die Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff eine Aufreinigung und/oder Trocknung der erhaltenen Aktivkohle erfolgt, insbesondere wobei die Aufreinigung mittels mindestens eines Waschvorgangs in einer Flüssigkeit, insbesondere Wasser, erfolgt und/oder insbesondere wobei die Trocknung unter Erwärmung der mit Stickstoff ausgerüsteten Aktivkohle, insbesondere auf Temperaturen im Bereich von 40°C bis 200°C, insbesondere 50°C bis 150°C, vorzugsweise 60°C bis 120°C, erfolgt.

24. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die mit Stickstoff ausgerüstete Aktivkohle einen Gehalt an flüchtigen Bestandteilen ("fB"), bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 20 Gew.-%, insbesondere 0,2 Gew.-% bis 15 Gew.-%, vorzugsweise 0,3 Gew.-% bis 12 Gew.-%, bevorzugt 0,5 Gew.-% bis 10 Gew.-%, besonders bevorzugt 1 Gew.-% bis 10 Gew.-%, aufweist.

25. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die mit Stickstoff ausgerüstete Aktivkohle einen Stickstoffgehalt, bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 30 Gew.-%, insbesondere 0,2 Gew.-% bis 25 Gew.-%, vorzugsweise 0,3 Gew.-% bis 20 Gew.-%, bevorzugt 0,5 Gew.-% bis 15 Gew.-%, besonders bevorzugt 1 Gew.-% bis 15 Gew.-%, aufweist, insbesondere wobei mindestens 50%, insbesondere mindestens 60%, vorzugsweise mindestens 70%, bevorzugt mindestens 80%, des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der mit Stickstoff ausgerüsteten Aktivkohle chemisch gebunden und/oder integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der mit Stickstoff ausgerüsteten Aktivkohle vorliegen und/oder insbesondere wobei 50% bis 99,9%, insbesondere 60% bis 99%, vorzugsweise 70% bis 95%, bevorzugt 80% bis 90%, des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der mit Stickstoff ausgerüsteten Aktivkohle chemisch gebunden und/oder integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der mit Stickstoff ausgerüsteten Aktivkohle vorliegen.

26. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass die mit Stickstoff ausgerüstete Aktivkohle ein Gesamtporenvolumen, insbesondere ein Gesamtporenvolumen nach Gurvich, im Bereich von 0,4 bis 4 cm^3/g, insbesondere 0,5 bis 3,5 cm^3/g, vorzugsweise 0,6 bis 3 cm^3/g, besonders bevorzugt 0,7 bis 2,5 cm^3/g, aufweist, insbesondere wobei 30% bis 99%, insbesondere 40% bis 99%, vorzugsweise 50% bis 95%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der mit Stickstoff ausgerüsteten Aktivkohle, durch Poren mit Porendurchmessern von ≤ 50 nm, insbesondere durch Mikro- und/oder Mesoporen, gebildet werden und/oder insbesondere wobei 10% bis 85%, insbesondere 20% bis 80%, vorzugsweise 30% bis 75%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der mit Stickstoff ausgerüsteten Aktivkohle, durch Poren mit Porendurchmessern im Bereich von 2 nm bis 50 nm, insbesondere durch Mesoporen, gebildet werden, und/oder
dass die mit Stickstoff ausgerüstete Aktivkohle ein durch Poren mit Porendurchmessern ≤ 2 nm gebildetes Porenvolumen, insbesondere Mikroporenvolumen nach Carbon Black, im Bereich von 0,05 bis 2 cm^3/g, insbesondere 0,1 bis 1,5 cm^3/g, vorzugsweise 0,2 bis 1,1 cm^3/g, besonders bevorzugt 0,3 bis 1 cm^3/g, aufweist und/oder dass 10% bis 95%, insbesondere 20% bis 95%, vorzugsweise 30% bis 90%, des Gesamtporenvolumens der mit Stickstoff ausgerüsteten Aktivkohle durch Poren mit Porendurchmessern von ≤ 2 nm, insbesondere durch Mikroporen, gebildet werden und/oder
dass die mit Stickstoff ausgerüstete Aktivkohle einen mittleren Porendurchmesser im Bereich von 1 bis 60 nm, insbesondere 1 bis 55 nm, bevorzugt 1,5 bis 50 nm, besonders bevorzugt 2 bis 45 nm, aufweist.

PAC ET AL. EXHIBIT 1019
Page 2235

27. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, dass als eingesetzte Aktivkohle ("Ausgangsaktivkohle") kornförmige, insbesondere kugelförmige Aktivkohle verwendet wird und/oder dass als eingesetzte Aktivkohle ("Ausgangsaktivkohle") eine derartige Aktivkohle verwendet wird, welche durch Carbonisierung eines Ausgangsmaterials, insbesondere von sulfonierten organischen Polymeren, vorzugsweise auf Basis von divinylbenzolvernetztem Polystyrol, und anschließende Aktivierung des carbonisierten Ausgangsmaterials erhalten wird.

28. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet,
dass die mit Stickstoff ausgerüstete Aktivkohle eine spezifische BET-Oberfläche im Bereich von 500 m^2/g bis 3.500 m^2/g, insbesondere 600 bis 3.000 m^2/g, vorzugsweise 700 bis 2.750 m^2/g, besonders bevorzugt 800 bis 2.500 m^2/g, aufweist und/oder
dass die mit Stickstoff ausgerüstete Aktivkohle eine durch Mikroporen gebildete Oberfläche von 400 bis 2.500 m^2/g, insbesondere 500 bis 2 300 m^2/g, vorzugsweise 600 bis 2.100 m^2/g, besonders bevorzugt 700 bis 1.900 m^2/g, aufweist und/oder
dass die mit Stickstoff ausgerüstete Aktivkohle eine Dichte von 1,1 bis 3,5 g/ml, insbesondere von 1,5 bis 3 g/ml, vorzugsweise von 1,75 bis 2,75 g/ml, bevorzugt von 2 bis 2,5 g/ml, aufweist und/oder
dass die mit Stickstoff ausgerüstete Aktivkohle eine Schüttdichte von 0,1 bis 1,5 g/ml, insbesondere von 0,15 bis 1 g/ml, vorzugsweise von 0,2 bis 0,8 g/ml, bevorzugt von 0,3 bis 0,6 g/ml, aufweist und/oder
dass die mit Stickstoff ausgerüstete Aktivkohle eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, von mindestens 5 Newton, insbesondere mindestens 10 Newton, vorzugsweise mindestens 15 Newton, bevorzugt mindestens 20 Newton, aufweist und/oder dass die Aktivkohle eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, im Bereich von 10 bis 50 Newton, insbesondere 10 bis 45 Newton, vorzugsweise 15 bis 40 Newton, aufweist.

29. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle, insbesondere mit katalytischen und/oder reaktiven Eigenschaften, vorzugsweise mit Stickstoff als katalytisch aktivem Heteroatom, wobei die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle durch Oberflächenoxidation einer als Ausgangsmaterial eingesetzten Aktivkohle ("Ausgangsaktivkohle") unter Verwendung und/oder in Gegenwart mindestens eines Oxidationsreagenzes ("OR") und nachfolgender Ausrüstung, insbesondere Modifizierung und/oder Funktionalisierung, mit Stickstoff der auf diese Weise erhaltenen, an ihrer Oberfläche oxidierten Aktivkohle unter Verwendung und/oder in Gegenwart mindestens eines Stickstoffmodifizierungsreagenzes ("SMR") erhältlich ist.

30. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle, insbesondere mit katalytischen und/oder reaktiven Eigenschaften, vorzugsweise mit Stickstoff als katalytisch aktivem Heteroatom, dadurch gekennzeichnet, dass Stickstoff unter Ausbildung chemischer Bindungen, vorzugsweise unter Ausbildung kovalenter chemischer Bindungen, an die Aktivkohle gebunden ist.

31. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 30, dadurch gekennzeichnet, dass Stickstoff in Form mindestens einer stickstoffhaltigen funktionellen Gruppe, insbesondere ausgewählt aus der Gruppe von Aminen, insbesondere primären, sekundären, tertiären und quartären Aminen, Iminen und Azinen sowie deren Kombinationen und/oder insbesondere ausgewählt aus der Gruppe von Amin-, Imin-, Azin-, Pyrrol-, Nitril-, Nitro-, Nitroso-, Pyridin-, Imid-, Amid-, Lactam- und Pyridongruppen sowie deren Kombinationen, vorliegt, insbesondere an die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle gebunden ist, vorzugsweise chemisch und/oder kovalent gebunden ist.

32. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 30 oder 31, dadurch gekennzeichnet, dass Stickstoff in das Kohlenstoffgerüst und/oder die Kohlenstoffmatrix der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle, vorzugsweise unter Ausbildung kovalenter chemischer Bindungen, insbesondere zwischen Stickstoff einerseits und Kohlenstoff andererseits, integriert und/oder eingebaut ist.

33. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 32, dadurch gekennzeichnet, dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle einen Gehalt an flüchtigen Bestandteilen ("fB"), bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 20 Gew.-%, insbesondere 0,2 Gew.-

PAC ET AL. EXHIBIT 1019
Page 2236

% bis 15 Gew.-%, vorzugsweise 0,3 Gew.-% bis 12 Gew.-%, bevorzugt 0,5 Gew.-% bis 10 Gew.-%, besonders bevorzugt 1 Gew.-% bis 10 Gew.-%, aufweist.

34. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 33, dadurch gekennzeichnet, dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle einen Stickstoffgehalt, bezogen auf das Trockengewicht der mit Stickstoff ausgerüsteten Aktivkohle, von mindestens 0,1 Gew.-%, insbesondere mindestens 0,2 Gew.-%, vorzugsweise mindestens 0,3 Gew.-%, bevorzugt mindestens 0,5 Gew.-%, besonders bevorzugt mindestens 1 Gew.-%, ganz besonders bevorzugt mindestens 2 Gew.-%, und/oder im Bereich von 0,1 Gew.-% bis 30 Gew.-%, insbesondere 0,2 Gew.-% bis 25 Gew.-%, vorzugsweise 0,3 Gew.-% bis 20 Gew.-%, bevorzugt 0,5 Gew.-% bis 15 Gew.-%, besonders bevorzugt 1 Gew.-% bis 15 Gew.-%, aufweist, insbesondere wobei mindestens 50%, insbesondere mindestens 60%, vorzugsweise mindestens 70%, bevorzugt mindestens 80%, des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle chemisch gebunden und/oder integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle vorliegen und/oder insbesondere wobei 50% bis 99,9%, insbesondere 60% bis 99%, vorzugsweise 70% bis 95%, bevorzugt 80% bis 90%, des Stickstoffs, bezogen auf den Gesamtstickstoffgehalt, in der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle chemisch gebunden und/oder integriert vorliegen und/oder nicht in Form von flüchtigen Bestandteilen ("fB") in der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle vorliegen.

35. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 34, dadurch gekennzeichnet,
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle ein Gesamtporenvolumen, insbesondere ein Gesamtporenvolumen nach Gurvich, im Bereich von 0,4 bis 4 cm^3/g, insbesondere 0,5 bis 3,5 cm^3/g, vorzugsweise 0,6 bis 3 cm^3/g, besonders bevorzugt 0,7 bis 2,5 cm^3/g, aufweist, insbesondere wobei 30% bis 99%, insbesondere 40% bis 99%, vorzugsweise 50% bis 95%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle, durch Poren mit Porendurchmessern von ≤ 50 nm, insbesondere durch Mikro- und/oder Mesoporen, gebildet werden und/oder insbesondere wobei 10% bis 85%, insbesondere 20% bis 80%, vorzugsweise 30% bis 75%, des Gesamtporenvolumens, insbesondere des Gesamtporenvolumens nach Gurvich, der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle, durch Poren mit Porendurchmessern im Bereich von 2 nm bis 50 nm, insbesondere durch Mesoporen, gebildet sind; und/oder
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle ein durch Poren mit Porendurchmessern ≤ 2 nm gebildetes Porenvolumen, insbesondere Mikroporenvolumen nach Carbon Black, im Bereich von 0,05 bis 2 cm^3/g, insbesondere 0,1 bis 1,5 cm^3/g, vorzugsweise 0,2 bis 1,1 cm^3/g, besonders bevorzugt 0,3 bis 1 cm^3/g, aufweist und/oder dass 10% bis 95%, insbesondere 20% bis 95%, vorzugsweise 30% bis 90%, des Gesamtporenvolumens der stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle durch Poren mit Porendurchmessern von ≤ 2 nm, insbesondere durch Mikroporen, gebildet sind und/oder
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle einen mittleren Porendurchmesser im Bereich von 1 bis 60 nm, insbesondere 1 bis 55 nm, bevorzugt 1,5 bis 50 nm, besonders bevorzugt 2 bis 45 nm, aufweist.

36. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 35, dadurch gekennzeichnet,
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle eine spezifische BET-Oberfläche im Bereich von 500 m^2/g bis 3.500 m^2/g, insbesondere 600 bis 3.000 m^2/g, vorzugsweise 700 bis 2.750 m^2/g, besonders bevorzugt 800 bis 2.500 m^2/g, aufweist und/oder dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle eine durch Mikroporen gebildete Oberfläche von 400 bis 2.500 m^2/g, insbesondere 500 bis 2.300 m^2/g, vorzugsweise 600 bis 2.100 m^2/g, besonders bevorzugt 700 bis 1.900 m^2/g, aufweist und/oder
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle eine Dichte von 1,1 bis 3,5 g/ml, insbesondere von 1,5 bis 3 g/ml, vorzugsweise von 1,75 bis 2,75 g/ml, bevorzugt von 2 bis 2,5 g/ml, aufweist und/oder
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle eine Schüttdichte von 0,1 bis 1,5 g/ml, insbesondere von 0,15 bis 1 g/ml, vorzugsweise von 0,2 bis 0,8 g/ml, bevorzugt von 0,3 bis 0,6 g/ml, aufweist und/oder
dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit) pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, von mindestens 5 Newton, insbesondere mindestens 10 Newton, vorzugsweise mindestens 15 Newton, bevorzugt mindestens 20 Newton, aufweist und/oder dass die Aktivkohle eine Druck- und/oder Berstfestigkeit (Gewichtsbelastbarkeit)

PAC ET AL. EXHIBIT 1019
Page 2237

pro Aktivkohlekorn, insbesondere pro Aktivkohlekügelchen, im Bereich von 10 bis 50 Newton, insbesondere 10 bis 45 Newton, vorzugsweise 15 bis 40 Newton, aufweist.

37. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 36, dadurch gekennzeichnet, dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle selbsttragend ist und/oder in Form einer insbesondere losen Schüttung vorliegt.

38. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 37, dadurch gekennzeichnet, dass die stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle auf einem Trägermaterial aufgebracht ist, insbesondere wobei das Trägermaterial gasdurchlässig, insbesondere luftdurchlässig, ausgebildet ist und/oder insbesondere wobei das Trägermaterial eine Gasdurchlässigkeit, insbesondere Luftdurchlässigkeit, von mindestens 10 $l \cdot m^{-2} \cdot s^{-1}$, insbesondere mindestens 30 $l \cdot m^{-2} \cdot s^{-1}$, vorzugsweise mindestens 50 $l \cdot m^{-2} \cdot s^{-1}$, besonders bevorzugt mindestens 100 $l \cdot m^{-2} \cdot s^{-1}$, ganz besonders bevorzugt mindestens 500 $l \cdot m^{-2} \cdot s^{-1}$, und/oder eine Gasdurchlässigkeit, insbesondere Luftdurchlässigkeit, von bis zu 10.000 $l \cdot m^{-2} \cdot s^{-1}$, insbesondere bis zu 20.000 l·m–2·s^{-1}, bei einem Strömungswiderstand von 127 Pa aufweist.

39. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 38, dadurch gekennzeichnet, dass das Trägermaterial eine dreidimensionale Struktur aufweist, insbesondere wobei das Trägermaterial als vorzugsweise offenporiger Schaumstoff, besonders bevorzugt Polyurethanschaumstoff, ausgebildet ist.

40. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 38, dadurch gekennzeichnet, dass das Trägermaterial eine zweidimensionale und/oder flächige Struktur aufweist, insbesondere wobei das Trägermaterial als vorzugsweise textiles Flächengebilde ausgebildet ist.

41. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 40, dadurch gekennzeichnet, dass das Trägermaterial als ein textiles Flächengebilde, vorzugsweise ein luftdurchlässiges Textilmaterial, bevorzugt ein Gewebe, Gewirke, Gestricke, Gelege oder Textilverbundstoff, insbesondere Vlies (Nonwoven), ausgebildet ist und/oder dass das Trägermaterial ein Flächengewicht von 5 bis 1.000 g/m^2, insbesondere 10 bis 500 g/m^2, bevorzugt 25 bis 450 g/m^2, aufweist.

42. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach Anspruch 40 oder 41, dadurch gekennzeichnet, dass das Trägermaterial ein natürliche Fasern und/oder synthetische Fasern (Chemiefasern) enthaltendes oder hieraus bestehendes textiles Flächengebilde ist, insbesondere wobei die natürlichen Fasern aus der Gruppe von Wollfasern und Baumwollfasern (CO) ausgewählt sind und/oder insbesondere wobei die synthetischen Fasern ausgewählt sind aus der Gruppe von Polyestern (PES); Polyolefinen, insbesondere Polyethylen (PE) und/oder Polypropylen (PP); Polyvinylchloriden (CLF); Polyvinylidenchloriden (CLF); Acetaten (CA); Triacetaten (CTA); Polyacryl (PAN); Polyamiden (PA), insbesondere aromatischen, vorzugsweise flammfesten Polyamiden; Polyvinylalkoholen (PVAL); Polyurethanen; Polyvinylestern; (Meth-)-Acrylaten; Polymilchsäuren (PLA); Aktivkohle; sowie deren Mischungen.

43. Stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 38 bis 42, dadurch gekennzeichnet, dass die Aktivkohle an und/oder auf dem Trägermaterial fixiert ist, vorzugsweise mittels Verklebung, insbesondere mittels eines Klebstoffs oder infolge von Eigenklebrigkeit oder Eigenadhäsion.

44. Schutzmaterialien, insbesondere für den zivilen oder militärischen Bereich, insbesondere Schutzbekleidung, wie Schutzanzüge, Schutzhandschuhe, Schutzschuhwerk, Schutzsocken, Kopfschutzbekleidung und dergleichen, sowie Schutzabdeckungen, vorzugsweise alle vorgenannten Schutzmaterialien für den ABC-Einsatz, hergestellt unter Verwendung einer stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle nach einem der Ansprüche 30 bis 43 und/oder aufweisend eine stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 43.

45. Filter und Filtermaterialien, insbesondere zur Entfernung von Schad-, Geruchs- und Giftstoffen aller Art, insbesondere aus Luft- und/oder Gasströmen, wie ABC-Schutzmaskenfilter, Geruchsfilter, Flächenfilter, Luftfilter, insbesondere Filter für die Raumluftreinigung, adsorptionsfähige Trägerstrukturen und Filter für den medizinischen Bereich, hergestellt unter Verwendung einer stickstoffmodifizierten und/oder stickstofffunktionalisierten Aktivkohle nach einem der Ansprüche 30 bis 43 und/oder aufweisend eine stickstoffmodifizierte und/oder stickstofffunktionalisierte Aktivkohle nach einem der Ansprüche 30 bis 43.

Es folgen 10 Blatt Zeichnungen

PAC ET AL. EXHIBIT 1019
Page 2238

Anhängende Zeichnungen

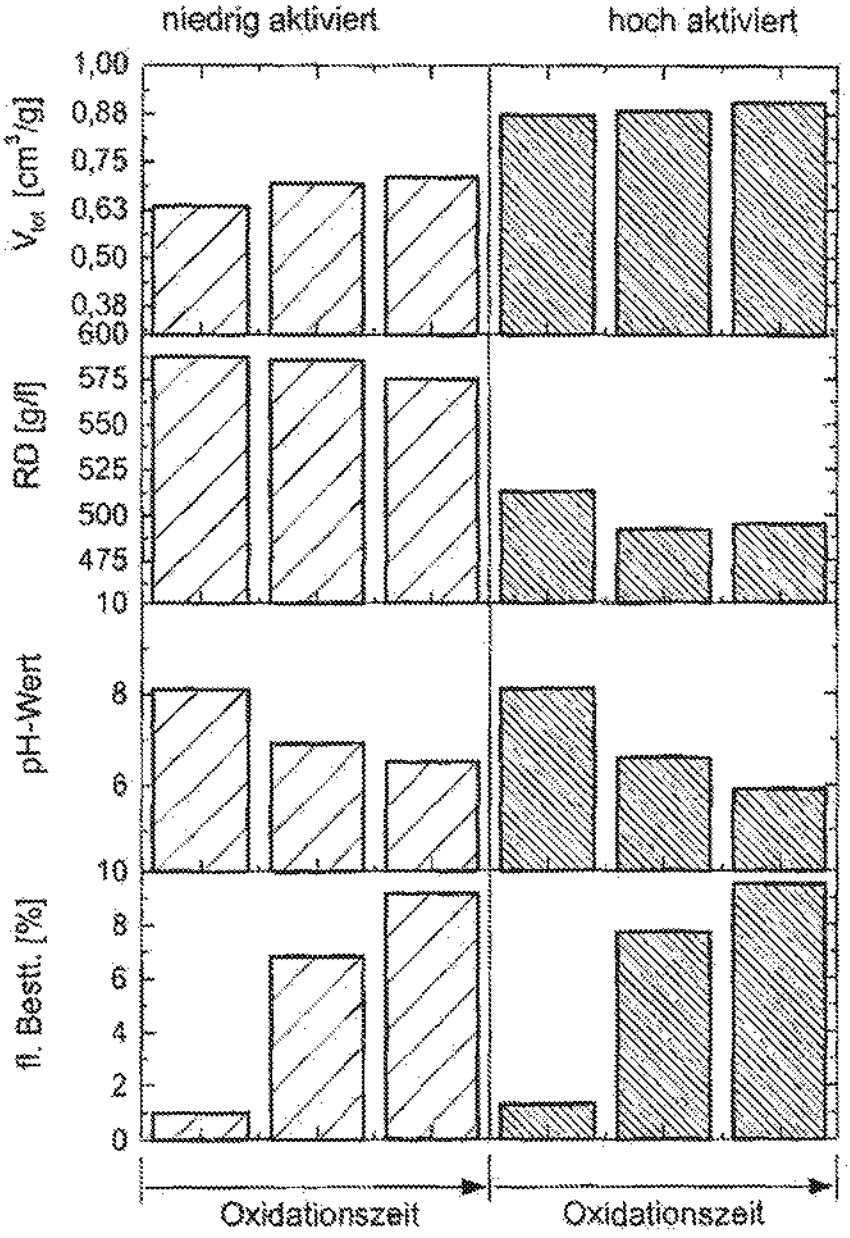


Fig. 1a

PAC ET AL. EXHIBIT 1019
Page 2239

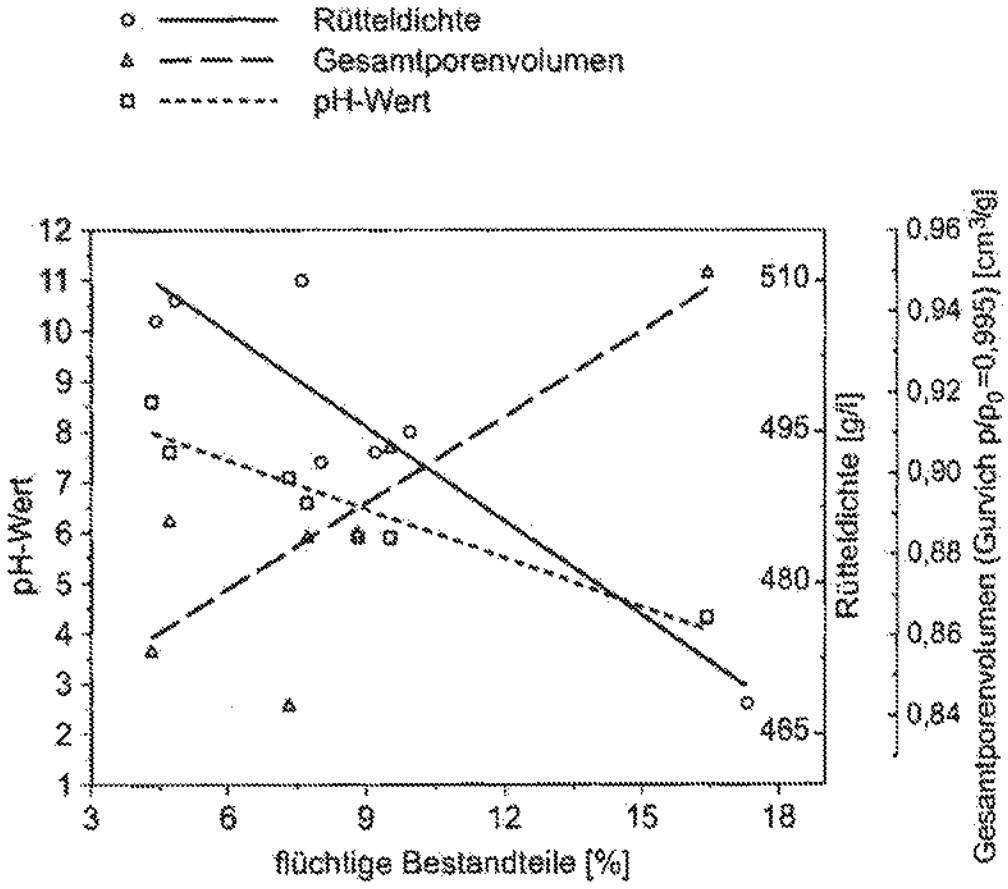

Rütteldichte
Gesamtporenvolumen
pH-Wert
pH-Wert
flüchtige Bestandteile [%]
Rütteldichte [g/l]
Gesamtporenvolumen (Gurvich p/ρ0=0,995) [cm³/g]
12
11
10
9
8
7
6
5
4
3
2
1
3
6
9
12
15
18
510
495
480
465
0,96
0,94
0,92
0,90
0,88
0,86
0,84

Fig. 1b

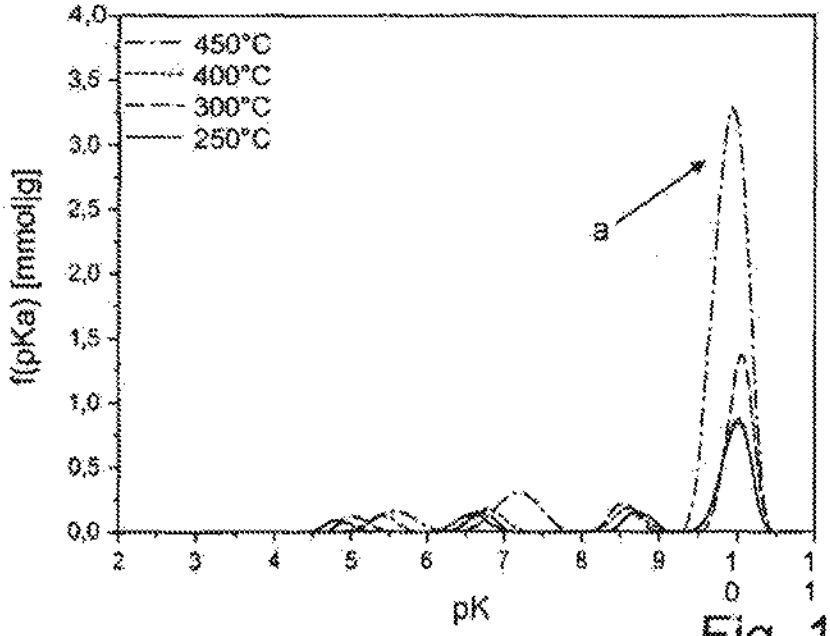


Fig. 1c

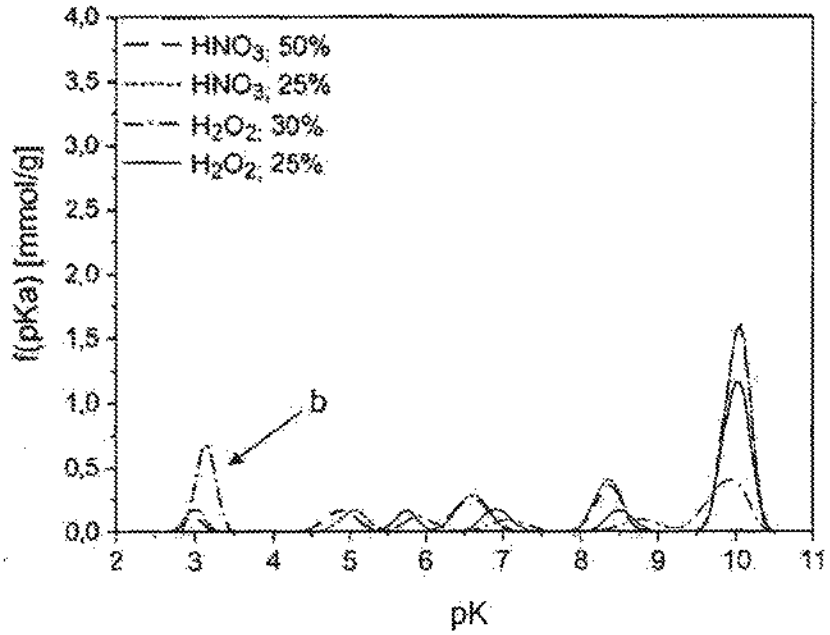


Fig. 1d

PAC ET AL. EXHIBIT 1019
Page 2241

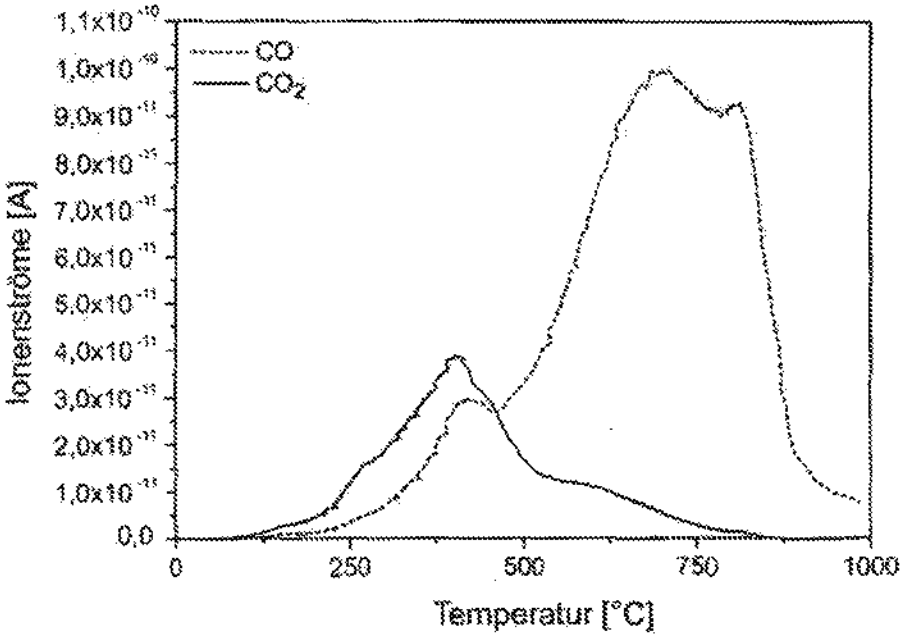


Fig. 1e

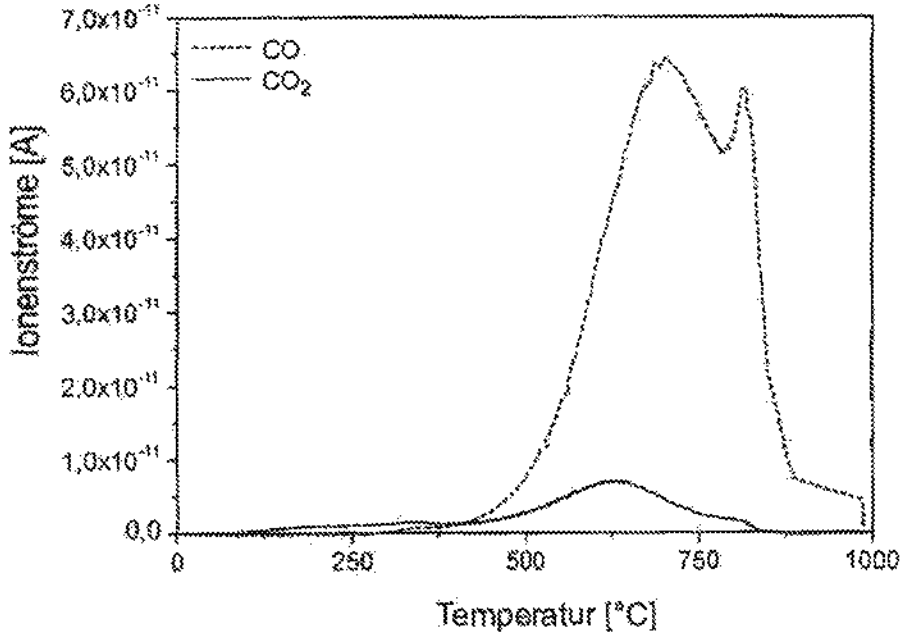


Fig. 1f

PAC ET AL. EXHIBIT 1019
Page 2242

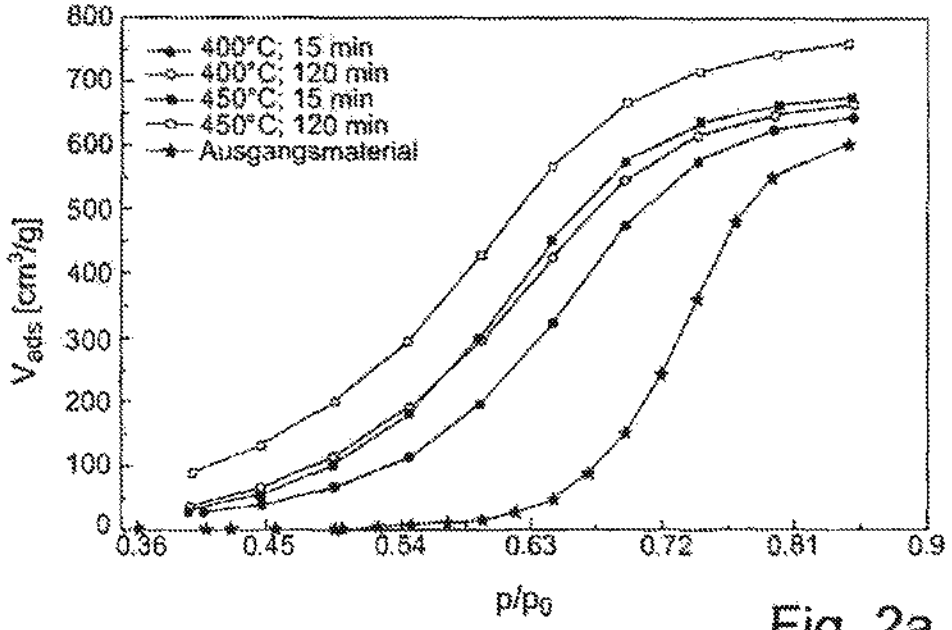


Fig. 2a

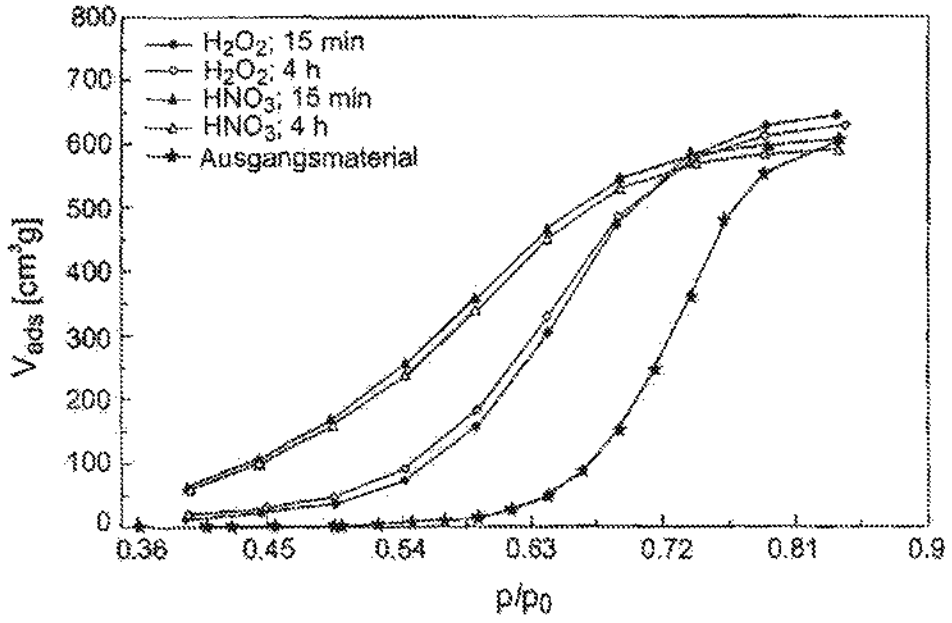


Fig. 2b

PAC ET AL. EXHIBIT 1019
Page 2243

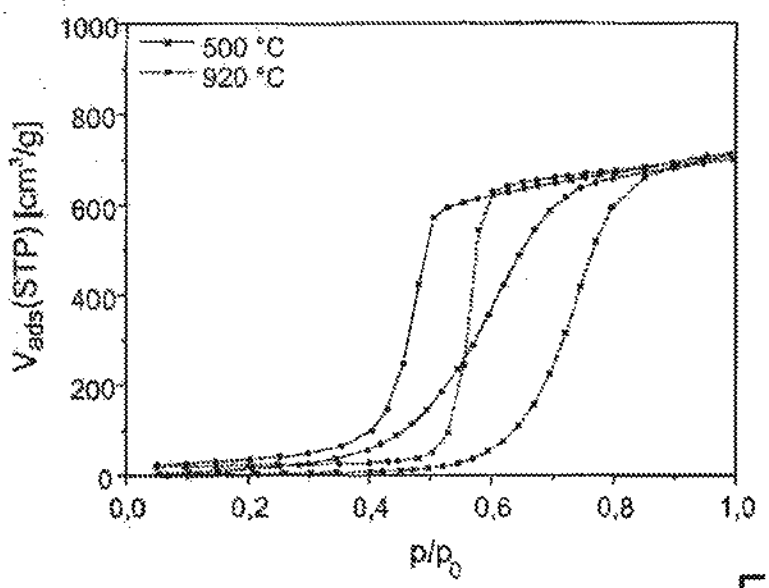


Fig. 3a

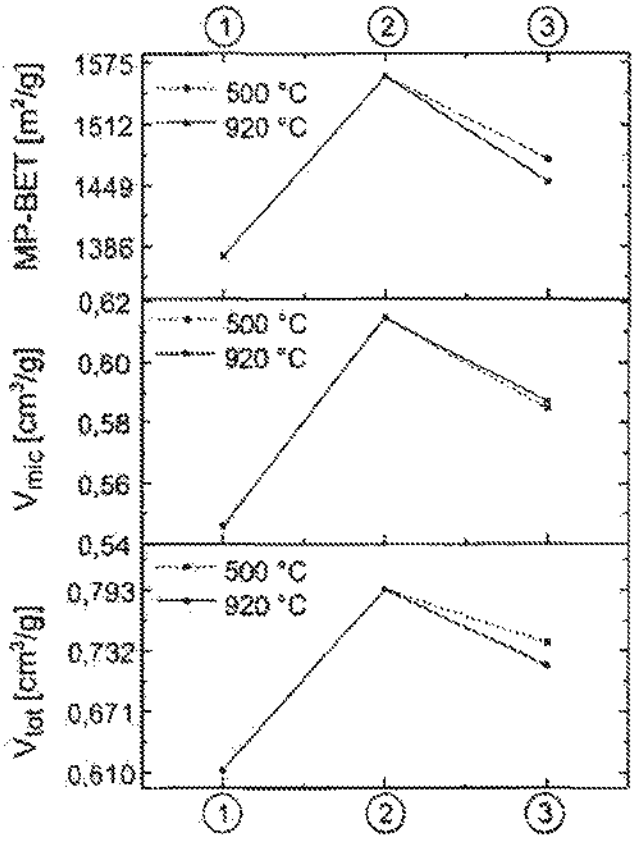


Fig. 3b

PAC ET AL. EXHIBIT 1019
Page 2244

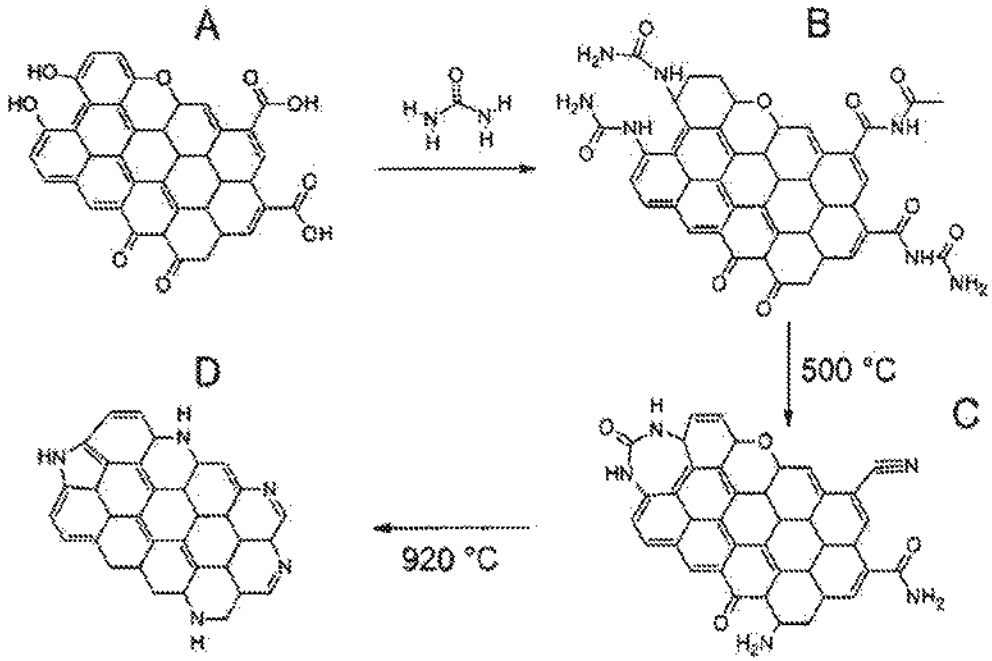

A
B
C
D
500 °C
920 °C

Fig. 4a

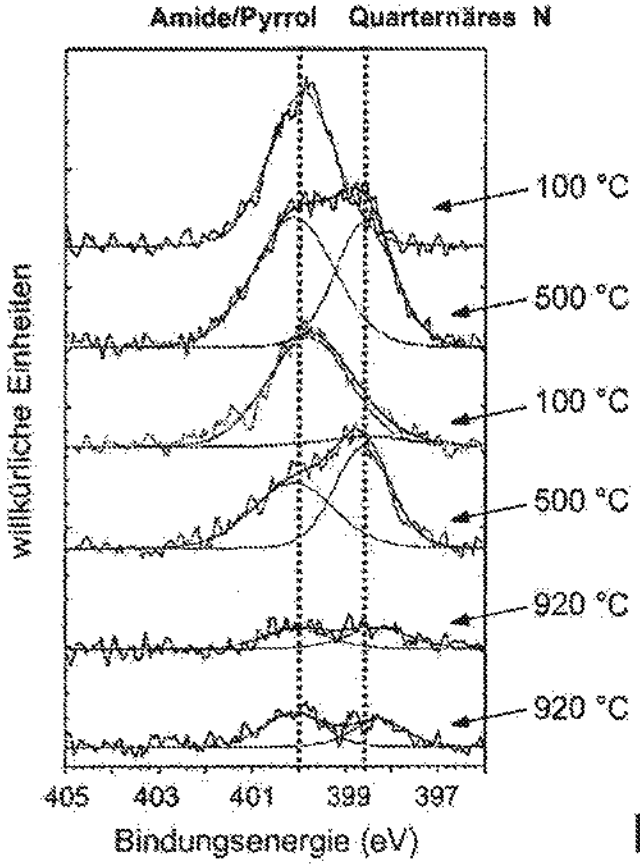

Amide/Pyrrol
Quarternäres N
willkürliche Einheiten
100 °C
500 °C
100 °C
500 °C
920 °C
920 °C
405
403
401
399
397
Bindungsenergie (eV)

Fig. 4b

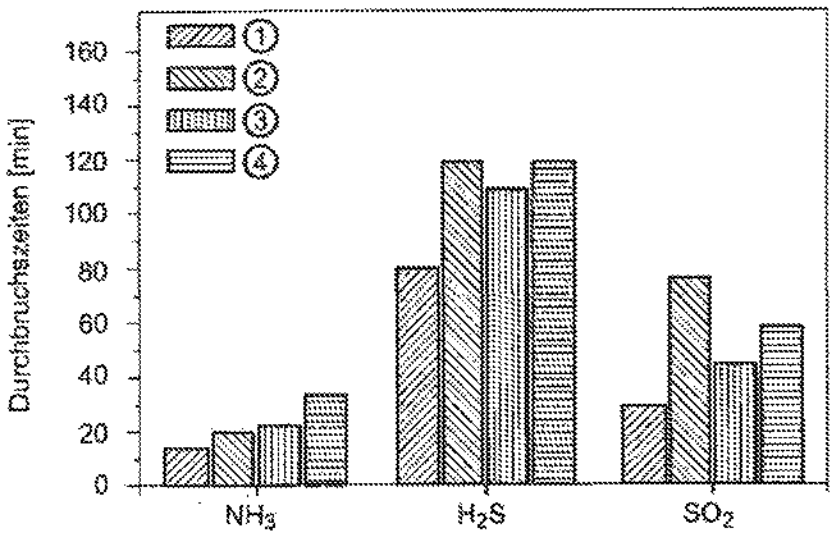


Fig. 5

PAC ET AL. EXHIBIT 1019
Page 2246

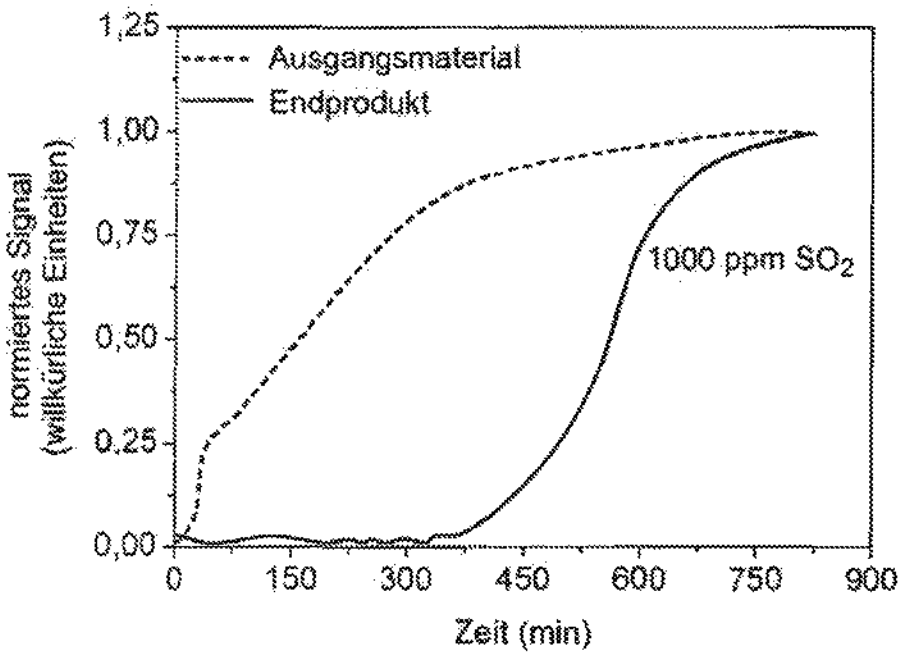


Fig. 6a

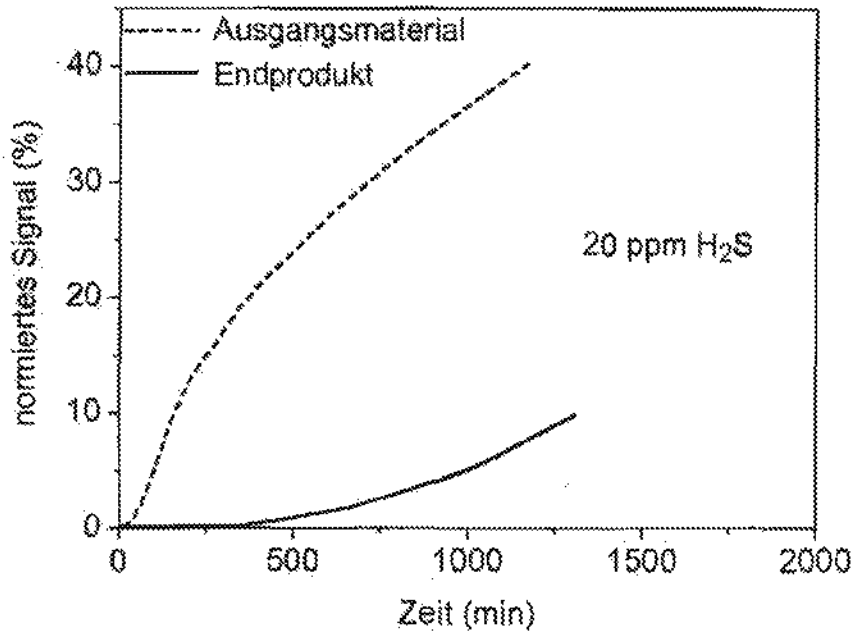


Fig. 6b

PAC ET AL. EXHIBIT 1019
Page 2247

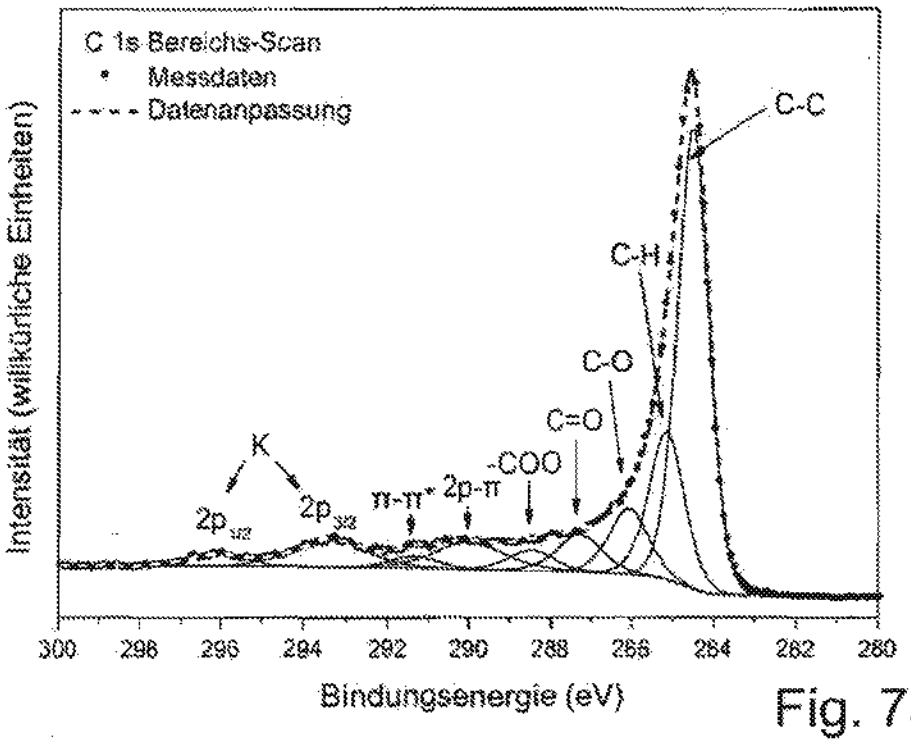


Fig. 7a

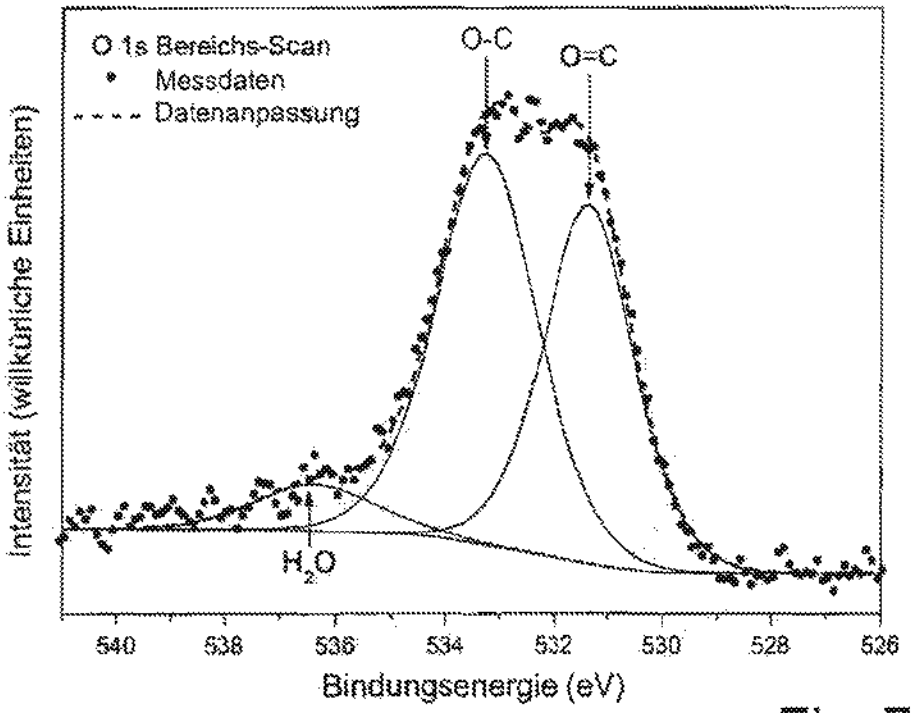


Fig. 7b

PAC ET AL. EXHIBIT 1019
Page 2248

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING TRANSMITTAL OF COPY OF INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (CHAPTER I OF THE PATENT COOPERATION TREATY)
(PCT Rule 44bis.1(c))

To:

MADDEN, Robert B.
Schwegman, Lundberg & Woessner
P.O. Box 2938
Minneapolis, Minnesota 55402
ETATS-UNIS D'AMERIQUE

SEP 21 2015

Date of mailing *(day/month/year)*	
17 September 2015 (17.09.2015)	
Applicant's or agent's file reference	IMPORTANT NOTICE
3338021WO1	

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2014/019916	03 March 2014 (03.03.2014)	06 March 2013 (06.03.2013)

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

The International Bureau transmits herewith a copy of the international preliminary report on patentability (Chapter I of the Patent Cooperation Treaty)

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Philippe Bécamel
Facsimile No. +41 22 338 82 70	e-mail: pt03.pct@wipo.int

Form PCT/IB/326 (January 2004)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference 3338021WO1	**FOR FURTHER ACTION**	See item 4 below
International application No. PCT/US2014/019916	International filing date *(day/month/year)* 03 March 2014 (03.03.2014)	Priority date *(day/month/year)* 06 March 2013 (06.03.2013)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION		

1. This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 *bis*.1(a).

2. This REPORT consists of a total of 13 sheets, including this cover sheet.

   In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.

3. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☒	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☒	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☒	Box No. VII	Certain defects in the international application
☒	Box No. VIII	Certain observations on the international application

4. The International Bureau will communicate this report to designated Offices in accordance with Rules 44*bis*.3(c) and 93*bis*.1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44*bis* .2).

	Date of issuance of this report 08 September 2015 (08.09.2015)
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. +41 22 338 82 70	Authorized officer Philippe Bécamel e-mail: pt03.pct@wipo.int

Form PCT/IB/373 (January 2004)

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43*bis*.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US2014/019916	03.03.2014	06.03.2013

International Patent Classification (IPC) or both national classification and IPC
INV. B01J20/20 B01D53/02 B01D53/10 B01J20/32 C01B31/08

Applicant
ENERGY & ENVIRONMENTAL RESEARCH CENTER FOUNDATION

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☒ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☒ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1*bis*(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:	Date of completion of this opinion	Authorized Officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	see form PCT/ISA/210	Pöhlmann, Robert Telephone No. +49 89 2399-2059

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:

   ☒ the international application in the language in which it was filed

   ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).

2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:

   a. (means)

      ☐ on paper

      ☐ in electronic form

   b. (time)

      ☐ in the international application as filed

      ☐ together with the international application in electronic form

      ☐ subsequently to this Authority for the purposes of search

4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

5. Additional comments:

Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non obvious), or to be industrially applicable have not been examined in respect of

☐ the entire international application

☒ claims Nos. 50-67(completely); 1-49(partially)

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international search *(specify)*:

☐ the description, claims or drawings *(indicate particular elements below)* or said claims Nos. are so unclear that no meaningful opinion could be formed *(specify)*:

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed *(specify)*:

☒ no international search report has been established for the whole application or for said claims Nos. 50-67(completely); 1-49(partially)

☐ a meaningful opinion could not be formed without the sequence listing; the applicant did not, within the prescribed time limit:

- ☐ furnish a sequence listing on paper complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ furnish a sequence listing in electronic form complying with the standard provided for in Annex C of the Administrative Instructions, and such listing was not available to the International Searching Authority in a form and manner acceptable to it.
- ☐ pay the required late furnishing fee for the furnishing of a sequence listing in response to an invitation under Rules 13*ter*.1(a) or (b).

☐ See Supplemental Box for further details

Box No. IV Lack of unity of invention

1. ☒ In response to the invitation (Form PCT/ISA/206) to pay additional fees, the applicant has, within the applicable time limit:

   ☐ paid additional fees

   ☐ paid additional fees under protest and, where applicable, the protest fee

   ☐ paid additional fees under protest but the applicable protest fee was not paid

   ☒ not paid additional fees

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose not to invite the applicant to pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rule 13.1, 13.2 and 13.3 is

   ☐ complied with

   ☒ not complied with for the following reasons:

   see separate sheet

4. Consequently, this report has been established in respect of the following parts of the international application:

   ☐ all parts.

   ☒ the parts relating to claims Nos. 1-49(partially)

Box No. V Reasoned statement under Rule 43*bis*.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	5-49(partially)
	No:	Claims	1-4(partially)
Inventive step (IS)	Yes:	Claims	10-15, 26-37, 40-47(all partially)
	No:	Claims	1-9, 16-25, 38, 39, 48, 49(all partially)
Industrial applicability (IA)	Yes:	Claims	1-49(partially)
	No:	Claims	

2. Citations and explanations

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item VIII

Certain observations on the international application

1 Clarity, Article 6 PCT)

1.1 General

The terms "about" (used in claims 4-6, 18-24, 34, 50, 58, 64), "substantially" (used in claims 5, 7-9, 50, 61-64, 67) and "core" (used in claims 3, 7, 18, 19, 51, 56, 61) are vague and unclear and leave the reader in doubt as to the meaning of the technical features to which they refer, thereby rendering the definition of the subject-matter of said claims unclear, Art. 6 PCT.

1.2 Claim 4

Claim 4 does not meet the requirements of Article 6 PCT because the matter for which protection is sought is not clearly defined. The claim attempts to define the subject-matter in terms of the result to be achieved (combines with at least 70 wt%), which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result (like but not limited to volume flows, distribution of sorbent, injection of sorbent, contact times, temperatures, other components in the mercury-containing gas).

1.3 Claim 7

It is unclear (Art. 6 PCT) how the nitrogen can be homogeneously distributed in the core of the particles and how at the same time there can be a concentration profile from the surface to the core (when referring to claim 3).

1.4 Claims 8, 9

Claims 8 and 9 do not meet the requirements of Art. 6 PCT because the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

1.5 Claim 18

It is unclear in claim 18 how a core of an activated carbon sorbent particle can comprise 99 wt% nitrogen (Art. 6 PCT). The core practically would consist of nitrogen only in this case.

1.6 Claim 20

It is unclear in claim 20 how a surface layer of an activated carbon sorbent particle can comprise 99 wt% nitrogen (Art. 6 PCT). The surface would consist of nitrogen only in this cas. Also it is unclear if the technical effect related to nitrogen being present at 0.001 wt% in the surface layer is still existing (Art.6 PCT).

1.7 Claim 22

The definition of the surface layer is unclear as a thickness of 99% of the radius of the particles is in fact the complete particle and not only a "surface layer" (Art. 6 PCT).

Re Item IV

2 **Lack of unity of invention**

Notwithstanding the objections under Article 6 PCT above, the application lacks unity within the meaning of Rule 13.1 PCT.

2.1 Reference is made to the following document:

D1 YUANJING ZHENG ET AL: "Review of technologies for mercury removal from flue gas from cement production processes",PROGRESS IN ENERGY AND COMBUSTION SCIENCE, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL,vol. 38, no. 5, 26 April 2012 (2012-04-26), pages 599-629, XP028415255,ISSN: 0360-1285, DOI: 10.1016/J.PECS.2012.05.001[retrieved on 2012-05-25]

D2 DE 20 2012 003747 U1 (BLUECHER GMBH [DE]) 15 November 2012 (2012-11-15)

2.2 **There are several groups of claims:**

- Group 1: Claims 1-49 (partially), in particular claims 2-9, 16-25, 38, 39, 48, 49
- Group 2: Claims 1-49 (partially), in particular claims 10-15, 26-37, 40, 41, 44, 45, claims 50-67 (completely)
- Group 3: Claims 1-49 (partially), in particular claims 42, 43
- Group 4: Claims 1-49 (partially), in particular claims claims 46, 47

2.3 **The common concept linking together the groups is the subject-matter of claim 1**. This common concept is not new over D1.

2.3.1 D1 discloses a method of reducing the mercury content in a mercury-containing gas (see page 600, para. 1.), the method comprising obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see page 615, para. 4.2.5.1 and page 616, left column, "...by impregnation of nitrogen-containing polymers or pitches ..."), contacting a pollutant-containing gas with the activated carbon sorbent to form a pollutant-sorbent composition (implicitly disclosed as for a sorbent based removal process the pollutant has to be contacted with the sorbent, the pollutant thereby always forms a pollutant-sorbent composition), and separating at least some of the pollutant-sorbent composition from the pollutant-containing gas, to give a separated gas (see page 622, figure 20).

Hence, D1 discloses all the features of claim 1.

2.3.2 D1 further discloses

- claim 3: the concentration of nitrogen in the surface layer of the sorbent particles to be higher than in a core of the particles (see page 615, right column, lines 1-4, nitrogenated function introduced on carbon surface, therefrom following a lower nitrogenous concentration in the core of the particles)

- claim 5, 6: the mercury-containing gas to comprise a sulfur(VI) concentration, like SO_3 (see page 616, right column, 2nd paragraph)

2.4 **The differentiating features are**

- Group 1: applying the method for gases with a sulfur(VI) concentration of more than 3 ppm by mole
- Group 2: obtaining or providing the activated carbon sorbent comprises promoting an unpromoted carbon sorbent and/or providing or obtaining the unpromoted carbon sorbent from a carbon precursor comprising nitrogen and/or the activated carbon sorbent comprising a stabilizing agent
- Group 3: adding an alkaline component into the pollutant containing gas
- Group 4: regenerating the activated carbon sorbent

2.5 **with following resulting technical effects:**

- Group 1: no surprising and unexpected technical effect distinguishable

- Group 2: further enhancement of the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: reduction of sulfuric compounds in the pollutant containing gas
- Group 4: saving financial means for sorbent

2.6 **Thus the problems solved may be regarded as**

- Group 1: finding an alternative mercury containing gas for which the method can be applied.
- Group 2: how to modify the method of D1 in order to further enhance the mercury sorption efficiency of the activated carbon sorbent comprising nitrogen
- Group 3: how to modify the method of D1 in order to reduce the sulfuric compounds in the pollutant containing gas
- Group 4: how to modify the method of D1 in order to save financial means for sorbent

2.7 **The special technical features (R. 13.2 PCT) are**

- Group 1: **no** special technical feature A as the alternative gas is considered to be obvious for the skilled person.
- Group 2: differentiating feature = special technical feature B as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 3: differentiating feature = special technical feature C as the feature is neither disclosed nor rendered obvious by D1 and therefore is considered to make a contribution over D1.
- Group 4: **no** special technical feature D as the regeneration and reuse of the sorbent is disclosed by D1 (see page 612, left column, paragraph before 4.2.2.3).

2.8 **Groups of (alleged) inventions**

The groups of technical features do not solve any common technical problem. Thus the groups of claims are neither linked by the same nor by corresponding special technical features and define different inventions not linked by a single general inventive concept (Rule 13.1 and 13.2 PCT) and therefore **the requirement for unity of invention referred to in Rule 13 PCT is not fulfilled.**

2.9 **Consequence**

A search has been performed for the invention first mentioned in the claims, here the subject-matter of the claims forming group 1. Correspondingly, in the following this written opinion is restricted to group 1.

Group 1 : Claims 1-9, 16-25, 38, 39, 48, 49 (partially)

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

3 Novelty Claim 1

3.1 As already shown under point 2.3.1 above the subject-matter of claim 1 is not new (Article 33(2) PCT).

4 Inventive Step Claim 1

Besides D1, which is considered to be the closest prior art to the subject-matter of claim 1, also D2 could be regarded as the closest prior art the subject-matter of claim 1.

4.1.1 D2 discloses

A method of reducing the pollutant content in a pollutant-containing gas (see §0142 and 0143), the method comprising:

obtaining or providing an activated carbon sorbent comprising activated carbon sorbent particles comprising nitrogen in a surface layer of the sorbent particles (see claim 1);

4.1.2 The subject-matter of claim 1 therefore differs from this known D2 in that

a pollutant-containing gas is contacted with the activated carbon sorbent, to form a pollutant-sorbent composition; and in that at least some of the pollutant-sorbent composition is separated from the pollutant-containing gas, to give a separated gas.

4.1.3 There is no unexpected technical effect related to that difference.

4.1.4 The problem to be solved by the present invention may therefore be regarded as how to to apply the method of D2 for reducing the pollutant content in a pollutant-containing gas.

4.1.5 The solution proposed in claim 1 of the present application cannot be considered to involve an inventive step (Article 33(3) PCT) for the following reasons:

It is common general knowledge for the skilled person to contact the sorbent with the gas to form a pollutant-sorbent composition and to separate the pollutant-sorbent composition from the gas to give a separated gas. Also, amongst many other documents he finds in D1 an indication (see cited passages) with which he would contact the sorbent with the gas, thereby forming a pollutant sorbent composition and separate this composition from the gas to give a separated gas, thereby arriving at the subject-matter of claim 1 without being inventive.

5 Dependent claims

Dependent claims 2-9, 16-25, 38, 39, 48, 49 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step.

5.1 Claims 2, 3

The subject-matter of said claims is neither new (see points 2.3.1 and 2.3.2 above), nor inventive (see D2, claim 1 and §0143, mercury being an obvious toxic substance whose removal from gas streams with activated carbon is widely known in industry).

5.2 Claims 5, 6

D1 discloses a sulfur(VI) concentration in the mercury-containing gas (see 2.3.2 above) and the claimed ranges for said concentration are considered to be merely an arbitrary selection out of a variety of possible mercury containing gases without showing an unexpected technical effect. The properties of the activated carbon sorbent of D1 are considered to achieve the results claimed in claim 5 with regard to corresponding activated carbon sorbents.

5.3 Claims 16, 17, 38, 39, 48, 49

It is well-known in the art to add the sorbent into the mercury-containing gas and to remove it after a certain distance by various means like bag houses, electrostatic precipitators, cyclones or the like. As well, it is common general knowledge to contact the gas with the sorbent in a fixed bed, a dry or aqueous scrubber, a filter or a moving bed.

Claim 19, 21

D2 discloses a wide variety of possible nitrogen concentrations of the activated carbon (see claim 25), which is also considered to be applicable either to the surface and/or to the core of carbon particles. Therefore, the claimed ranges are not inventive.

Claim 24, 25

The claimed range of particle diameters is considered an arbitrary selection and activated carbon particles in this range are known to the skilled person (see for reference D2, §0106). Furthermore, every surface is considered to be continuous and therefore also a surface layer.

Re Item VII

Certain defects in the international application

6 The requirements of Rule 6.3(b) PCT (two-part form of independent claims) and Rule 5.1(a)(ii) and (iii) PCT (acknowledgement of prior art D1) are not met.

Electronic Acknowledgement Receipt

EFS ID:	32669333
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jordan Rivard Golomb/Jamie Johnson
Filer Authorized By:	Jordan Rivard Golomb
Attorney Docket Number:	4820.001US9
Receipt Date:	18-MAY-2018
Filing Date:	
Time Stamp:	19:17:25
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Foreign Reference	0019_de_202012003747u1.pdf	17736678 a8ac82dab8cca6bb0e59385100faee0e26520ff8	no	94

Warnings:

Information:					
2	Non Patent Literature	0153_3338016us2_rerr_031616.pdf	704560 622a2d6f91316889c00637655baf2a13f49160b3	no	5
Warnings:					
Information:					
3	Non Patent Literature	0154_4820001us7_adar_021218.pdf	1084770 3deb780868280eccbb9ac6485185d2f0e63d7bc1	no	8
Warnings:					
Information:					
4	Non Patent Literature	0155_4820001us7_exir_030518.pdf	380728 8a69f63e35989b9c6b943677fe31957740272772	no	3
Warnings:					
Information:					
5	Non Patent Literature	0156_4820001us7_foar_120617.pdf	1121711 8923381e13467a7a4de360ab8733d3eb77851041	no	9
Warnings:					
Information:					
6	Non Patent Literature	0157_4820001us7_oarn_070617.pdf	887769 653864e3edab9ff2093212c29c0a2a5e441d652d	no	7
Warnings:					
Information:					
7	Non Patent Literature	0166_4820005us1_adar_04242018.pdf	499388 b89373bf64f7ece3439a194a58b30d21b92789c9	no	3
Warnings:					
Information:					
8	Non Patent Literature	0167_4820005us1_foar_021518.pdf	1470658 5f7c9d4650588bd546d67c70f68958465650859	no	13
Warnings:					
Information:					

9	Non Patent Literature	0168_4820005us1_oarn_092717.pdf	1936500 347021e2600464042c89a8d5e1e22331376 9f4b4	no	17
Warnings:					
Information:					
10	Non Patent Literature	0173_4820003us2_oarn_022118.pdf	1669971 bad0b54720cf47f7fa8e175b7ee0e7197805 3716	no	15
Warnings:					
Information:					
11	Non Patent Literature	0176_3338021wo1_p326_091715.pdf	1879833 2cb837ba8523d410171dfc08d714497b2aa a902a	no	14
Warnings:					
Information:					
12	Non Patent Literature	0191_4820006ca1_oarmisc_083117.pdf	364865 0d2d1a2fb794e59dd90ad3cf2b891a8f1f1e cbf3	no	4
Warnings:					
Information:					
13	Non Patent Literature	0193_3338016ca1_oarmisc_122216.pdf	1805782 e3ba06c1df6432974ef485fab6855870a0b9 4974	no	5
Warnings:					
Information:					
14	Non Patent Literature	0194_2871422aarmisc_022718_20180226.pdf	713571 25f4fb8bdf83042cc6052a75ef4c420b2548 dcd3	no	53
Warnings:					
Information:					
15	Non Patent Literature	0195_2871422aarmisc20170621_response_as_filed_00406200_4220170621.pdf	2381254 b2ba89be1fa4f2883fecf2bf3afe183873845 610	no	41
Warnings:					
Information:					

16	Non Patent Literature	0198_cn_response_1_20_12.pdf	163517 51bfdba965131660ac37a51da0694c8added87d4	no	10
Warnings:					
Information:					
17	Non Patent Literature	0203_4820003cn1_oarmisc_071217.pdf	697630 c2b12372892bc938c9a9fd2fbb350db10d1b6609	no	8
Warnings:					
Information:					
18	Non Patent Literature	0205_3338021cn1_oarmisc_122316.pdf	3209592 277daba330f8d9b4d026685b9caec84816a4d171	no	39
Warnings:					
Information:					
19	Non Patent Literature	0209_norit_darco_fgd_product_sheet.pdf	6905 cd5aa2be10f7b669ae20249015584 53bd14ad709	no	2
Warnings:					
Information:					
20	Non Patent Literature	0250_4820006ep1_oarmisc_042417.pdf	655151 afec2b28863ed88e1aa0b580720f4be3f153ae97	no	8
Warnings:					
Information:					
		Total Files Size (in bytes):	39370833		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s): Edwin S. Olson et al.	Examiner: UNKNOWN
Serial No.: 15/974,343	Group Art Unit: UNKNOWN
Filed: 5/8/2018	Docket: 4820.001US9
Customer No.: 21186	Confirmation No.: UNKNOWN

Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

PRELIMINARY AMENDMENT

MS Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Prior to taking up this application for examination, please enter the following amendments:

IN THE CLAIMS

1. (Currently Amended) A method for separating mercury from a mercury-containing gas, the method comprising:

combusting a mixture of coal and an additive that has been added to the coal, the additive comprising a bromide compound, to form the mercury-containing gas, ~~wherein the additive is chosen from halides, halogens, salts thereof, and combinations thereof~~;

adding a particulate sorbent material comprising activated carbon into the mercury-containing gas;

promoting at least a portion of the sorbent material by chemically reacting the sorbent material with ~~the additive~~Br_2, HBr, Br^-, or a combination thereof, in-flight ~~the mercury-containing gas~~, to form a promoted sorbent material;

chemically reacting mercury in the mercury-containing gas with the promoted sorbent material, to form a mercury-sorbent; and

separating the mercury-sorbent from the mercury-containing gas.

2. (Original) The method of claim 1, further comprising mixing the additive and the coal before combusting the coal.

3. (Original) The method of claim 2, wherein the additive mixed with the coal is in a liquid.

4. (Original) The method of claim 3, wherein the liquid is a hydrocarbon, a chlorinated hydrocarbon, supercritical carbon dioxide, water, salt solution, or a combination thereof.

5. (Original) The method of claim 1, wherein the promoted sorbent material comprises active sites, wherein the active sites comprise halide anions bound to the activated carbon.

6. (Original) The method of claim 1, wherein the promoted sorbent material comprises active sites, wherein the active sites comprise carbocations bound to halide anions.

7. (Original) The method of claim 1, wherein chemically reacting the sorbent material with the additive in the mercury-containing gas comprises chemically reacting carbene species edge sites in the activated carbon with the additive.

8. (Original) The method of claim 1, wherein carbocations in the activated carbon of the mercury-sorbent accept electrons from mercury atoms of the mercury-sorbent.

9. (Original) The method of claim 1, wherein the additive is substantially in vapor form in the mercury-containing gas.

10. (Currently Amended) The method of claim 1, wherein the additive ~~is chosen from Cl_2, HCl, sodium chloride, calcium chloride, and a combination thereof~~comprises Ca, Na, or a combination thereof.

11-13. (Canceled)

14. (Original) The method of claim 1, wherein the activated carbon is chosen from powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, and combinations thereof.

15-20. (Canceled)

21. (New) The method of claim 1, wherein the coal and the additive are mixed at a location upstream of a combustion furnace where combustion occurs.

22. (New) The method of claim 1, comprising separating greater than 70 wt% of the mercury from the mercury-containing gas.

23. (New) The method of claim 1, comprising separating greater than 70 wt% of the mercury from the mercury-containing gas on the sorbent.

24. (New) The method of claim 1, wherein the sorbent material has a composition comprising from about 1 to about 30 grams of additive per 100 grams of activated carbon.

25. (New) The method of claim 1, wherein the method is a method for reducing mercury in the mercury-containing gas to a desired level, wherein separating the mercury-sorbent from the mercury-containing gas forms a cleaned gas, the method further comprising:

monitoring the mercury content of the cleaned gas; and

controlling, in response to the monitored mercury content of the cleaned gas, an injection rate of injecting the sorbent into the mercury-containing gas, the sorbent composition, or a combination thereof, so that the mercury content of the cleaned gas is maintained at or below the desired level.

REMARKS

Claims 1 and 10 are amended, claims 11-13 and 15-20 are canceled, and claims 21-25 are added; as a result, claims 1-10, 14, 21-25 are now pending in this application.

Claim 1 is amended to recite "…an additive that has been added to the coal…." Support can be found in the application as filed at Figure 11.

Claim 1 is amended to recite "…the additive comprising a bromide compound…." Support can be found in the application as filed at page 50 line 10.

Claim 1 is amended to recite "…chemically reacting the sorbent material with ~~the additive~~Br_2, HBr, Br^-, or a combination thereof…." Support can be found in the application as filed at page 18 lines 25-26 and at page 19 lines 2-7.

Claim 1 is amended to recite that the sorbent material is reacted with the Br_2, HBr, Br^-, or combination thereof "…in-flight ~~the mercury-containing gas~~, to form a promoted sorbent material…." Support can be found in the application as filed at page 20 lines 9 to 19 and FIG. 11.

Claim 10 is amended to recite "…wherein the additive ~~is chosen from Cl_2, HCl, sodium chloride, calcium chloride, and a combination thereof~~comprises Ca, Na, or a combination thereof." Support can be found in the application as filed at page 42, lines 10-11.

No new matter is added via the amendments or new claims herein.

CONCLUSION

Applicant respectfully submits that the claims are in condition for allowance and notification to that effect is earnestly requested. The Examiner is invited to telephone Applicant's attorney at (612) 349-9580 to facilitate prosecution of this application.

If necessary, please charge any additional fees or credit overpayment to Deposit Account No. 19-0743.

Respectfully Submitted,

SCHWEGMAN, LUNDBERG & WOESSNER, P.A.
P.O. Box 2938
Minneapolis, MN 55402
(612) 349-9580

Date May 15, 2018 By /Nicholas P. Lanzatella/
Nicholas P. Lanzatella
Reg. No. 63,803

Electronic Acknowledgement Receipt

EFS ID:	32628572
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jose M. Nunez/Megan Reed
Filer Authorized By:	Jose M. Nunez
Attorney Docket Number:	4820.001US9
Receipt Date:	15-MAY-2018
Filing Date:	
Time Stamp:	14:44:37
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		SIGNED_4820_001US9_Prelim Amdmt.pdf	116961 724cb8457ae8f49b787eb1f867404686297fe6a6	yes	8

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Transmittal Letter	1	1
	Preliminary Amendment	2	2
	Claims	3	6
	Applicant Arguments/Remarks Made in an Amendment	7	8
Warnings:			
Information:			
	Total Files Size (in bytes):	116961	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s): Edwin S. Olson et al.
Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

Docket No.:	4820.001US9	Serial No.:	15/974,343
Filed:	May 8, 2018	Due Date:	May 25, 2018
Examiner:	Unknown	Group Art Unit:	Unknown
Customer No.:	21186	Confirmation No.:	1072

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

We are transmitting herewith the following attached items (as indicated with an "X"):

X Preliminary Amendment (7 pgs.)

If not provided for in a separate paper filed herewith, please consider this a PETITION FOR EXTENSION OF TIME for sufficient number of months to enter these papers and please charge any additional fees or credit overpayment to Deposit Account No. 19-0743. If applicable, any papers or fees supplied herewith are considered to be timely filed pursuant to 37 C.F.R. § 1.7(a), the response period falling on a Federal Holiday, Saturday or Sunday being extended to the next succeeding business day.

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
Customer No.: 21186

By /Nicholas P. Lanzatella/
Nicholas P. Lanzatella
Reg. No. 63,803

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s): Edwin S. Olson et al.
Title: SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
Attorney Docket No.: 4820.001US9
Customer No.: 21186

PATENT APPLICATION TRANSMITTAL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

We are transmitting herewith the following attached items and information (as indicated with an "X"):

X **CONTINUATION under 37 CFR 1.53(b) of prior Patent Application No. comprising:**
- X Application Data Sheet (8 pgs).
- X Specification (61 pgs, including claims numbered 1 through 20 and a 1 page Abstract).
- X Formal Drawing(s) (11 sheets).
- X Copy of signed Declaration (3 pgs) from prior application.
- X Certification and Request for Prioritized Examination (Track 1) (1 pg), including authorization to charge Deposit Account 19-0743 in the amount of $4000.00 for the Prioritized Examination (Track 1) filing fee as set forth in 37 C.F.R. § 1.17(c); and Authorization to charge Deposit Account 19-0743 for the Processing Fee (Track 1) set forth in 37 C.F.R. § 1.17(i) in the amount of $140.00.
- X **Authorization to charge Deposit Account 19-0743 in the amount of $5,860.00**

The filing fee has been calculated below as follows:

	No. Filed	No. Extra	Rate	Fee
TOTAL CLAIMS	20- 20	0	x $100.00 =	$0.00
INDEPENDENT CLAIMS	2 - 3	0	x $460.00 =	$0.00
[]MULTIPLE DEPENDENT CLAIMS PRESENTED				$0.00
BASIC FEE				$300.00
SEARCH FEE				$660.00
EXAMINATION FEE				$760.00
PRIORITIZED EXAMINATION (TRACK 1) FILING FEE				$4,000.00
PROCESSING FEE (TRACK 1)				$140.00
	No. of pages (75% for e-filing)	Extra sets of 50 pages	Rate	
APPLICATION SIZE FEE	(54 - 100) / 50	0	$400.00	$0.00
TOTAL				$5,860.00

Please charge any additional required fees or credit overpayment to Deposit Account No. 19-0743. If applicable, any papers or fees supplied herewith are considered to be timely filed pursuant to 37 C.F.R. § 1.7(a), the response period falling on a Federal Holiday, Saturday or Sunday being extended to the next succeeding business day.

SCHWEGMAN LUNDBERG & WOESSNER, P.A.
Customer Number: 21186

By: /Ryan J. Connell/
Ryan J. Connell
Reg. No. 74,611

Date of Deposit: May 8, 2018
This paper or fee is being filed on the date indicated above using the USPTO's electronic filing system EFS-Web, and is addressed to The Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

CERTIFICATION AND REQUEST FOR PRIORITIZED EXAMINATION UNDER 37 CFR 1.102(e)

(Page 1 of 1)

First Named Inventor:	Edwin S. Olson	Nonprovisional Application Number (if known):	Unknown
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	Docket No.:	4820.001US9

APPLICANT HEREBY CERTIFIES THE FOLLOWING AND REQUESTS PRIORITIZED EXAMINATION FOR THE ABOVE-IDENTIFIED APPLICATION.

1. The processing fee set forth in 37 CFR 1.17(i)(1) and the prioritized examination fee set forth in 37 CFR 1.17(c) have been filed with the request. The publication fee requirement is met because that fee, set forth in 37 CFR 1.18(d), is currently $0. The basic filing fee, search fee, and examination fee are filed with the request or have been already been paid. I understand that any required excess claims fees or application size fee must be paid for the application.

2. I understand that the application may not contain, or be amended to contain, more than four independent claims, more than thirty total claims, or any multiple dependent claims, and that any request for an extension of time will cause an outstanding Track I request to be dismissed.

3. **Original Application(Track One) – Prioritized Examination under § 1.102(e)(1)**

   i. (a) The application is an original nonprovisional utility application filed under 35 U.S.C. 111(a). This certification and request is being filed with the utility application via EFS-Web.

   ---OR---

   (b) The application is an original nonprovisional plant application filed under 35 U.S.C. 111(a). This certification and request is being filed with the plant application in paper.

   ii. An executed inventor's oath or declaration under 37 CFR 1.63 or 37 CFR 1.64 for each inventor, **or** the application data sheet meeting the conditions specified in 37 CFR 1.53(f)(3)(i) is filed with the application.

Signature /Ryan J. Connell/	Date 5/8/18
Name (Print/Typed) Ryan J. Connell	Practitioner Registration Number: 74,611

Note: *This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4(d) for signature requirements and certifications. Submit multiple forms if more than one signature is required, see below*.*

*Total of 1 forms are submitted.

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2:

☐ **Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)**

Inventor Information:

Inventor 1: Edwin S. Olson

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Edwin	S.	Olson	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	Grand Forks	State/Province	ND	Country of Residence	United States of America

Mailing Address of Inventor:

Address 1	223 Circle Hills Drive		
Address 2			
City	Grand Forks	State/Province	ND
Postal Code	58201	Country	United States of America

Inventor 2: Michael J. Holmes

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Michael	J.	Holmes	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	Thompson	State/Province	ND	Country of Residence	United States of America

Mailing Address of Inventor:

Address 1	614 6th Avenue Northeast		
Address 2			
City	Thompson	State/Province	ND
Postal Code	58278	Country	United States of America

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Inventor 3: John H. Pavlish

Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	John	H.	Pavlish	

Residence Information (Select One) ☒ US Residency ☐ Non US Residency ☐ Active US Military Service

City	East Grand Forks	State/Province	MN	Country of Residence	United States of America

Mailing Address of Inventor:

Address 1	42204 210th Street SW		
Address 2			
City	East Grand Forks	State/Province	MN
Postal Code	56721	Country	United States of America

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ An Address is being provided for the correspondence Information of this application.

Customer Number	21186
Email Address	request@slwip.com

Application Information:

Title of the Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY		
Attorney Docket Number	4820.001US9	Small Entity Status Claimed	☐
Application Type	Non-Provisional		
Subject Matter	Utility		
Suggested Class (if any)		Sub Class (if any)	
Suggested Technology Center (if any)			
Total Number of Drawing Sheets (if any)	11	Suggested Figure for Publication (if any)	

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Filing By Reference:

Only complete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). **Do not** complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country Publication

Publication Information:

☐ **Request Early Publication (Fee required at time of Request 37 CFR 1.219)**

☐ **Request Not to Publish. I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application has not and will not be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.**

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32). Entereither Customer Number or complete the Representative Name section below. If bothsections are completed the Customer Number will be used for the Representative Information during processing.

Please Select One:	☒ Customer	☐ US Patent Practitioner	☐ Limited Recognition (37 CFR 11.9)
Customer Number	21186		

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78(a)(2) or CFR 1.78(a)(4), and need not otherwise be made part of the specification.

Prior Application Status	Pending		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
This Application	continuation of	15/951,970	2018-04-12
Prior Application Status	Pending		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
15/951,970	continuation of	14/712,558	2015-05-14
Prior Application Status	Pending		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
14/712,558	continuation of	14/318,270	2014-06-14
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
14/318,270	continuation of	13/966,768	2013-08-14
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
13/966,768	continuation of	13/427,665	2012-03-22
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
13/427,665	continuation of	12/419,219	2009-04-06
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
12/419,219	continuation of	12/201,595	2008-08-29
Prior Application Status	Patented		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
12/201,595	continuation of	11/209,163	2005-08-22
Prior Application Status	Expired		
Application Number	**Continuity Type**	**Prior Application Number**	**Filing or 371(c) Date (YYYY-MM-DD)**
11/209,163	Claims benefit of provisional	60/605,640	2004-08-30

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Foreign Priority Information:

This section allows for the applicant to claim priority to a foreign application. Providing this information in the application data sheet constitutes the claim for priority as required by 35 U.S.C. 119(b) and 37 CFR 1.55(d). When priority is claimed to a foreign application that is eligible for retrieval under the priority document exchange program (PDX)i the information will be used by the Office to automatically attempt retrieval pursuant to 37 CFR 1.55(h)(1) and (2). Under the POX program, applicant bears the ultimate responsibility for ensuring that a copy of the foreign application is received by the Office from the participating foreign intellectual property office, or a certified copy of the foreign priority application is filed, within the time period specified in 37 CFR 1.55(g)(1).

Application Number	Country	Parent Filing Date (YYYY-MM-DD)	Access Code (if applicable)

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Authorization or Opt-Out of Authorization to Permit Access:

When this Application Data Sheet is properly signed and filed with the application, applicant has provided written authority to permit a participating foreign intellectual property (IP) office access to the instant application-as-filed (see paragraph A in subsection 1 below) and the European Patent Office (EPO) access to any search results from the instant application (see paragraph B in subsection 1 below).

Should applicant choose not to provide an authorization identified in subsection 1 below, applicant must opt-out of the authorization by checking the corresponding box A or B or both in subsection 2 below.

NOTE: This section of the Application Data Sheet is ONLY reviewed and processed with the INITIAL filing of an application. After the initial filing of an application, an Application Data Sheet cannot be used to provide or rescind authorization for access by a foreign IP office(s). Instead, Form PTO/SB/39 or PTO/SB/69 must be used as appropriate.

1. Authorization to Permit Access by a Foreign Intellectual Property Office(s)

A. Priority Document Exchange (PDX) - Unless box A in subsection 2 (opt-out of authorization) is checked, the undersigned hereby grants the USPTO authority to provide the European Patent Office (EPO), the Japan Patent Office (JPO), the Korean Intellectual Property Office (KIPO), the State Intellectual Property Office of the People's Republic of China (SIPO), the World Intellectual Property Organization (WIPO), and any other foreign intellectual property office participating with the USPTO in a bilateral or multilateral priority document exchange agreement in which a foreign application claiming priority to the instant patent application is filed, access to: (1) the instant patent application-as-filed and its related bibliographic data, (2) any foreign or domestic application to which priority or benefit is claimed by the instant application and its related bibliographic data, and (3) the date of filing of this Authorization. See 37 CFR 1.14(h)(1).

B. Search Results from U.S. Application to EPO - Unless box B in subsection 2 (opt-out of authorization) is checked, the undersigned hereby grants the USPTO authority to provide the EPO access to the bibliographic data and search results from the instant patent application when a European patent application claiming priority to the instant patent application is filed. See 37 CFR 1.14(h)(2).

The applicant is reminded that the EPO's Rule 141(1) EPC (European Patent Convention) requires applicants to submit a copy of search results from the instant application without delay in a European patent application that claims priority to the instant application.

2. Opt-Out of Authorizations to Permit Access by a Foreign Intellectual Property Office(s)

☐ **A. Applicant DOES NOT authorize the USPTO to permit a participating foreign IP office access to the instant application-as-filed. If this box is checked, the USPTO will not be providing a participating foreign IP office with any documents and information identified in subsection 1A above.**

☐ **B. Applicant DOES NOT authorize the USPTO to transmit to the EPO any search results from the instant patent application. If this box is checked, the USPTO will not be providing the EPO with search results from the instant application.**

NOTE: Once the application has published or is otherwise publicly available, the USPTO may provide access to the application in accordance with 37 CFR 1.14.

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Applicant Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Applicant: Midwest Energy Emissions Corp

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

☒ Assignee	☐ Legal Representative under 35 U.S.C. 117	☐ Joint Inventor
☐ Person to whom the inventor is obligated to assign	☐ Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

☐ Deceased	☐ Legally incapacitated

Name of the Deceased or Legally Incapacitated Inventor :

If the Applicant is an Organization check here: ☒

Organization Name: Midwest Energy Emissions Corp

Prefix	Given Name	Middle Name	Family Name	Suffix

Mailing Address Information:

Address 1	670 D Enterprise Dr		
Address 2			
City	Lewis Center	State/Province	OH
Country	United States of America	Postal Code	43035
Phone Number			
Email Address			

Modified PTO/AIA/14 (12-13)
Approved for use through 04/30/2017. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	4820.001US9
	Application Number	Unknown
Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY	

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Assignee Information including Non-Applicant Assignee Information:

Providing assignment information in this section does not substitute for compliance with any requirement of part 3 of Title 37 of CFR to have an assignment recorded by the Office.

Complete this section if assignee information, including non-applicant assignee information, is desired to be included on the patent application publication. An assignee-applicant identified in the "Applicant Information" section will appear on the patent application publication as an applicant. For an assignee-applicant, complete this section only if identification as an assignee is also desired on the patent application publication.

If the Assignee or Non-Applicant Assignee is an Organization check here. ☐

Prefix	Given Name	Middle Name	Family Name	Suffix

Mailing Address Information For Assignee including Non-Applicant Assignee:

Address 1			
Address 2			
City		State/Province	
Country		Postal Code	
Phone Number		Fax Number	
Email Address			

Signature:

NOTE: This Application Data Sheet must be signed in accordance with 37 CFR 1.33(b). **However, if this Application Data Sheet is submitted with the INITIAL filing of the application and either box A or B is not checked in subsection 2 of the "Authorization or Opt-Out of Authorization to Permit Access" section, then this form must also be signed in accordance with 37 CFR 1.14(c).**

This Application Data Sheet **must** be signed by a patent practitioner if one or more of the applicants is **a juristic entity** (e.g., corporation or association). If the applicant is two or more joint inventors, this form must be signed by a patent practitioner, **all** joint inventors who are the applicant, or one or more joint inventor-applicants who have been given power of attorney (e.g., see USPTO Form PTO/AIA/81) on behalf of **all** joint inventor-applicants.

See 37 CFR 1.4(d) for the manner of making signatures and certifications.

Signature	/Ryan J. Connell/			Date (YYYY-MM-DD)	5/8/18
First Name	Ryan	Last Name	Connell	Registration Number	74,611

This collection of information is required by 37 CFR 1.76. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 23 minutes to complete, including gathering, preparing, and submitting the completed application data sheet form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-14**

SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. Patent Application Serial No. 15/951,970, filed April 12, 2018, which is a continuation of U.S. Patent Application Serial No. 14/318,270, filed June 27, 2014, which is a continuation of U.S. Patent Application Serial No. 13/966,768, filed August 14, 2013, issued as U.S. Patent No. 8,821,819, which is a continuation of U.S. Patent Application Serial No. 13/427,665, filed March 22, 2012, issued as U.S. Patent No. 8,512,655, which is a continuation of U.S. Patent Application Serial No. 12/419,219, filed April 06, 2009, issued as U.S. Patent No. 8,168,147, which is a continuation of U.S. Patent Application Serial No. 12/201,595, filed August 29, 2008, which is a division of U.S. Patent Application Serial No. 11/209,163, filed August 22, 2005, issued as U.S. Patent No. 7,435,286, which application claims the benefit under 35 U.S.C. § 119 (e) of U.S. Provisional Patent Application No. 60/605,640 filed Aug. 30, 2004, the disclosure of which is hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with United States Government support under Grant Numbers R 827649-01 and CR 830929-01 awarded by the United States Environmental Protection Agency and under Contract Number DE-FC26-98FT40320 awarded by the United States Department of Energy. The United States Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

1. Technical Field of the Invention

The present invention relates to methods and materials for the removal of pollutants from flue gas or product gas from a gasification system. In particular, mercury is removed from gas streams generated during the burning or gasification of fossil fuels by highly reactive regenerable sorbents.

PAC ET AL. EXHIBIT 1019
Page 2288

2. Background of the Invention

The combustion and gasification of fossil fuel such as coal generates flue gas that contains mercury and other trace elements that originate from the fuel. The release of the mercury (and other pollutants) to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. Mercury is initially present in the elemental form during combustion and gasification. In downstream process sections, such as in the ducts and stack of a combustion system, some of the elemental mercury is oxidized. The amount that is oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the fuel, but concentrations of mercury in the stream of flue gas from coal combustion are typically less than 5 parts per billion (ppb). Large coal combustion facilities such as electric utilities may emit a pound of mercury, or more, per day. Mercury removal applications include, without limitation, flue gas from coal (or other fossil fuel) combustion, waste incineration, product gas from gasification, as well as off gases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories.

Mercury Sorbent Technologies

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles, and basic silicate or oxide sorbents. When particle injection is employed, the mercury captured on the sorbent particles is removed from the gas stream in a bag house or electrostatic precipitator (ESP) and collected along with ash particulate. The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of only about 60% is attained for some applications with a FF (fabric filter) to collect carbon and ash. Even lower removal rates have been

PAC ET AL. EXHIBIT 1019
Page 2289

observed when using an ESP to collect the carbon because the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after extended exposure to the flue gas does the sorbent become effectively seasoned and provide increased reactivity with the mercury in the gas. Consequently, these sorbents must be used in large amounts, at high sorbent-to-mercury ratios, to effectively capture the mercury. These sorbents tend to be relatively expensive and cannot be easily separated from the ash for regeneration and reuse. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash, preventing its use in various applications.

Accordingly, there remains a need for more economical and effective mercury removal technology. This invention provides for cost-effective removal of pollutants including mercury, using sorbent enhancement additives and/or highly reactive sorbents, with contact times of seconds (or less), and that may be regenerated and reused.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to overcome the deficiencies of the prior art and thereby to provide new and economical methods for the removal of mercury from the gases produced in the utilization of fossil fuels.

A halogen/halide promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new halide-modified carbon form containing a reactive compound produced by the reaction of bromine (or halide or other halogen) with the carbon. Optional secondary components and alkali may be added to further increase reactivity and mercury capacity. Mercury removal efficiencies obtained exceed or match conventional methods with added benefits such as reduced costs. Optionally, the sorbent can be regenerated and reused. Sorbent treatment and/or preparation methods are also described. New methods for in-flight preparation, introduction,

PAC ET AL. EXHIBIT 1019
Page 2290

and control of the active sorbent into the mercury contaminated gas stream are described.

In some embodiments, a promoted carbon sorbent is provided comprising a base activated carbon that has reacted with a promoter selected from the group consisting of halides, halogens, and combinations thereof, such that the reaction product is effective for the removal of mercury from a gas stream.

In an embodiment, a promoted carbon sorbent is provided wherein the base activated carbon is selected from the group consisting of powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, activated carbon with an average particle size greater than that of flyash produced such that it is physically separable therefrom, and combinations thereof, and the promoter is selected from the group consisting of molecular halogens, Group V (CAS nomenclature is used throughout) halides, Group VI halides, hydrohalides, and combinations thereof. In an embodiment, the base activated carbon may have an mass mean particle diameter such that it can be substantially separated by physical means from entrained ash in the gas stream from which mercury is to be removed. In an embodiment, the base activated carbon may have a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the sorbent comprises from about 1 to about 30 grams promoter per 100 grams of base activated carbon. Another embodiment further comprises an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are enhanced.

In another embodiment, the concentration of the optional secondary component on the finished sorbent is within the range of from about 1 to about 15 wt-% of the concentration of the promoter on the finished sorbent.

In another embodiment, an optional alkali component may preferably be added to provide a synergistic effect through combination of this alkali with the primary sorbent.

In another embodiment, the optional secondary component is selected from the group consisting of Group V halides, Group VI halides, HI, HBr, HCl, and

PAC ET AL. EXHIBIT 1019
Page 2291

combinations thereof. In another embodiment, the promoter is substantially in vapor form when combined with the base activated carbon. In another embodiment, the promoter is combined with an organic solvent prior to reaction with the base activated carbon. In another embodiment, the promoter and optional secondary component are combined with the base activated carbon substantially simultaneously. Another embodiment further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. Another embodiment further comprises adding an optional alkali component.

In an embodiment, a method is provided comprising providing a granular activated carbon; reacting the activated carbon with a promoter selected from the group consisting of halogens, halides, and combinations thereof, such that the reaction product comprises a promoted carbon sorbent effective for removal of mercury from a gas stream. In a further embodiment, the reaction product comprises from about 1 to about 30 grams promoter per 100 grams activated carbon. In another embodiment the reaction product has an average particle size distribution greater than the average size of entrained ash particles in the gas stream from which mercury is to be removed, such that the reaction product can be substantially removed from the entrained ash particles by physical means. In another embodiment the reaction product has a mass mean particle diameter greater than about 40 micrometers.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment the promoter is in the gas phase when contacting the activated carbon. In another embodiment, the promoter is in an organic solvent when contacting the activated carbon.

In another embodiment, the promoter is selected from the group consisting of Br_2, a Group V bromide, a Group VI bromide, and combinations thereof.

In another embodiment, the method further comprises reacting the granular activated carbon with an optional secondary component comprising a halogen or a hydrohalide such that the reactivity and mercury capacity of the sorbent are

PAC ET AL. EXHIBIT 1019
Page 2292

enhanced. In another embodiment, the promoter and optional secondary component are contacted simultaneously with the activated carbon. In another embodiment the method further comprises adding a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof. In an embodiment, a method is provided for control of mercury in a flue gas with substantially lower sorbent requirements. Through enhanced sorbent reactivity, mercury removal per gram of sorbent is increase, thereby decreasing the capital and operating costs by decreasing sorbent requirements.

In an embodiment, a method is provided for reducing mercury in flue gas comprising providing a sorbent, injecting the sorbent into a mercury-containing flue gas stream, collecting greater than 70 wt-% of the mercury in the flue gas on the sorbent to produce a cleaned flue gas, and substantially recovering the sorbent from the cleaned flue gas. In embodiments where less than 70 wt-% mercury removal is desired, the required removal may preferably be attained using less than half as much carbon as would be required with standard (non-enhanced) carbon. In a further embodiment, the method further comprises monitoring the mercury content of the clean flue gas, regenerating the recovered sorbent, and using the monitored mercury content of the cleaned flue gas to control the rate of injection of the sorbent. In another embodiment the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

In another embodiment, the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof. In another embodiment, the promoter is reacted in the gas phase or as a vapor. In another embodiment, the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon.

In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon, a promoter, and an optional secondary component to enhance the reactivity and capacity of the sorbent within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream.

PAC ET AL. EXHIBIT 1019
Page 2293

In another embodiment, the optional secondary component is selected from the group consisting of iodine, hydrohalides, Group V halides, Group VI halides, and combinations thereof. In another embodiment, the optional secondary component is added at from about 1 to about 15 wt% of the promoter content. In another embodiment, the method further comprises adding to the sorbent a mercury-stabilizing reagent selected from the group consisting of S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

In an embodiment, the method further comprises co-injecting an optional alkaline material, including without limitation alkaline and alkaline earth components, to improve the efficiency of mercury capture by capturing oxidized mercury and/or capturing gaseous components that might otherwise reduce sorbent capacity. In another embodiment, the optional alkaline material may preferably comprise calcium oxide, sodium carbonate, and the like, as are known in the art.

In another embodiment, the method further comprises using the monitored mercury content of the cleaned flue gas to control the composition of the sorbent. In another embodiment, the injected sorbent is prepared in-flight by reacting an activated carbon and a promoter within a pneumatic transport line from which the reaction product is injected to the mercury-containing flue gas stream, wherein the promoter is selected from the group consisting of molecular halogens, halides, and combinations thereof, wherein the promoter is reacted in the gas phase or as a vapor, wherein the promoter is added at from about 1 to about 30 grams per 100 grams of activated carbon, wherein the rate at which the promoter is added and the rate of sorbent injection are determined by a digital computer based at least in part on the monitored mercury content of the cleaned flue gas.

In an embodiment, a method for reducing the mercury content of a mercury and ash containing gas stream is provided wherein particulate activated carbon sorbent with a mass mean size greater than 40 μm is injected into the gas stream, mercury is removed from the gas by the sorbent particles, the sorbent particles are separated from the ash particles on the basis of size, and the sorbent particles are re-injected to the gas stream. In another embodiment, the mercury-containing sorbent particles are regenerated to remove some or substantially all of the mercury. In

PAC ET AL. EXHIBIT 1019
Page 2294

another embodiment, an alkaline component is co-injected into the gas stream. In another embodiment, the sorbent may further comprise a promoter. The promoter may preferably comprise a halide, a halogen, or both.

As will be described in more detail below, the present invention thus provides several advantages over previously known techniques, including significantly more effective and economical mercury sorbents for effluent gases, advantageously applicable to treating gas streams from fired equipment and gasification systems.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the preferred embodiments of the present invention, reference will now be made to the accompanying drawings.

FIG. 1 schematically illustrates methods for preparation of promoted carbon sorbents in accordance with the present invention.

FIG. 2 illustrates a proposed mechanistic model of the chemical reactions resulting in the oxidation and capture of mercury.

FIG. 3 schematically illustrates preparation of promoted carbon sorbents and processes for flue gas mercury reduction in flue gases and/or product gases from a gasification system in accordance with the present invention, including in-flight preparation of promoted carbon sorbent.

PAC ET AL. EXHIBIT 1019
Page 2295

FIG. 4 is a diagram illustrating breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 5 is a diagram illustrating breakthrough curves for non-halogenated NORIT Darco FGD sorbent (37 mg+113 mg sand) in low-HCl (1 ppm) synthetic flue gas.

FIG. 6 is a bar chart illustrating pilot-scale mercury removal results, including large-size sorbent results.

FIG. 7 is a diagram illustrating the effects of sorbent size and injection rate on mercury removal for ESPs and fabric filters.

FIG. 8 is a diagram illustrating the breakthrough curves for a brominated NORIT Darco FGD sorbent with inert sand.

FIG. 9 is a diagram illustrating the breakthrough curves for brominated NORIT Darco FGD sorbent with a co-injected alkali material.

FIG. 10 is a plot of mercury removal vs. carbon injection rate with and without co-injection of alkali material.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein will be described in detail specific preferred embodiments of the present invention, with the understanding that the present disclosure is to be considered an exemplification of the principles of the invention, and is not intended to limit the invention to that illustrated and described herein. The present invention is susceptible to preferred embodiments of different forms or order and should not be interpreted to be limited to the specifically expressed methods or compositions contained herein. In particular, various preferred embodiments of the present invention provide a number of different configurations and applications of the inventive method, compositions, and their uses.

The present invention provides a cost-effective way to capture pollutants by utilizing exceptionally reactive halogen/halide promoted carbon sorbents using a

PAC ET AL. EXHIBIT 1019
Page 2296

bromide (or other halogen/halide) treatment of the carbon, that capture mercury via mercury-sorbent surface reactions, at very short contact times of seconds or less. The sorbent does not require in situ activation (no induction period) in the gas stream to achieve high reactivity, as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants is greatly enhanced and the sorption capacity can be regenerated, the promoted sorbent may be regenerated, recycled and/or reused.

The treated carbons, treatment techniques, and optional additives discussed herein have applicability to mercury control from the product or effluent gas or gases from gasification systems, syngas generators, and other mercury-containing gas streams, in addition to the flue gas from combustion systems. Thus, it should be understood that the terms combustion system and flue gas as used throughout this description may apply equally to gasification systems and syngas or fuel gas, as will be understood by those skilled in the art.

Referring now to FIG. 1, there is shown a block flow diagram illustrating some preferred embodiments of the process of the present invention to prepare promoted sorbents useful for mercury capture from flue gas and/or product gas form a gasification system streams. In a preferred embodiment illustrated by path 10-20, block 10 illustrates providing a base activated carbon, and adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, to produce a product promoted carbon sorbent. In embodiments where the halogen or halide is added, for example, as a vapor, no further steps may be necessary. In embodiments where the halogen or halide is added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 20A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-20-30, comprising providing a base activated carbon as shown by block 10, adding a halogen or halide promoter that reacts with the carbon, illustrated at block 20, and adding a secondary component illustrated at block 30 that reacts with the result of block 20 to produce a product promoted carbon sorbent. In embodiments where both the halogen or halide promoter and the secondary component are added, for example, as a vapor, no

PAC ET AL. EXHIBIT 1019
Page 2297

further steps may be necessary. In embodiments where the halogen or halide promoter and/or secondary component are added in, for example, a solvent, it may be desirable to employ solvent removal as illustrated by block 30A.

Referring still to FIG. 1, another preferred embodiment of the process of the present invention is illustrated by path 10-40, comprising providing a base activated carbon as illustrated at block 10, and adding a halogen or halide promoter and a secondary component to the activated carbon together, with which they react as illustrated by block 40, producing a product promoted carbon sorbent. As above, in embodiments where vapor additions are made to the activated carbon no further steps may be desired. In embodiments where one or more components are added in solvent, a solvent removal step may be provided as illustrated by block 40A.

Referring still to FIG. 1, also illustrated are preferred embodiments in which, as illustrated by block 50, a flue gas stream is treated with product promoted carbon sorbent prepared as described above.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, regenerated activated carbon from product promoted carbon sorbent, or other types as known in the art.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure, aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle size greater than fly ash in a flue gas stream to be treated.

In some preferred embodiments the activated carbon provided may preferably be any of several types, as understood by those skilled in the art. For example, the activated carbon may include powdered activated carbon, granular activated carbon, carbon black, carbon fiber, carbon honeycomb or plate structure,

PAC ET AL. EXHIBIT 1019
Page 2298

aerogel carbon film, pyrolysis char, an activated carbon or regenerated activated carbon with a mass mean particle diameter preferably greater than 40 micrometers, more preferably greater than 60 micrometers, or a particle size distribution greater than that of the fly ash or entrained ash in a flue gas stream to be treated, such that the activated carbon and ash can be separated by physical means.

In some preferred embodiments, the halogen or halide promoter that is added to, and reacts with, the base activated carbon may preferably comprise, by way of illustration and not limitation, a molecular halogen in vapor or gaseous form, a molecular halogen in an organic solvent, a Group V or Group VI halide, such as PBr_3 or SCl_2, respectively, in vapor, liquid, or solution form (though not in an aqueous solvent).

Embodiments are also provided in which the organic solvent may preferably comprise a chlorinated hydrocarbon, such as dichloromethane, a hydrocarbon solvent, including for example, petroleum ether, ligroin, pentane, hexane, toluene, and benzene, carbon disulfide, a waste solvent, an ether, a recycled solvent, a supercritical solvent, such as supercritical CO_2, water (though not in the case of a Group V or Group VI halide), and others as will be apparent to those of skill in the art.

Referring now to FIG. 2, there is illustrated a theory developed from scientific evidence to explain the nature of the promoting compounds. For example, as illustrated in FIG. 2, hydrogen bromide reacts with the unsaturated structure of the activated carbon. This may be, by way of illustration only, a carbene species on the edge of the graphene sheet structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury with subsequent capture by the sorbent.

It has now been found that the formation of the new bromide compound with carbon increases their reactivity toward mercury and other pollutants. Additionally, the resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation apparently results from the promotion effect of the halide, exerted on the developing positive charge on the mercury during the oxidation, known in the chemical art as a specific catalytic effect. Thus, as the

PAC ET AL. EXHIBIT 1019
Page 2299

mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, stabilizing the positive charge developing on the mercury and lowering the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Referring now to FIG. 3, a schematic flow diagram is provided of mercury control system 100 comprising preparation of promoted carbon sorbents, and flue gas mercury reduction, in accordance with preferred embodiments of the present invention. There is provided base activated carbon reservoir 110, an optional halogen/halide promoter reservoir 120, an optional secondary component reservoir 130, and an optional akali component reservoir 180, each of which with corresponding flow control device(s) 201, 202, 203, and 208/209, respectively. In conjunction with the optional alkali component reservoir 180, optional flow control devices 208 and 209 can be used independently, together, or not at all.

Reservoirs 110, 120, 130, and 180 connect through their respective flow control devices and via associated piping, to transport line 115. Optional alkali component reservoir 180 may also connect, through respective flow control devices and via associated piping, to transport line 118. A source of air, nitrogen, or other transport gas(es) is provided by gas source 170 to transport line 115 for the purpose of entraining materials discharged from reservoirs 110, 120, 130, and 180 and injecting such materials, via injection point 116, into contaminated flue gas stream 15. A source of air, nitrogen, or other transport gas(es) may be provided by gas source 171 to transport line 118 for the purpose of entraining materials discharged from reservoirs 180 and injecting such materials, via injection point 119, into flue gas stream 15. Gas sources 170 and 171 may be the same or different, as desired. Alternatively, transport gas(es) may be provided to both transport lines 115 and 118 by gas source 170 (connection from source 170 to line 118 not shown). Although gas sources 170 and 171 are shown in FIG. 3 as compressors or blowers, any source

PAC ET AL. EXHIBIT 1019
Page 2300

of transport energy known in the art may be acceptable, as will be appreciated by those of skill in the art.

For clarity, single injection points 116 or 119 are shown in FIG. 3, although one skilled in the art will understand that multiple injection points are within the scope of the present invention. Optical density measuring device(s) 204 is connected to transport line 115 and/or 118 to provide signals representative of the optical density inside transport line 115 and/or 118 as a function of time.

Downstream from injection point 116 and 119 is provided particulate separator 140. By way of illustration and not limitation, particulate separator 140 may comprise one or more fabric filters, one or more electrostatic precipitators (hereinafter "ESP"), or other particulate removal devices as are known in the art. It should be further noted that more than one particulate separator 140 may exist, sequentially or in parallel, and that injection point 116 and 119 may be at a location upstream and/or downstream of 140 when parallel, sequential, or combinations thereof exist. Particulate separator 140 produces at least a predominantly gaseous ("clean") stream 142, and a stream 141 comprising separated solid materials. A sorbent/ash separator 150 separates stream 141 into a largely ash stream 152, and a largely sorbent stream 151. Stream 151 may then preferably be passed to an optional sorbent regenerator 160, which yields a regenerated sorbent stream 161 and a waste stream 162.

An optional Continuous Emission Monitor (hereinafter "CEM") 205 for mercury is provided in exhaust gas stream 35, to provide electrical signals representative of the mercury concentration in exhaust stream 35 as a function of time. The optional mercury CEM 205 and flow controllers 201, 202, 203, 208, and 209 are electrically connected via optional lines 207 (or wirelessly) to an optional digital computer (or controller) 206, which receives and processes signals and preferably controls the preparation and injection of promoted carbon sorbent into contaminated flue gas stream 15.

In operation, promoted carbon sorbent and/or an optional alkali component is injected into contaminated flue gas stream 15. After contacting the injected material with the contaminated flue gas stream 15, the injected material reduces the

PAC ET AL. EXHIBIT 1019
Page 2301

mercury concentration, transforming contaminated flue gas into reduced mercury flue gas, 25. The injected material is removed from the flue gas 25, by separator 140, disposed of or further separated by optional separator 150, and disposed of or regenerated by an optional regenerator 160, respectively. The reduced mercury "clean" flue gas stream 142 is then monitored for mercury content by an optional CEM 205, which provides corresponding signals to an optional computer/controller 206. Logic and optimization signals from 206 then adjust flow controllers 201, 202, 203, 208, 209 to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art. Flow controllers 201, 202, 203, 208, 209 can also be adjusted manually or be some other automated means to maintain the mercury concentration in exhaust stream 35 within desired limits, according to control algorithms well known in the art.

Referring still to FIG. 3, there are illustrated several preferred embodiments for preparation and injection of promoted carbon sorbents and/or alkali components in accordance with the present invention. Stream 111 provides for introduction of base activated carbon from reservoir 110, as metered by flow controller 201 manually or under the direction of computer 206. The halogen/halide may be combined and react with the base activated carbon according to any of several provided methods. The halogen/halide may preferably be combined via line 121 directly into transport line 115, within which it contacts and reacts with the base activated carbon prior to injection point 116. This option is one form of what is referred to herein as "in-flight" preparation of a promoted carbon sorbent in accordance with the invention. Further, the halogen/halide may be combined via line 121*b* with base activated carbon prior to entering transport line 115. Still further, the halogen/halide may be contacted and react with the base activated carbon by introduction via line 121*c* into reservoir 110. This option is preferably employed when, for example, reservoir 110 comprises an ebullated or fluidized bed of base activated carbon, through which halogen/halide flows in gaseous form or as a vapor. Of course, the halogen/halide may also preferably be contacted with the base activated carbon in liquid form or in a solvent, as discussed previously, and

PAC ET AL. EXHIBIT 1019
Page 2302

solvent removal (not shown in FIG. 3) may then be provided if necessary as mentioned with respect to embodiments discussed with reference to FIG. 1.

Similarly, the optional secondary component may be contacted and react directly in transport line 115 via line 131, or optionally as described above with respect to the halogen/halide, via lines 131*b* and 131*c*.

Similarly, the optional alkali component from 180 may either be added in transport line 115 directly, or may be injected separately by transport line 118, combining downstream in flue gas 15 for synergistic effects with base activated carbon, promoted carbon, or optional secondary components. Being able to vary onsite the amount of the optional alkali component relative to base activated carbon, promoted carbon, or optional secondary components is a key feature to overcome and optimize for site-specific operating and flue gas conditions.

In some preferred embodiments wherein contacting between components and reaction is performed in a liquid or solvent phase, stirring of such liquid and/or slurry mixtures may be provided. In other embodiments, the halogen/halide promoter and optional secondary component(s) may preferably be sprayed in solution form into or on the base activated carbon. In some such embodiments, drying, filtering, centrifugation, settling, decantation, or other solvent removal methods as are known in the art may then be provided.

In embodiments wherein the halogen/halide promoter is in gaseous or vapor form, it may be diluted in air, nitrogen, or other gas as appropriate. The halide/halogen gas, for example, gaseous HBr or Br_2, may be passed through an ebullated or fluidized bed of granular or fibrous activated carbon, with the promoted carbon sorbent so produced removed from the top of the bed via gas entrainment for injection.

In some embodiments, the secondary component(s) may preferably comprise iodine or other halogens, hydrohalides, including without limitation HI, HBr, HCl, a Group V or Group VI element with a molecular halogen, such as SCl_2 and others. In some preferred embodiments, the promoted carbon sorbent may comprise from about 1 to about 30 g halogen/halide per 100 g base activated carbon. In some preferred embodiments, the promoted carbon sorbent may comprise an secondary

PAC ET AL. EXHIBIT 1019
Page 2303

component in concentration of from about 1 to about 15 wt-% of the concentration of the halogen/halide component.

In still other embodiments, the product promoted carbon sorbent may be applied to a substrate. In other embodiments, such prepared substrate(s) may be caused to contact a contaminated flue gas or gasification system product gas stream for mercury reduction purposes. Such substrates may be monolithic, rotating, or exposed to the gas stream in any number of ways known to those skilled in the art.

In some embodiments, a method is provided whereby a mercury stabilizing reagent is added to a promoted carbon sorbent to produce a bifunctional sorbent. Such stabilizing reagent(s) may be sequentially added, either before or after the addition and reaction of the halogen/halide. In some preferred embodiments, the halogen/halide preferably comprises Br or HBr, and the mercury-stabilizing reagent may comprise S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have been problematic, owing to their reactivity with other gases and metals, resulting in corrosion and health issues. A "halogen" is defined as a member of the very active elements comprising Group VIIA (CAS nomenclature is used throughout; Group VIIA (CAS) corresponds to Group VIIB (IUPAC)) of the periodic table. In the molecular elemental form of the halogens, including F_2, Cl_2, Br_2, and I_2, the reaction with a hot flue gas components leave little to react with elemental mercury. The atomic elemental halogen form, which includes the fluorine, chlorine, bromine, and iodine atoms, is about a million times more reactive to mercury but the concentration of the atomic forms is typically extremely low. In a large portion of electric utility coal combustion facilities, the concentrations are generally not sufficient to oxidize a significant amount of mercury.

The term "halide" as used herein is defined as a compound formed from the reaction of a halogen with another element or radical. In general, halide compounds are much less reactive than the molecular halogens, having a low chemical potential. Halides are considered reduced forms that do not, alone, oxidize other compounds.

PAC ET AL. EXHIBIT 1019
Page 2304

In the conventional view therefore, a halide-salt-treated activated carbon will not effectively oxidize elemental mercury and capture elemental mercury.

Halogen Promoted Sorbent Characteristics

The sorbent described here has a very high initial reactivity for oxidizing mercury and therefore can be used in very small amounts to achieve very high capture efficiencies, thus lowering operation costs and lessening waste disposal problems. In addition, further disposal reductions are obtainable by regenerating and reusing the sorbents produced using the inventive technology. The time interval required for the mercury and the promoted carbon sorbents of the present invention to successfully interact in a flue gas duct, with the subsequent collection of the mercury on the sorbent and ash is very short—less than seconds. Clearly, such collection times require the sorbent to have both high capacity and high reactivity toward mercury. The promoted carbon sorbent can be utilized in a very finely powdered form to minimize mass transfer limitations. However, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. Additionally, use of these enhancement technologies allows capture to be effective for larger sorbent particles which also allows separation of the sorbent from the ash to enable subsequent regeneration as well as ash utilization. One feature of this invention is the process to prepare a sorbent containing a halide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for very effective capture of the mercury.

It appears that the inventive sorbents chemically combine molecular bromine, for example, from solution, with activated carbon (edge sites). X-ray photoelectron spectroscopy has established that the addition of bromine, chlorine, HBr, or HCl formed a chemical compound in the carbon structure. Thus, the sorbent produced from halogen and activated carbon does not represent a molecular halogen form, but rather a new chemically modified carbon (or halocarbon) structure. This phenomenon may not occur with the less reactive iodine, where an I_2 molecular complex can exist on the carbon basal plane. In the case of bromine, modified cationic carbon has a high chemical potential for oxidation of mercury. Thus, an

PAC ET AL. EXHIBIT 1019
Page 2305

entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can preferably be generated by the addition of bromine, hydrogen bromide, or combinations of bromine and other elements, as described herein. Halogen treatment resulted in higher-activity carbons because the halide anions (especially bromide and iodide) were effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

Optional Second Component

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, typically exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound derived from a second halogen, such as HI. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus, the second component is an element with more polarized electrons (4p and 5p).

Optional Alkali Component

It has been demonstrated that addition of an optional alkali component with a base or promoted activated carbon results in improved mercury capture, typically exceeding that of both the untreated carbon and the promoted carbon. Test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This suggests the need to be able to adjust and tailor the alkali-to-activated-carbon ratio onsite in order to overcome and optimize for a given set of site conditions.

The synergy that can be gained when co-injecting the two materials can be explained as follows. First, testing shows that binding sites on activated carbon (hereinafter "AC") can be consumed by chlorine species, sulfur species (i.e. sulfates), and other flue gas contaminants (arsenates, selenates, etc). The addition of optional alkali material will interact and react with these species/contaminants thus

PAC ET AL. EXHIBIT 1019
Page 2306

minimizing their consumption of AC mercury binding sites. Second, testing also shows that standard AC will continue to oxidize mercury, even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by particulate control devices. Consequently, the addition of the optional alkali component acts to protect mercury binding sites and capture oxidized mercury, thereby resulting in improved mercury reduction at lower cost. Alkali is generally much lower in cost (~an order of magnitude less) than activated carbon, thus more of it can be used still resulting in overall lower costs.

"In-Flight" Sorbent Preparation

Furthermore, we have demonstrated that the halogen promoted carbon sorbent can be readily produced "in-flight". This is accomplished by, for example, contacting the vapors of any combination of halogens and optionally a second component, in-flight, with very fine carbon particles. The particles may be dispersed in a stream of transport air (or other gas), which also conveys the halogen/halide promoted carbon sorbent particles to the flue gas duct, or other contaminated gas stream, from which mercury is to then be removed. There is no particular temperature requirement for this contact. This technology is obviously very simple to implement, and results in a great cost savings to facilities using this technology for mercury capture.

Advantages of On-Site Preparation

In-flight preparation of the halogen/halide promoted carbon sorbent on location produces certain advantages. For example, the treatment system can be combined with the carbon injection system at the end-use site. With this technique, the halogen/halide is introduced to the carbon-air (or other gas) mixture in a transport line (or other part of the sorbent storage and injection system). This provides the following benefits over current conventional concepts for treating sorbents off-site:

Capital equipment costs at a treatment facility are eliminated.

Costs to operate the treatment facility are eliminated.

There are no costs for transporting carbon and additive to a treatment facility.

PAC ET AL. EXHIBIT 1019
Page 2307

The inventive process uses existing hardware and operation procedures.

The inventive technology ensures that the sorbent is always fresh, and thus, more reactive.

No new handling concerns are introduced.

There are no costs for removing carbon from treatment system.

The inventive process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as may be needed when changing fuels or reducing loads, thus further optimizing the economics.

The inventive technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the present invention, embodiments including a process for preparing and regenerating halogen/halide promoted carbon sorbents, whose activity for mercury capture is enhanced by the addition of halogen (e.g. bromine) to the carbon structure.

Sorbent Injection Location

Some of the preferred embodiments contemplate the use of a halogen promoted sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Other embodiments of the inventive composition of the halogen promoted carbon sorbent comprise a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Other embodiments allow the addition of the optional alkali component in conjunction with a base activated carbon and/or with the use of a halogen based sorbent and any other combinations of the sorbent technologies provided in this patent. Alternatively, embodiments include methods wherein the sorbent is on a moving contactor consisting of particles or fibers containing one or more of the compositions listed above.

Sorbent Regeneration

Any of the above embodiments of the halogen/halide promoted carbon sorbent can be easily regenerated; the poisoning contaminants from the flue gas are

PAC ET AL. EXHIBIT 1019
Page 2308

preferably removed and an inexpensive promoting agent added, to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive, conventional methods of adding a reagent (such as peroxide, gold, triiodide, etc.) to a sorbent. The halogen/halide promoted carbon sorbent of the present invention, treated with bromine and/or optional components, is noncorrosive. Detailed examples of sorbent regeneration techniques are described in co-pending, commonly owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is hereby incorporated by reference in its entirety.

Sorbent Injection Control Schemes

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize certain aspects of the invention. Where possible and desirable, the mercury control technology of the present invention may preferably utilize continuous measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent and optional component(s) levels can be achieved in this way, which will ensure mercury removal requirements are met with minimal material requirements, thus minimizing the associated costs. In an embodiment, the mercury emissions are continuously measured downstream of the injection location, preferably in the exhaust gas at the stack.

Promoted Carbon Sorbents

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, gallium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accepts electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine,

PAC ET AL. EXHIBIT 1019
Page 2309

yet provides a highly reactive bromine-containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

EXAMPLES

To more clearly illustrate the present invention, several examples are presented below. These examples are intended to be illustrative and no limitations to the present invention should be drawn or inferred from the examples presented herein.

Example 1

Preparation and Testing of Halogenated Carbon (& Comparative Example) Gas Phase Halogenation

Finely powdered activated carbon (such as NORIT Darco FGD, NORIT Americas, Inc., Marshall, Tex. (USA), although others are suitable, as will be recognized by those skilled in the art), was placed in a rotating plastic barrel with side blades (a 5 ft^3 (0.14 m^3) cement mixer) fitted with a tight plastic lid to prevent loss of the fine powder during the preparation. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that is warmed to about 40°-50° C. The vapor pressure of the bromine was such that a dark red gas is generated and passed out of the generator. The outlet from the gaseous bromine generator is connected via a 1/4 inch (0.64 cm) plastic hose to a stationary metal tube inserted through a flange in the center of the plastic lid and passing into the center of the barrel. The flange is not air tight so that the excess of nitrogen is released after the bromine is transferred to the tumbling carbon. Thus, the bromine gas stream continuously passed into the rotating barrel where it contacted the tumbling carbon. The unit is then operated until the desired amount of bromine has combined with the carbon. Typically, this is 0.4 to 1 kg of bromine to 20 kg of carbon (2-5 wt. %). When the reaction is completed, the carbon is weighed. The treated carbon is odorless and does not cause skin irritation since

PAC ET AL. EXHIBIT 1019
Page 2310

the bromine has completely reacted with the carbon to produce the brominated carbon.

XPS spectra demonstrate that the brominated carbon contains both covalent carbon-bound (organic) bromide as well as anionic bromide. The product contains the same moisture originally present in the activated carbon (5-17 wt %), but does not require further drying for use. The moisture is driven out at higher temperatures (>150° C.), and the bromine was not released until very high temperatures

Bench-Scale Testing of Mercury Oxidation and Capture Efficiency

A bench-scale apparatus and procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including bromine-containing activated carbons prepared from a variety of carbons, including commercially available sorbents, aerogel film sorbents, and the original precursor carbons for comparison.

A detailed description of the apparatus and its operation is provided in Dunham, G.E.; Miller, S. J. Chang, R.; Bergman, P. *Environmental Progress* 1998, 17, 203, which is incorporated herein by reference in its entirety. The bench scale mercury sorbent tests in the flue gas compositions were performed with finely (--400 mesh) powdered sorbents (37 mg) mixed with 113 mg sand and loaded on a quartz filter (2.5 inch (6.35 cm)). The loaded filter and holder were heated in an oven (125° C.) in the simulated flue gas stream (30 SCFH (standard cubic feet/hr) or 0.79 NCMH (normal cubic meters per hour)) containing the following: O_2 (6%), CO_2 (12%), SO_2 (600 ppm), NO (120 ppm) NO_2 (6 ppm), HCl (1 ppm), Hg^0 (11 $\mu g/m^3$), H_2O (15%), and N_2 (balance). Elemental mercury was provided by a standard permeation tube source placed in a double jacketed glass condenser, and heated to the desired temperature. Mercury concentrations in the gas streams were determined with a continuous mercury emission monitor (Sir Galahad mercury CEM mfr. P.S. Analytical Deerfield Beach Fla. USA), and a $SnCl_2$ cell was used to convert oxidized species to elemental, so that both elemental and oxidized mercury concentration data could be obtained for both the influent and the effluent concentrations from the sorbent bed. Mercury concentrations were calibrated for the

PAC ET AL. EXHIBIT 1019
Page 2311

flow rates used. Spent sorbents were analyzed for mercury to determine the mass balance.

Referring now to FIG. 4, the effluent mercury concentration data are plotted as a percent of the influent mercury versus time. The resulting curve (breakthrough curve) for the halogenated sorbents typically showed 0%-1% Hg in the effluent (99+% capture) at the beginning, and increasing only after 30-60 minutes (breakthrough point), depending on the sorbent. FIG. 4 illustrates the breakthrough curves for 5 wt/wt % brominated NORIT Darco FGD sorbent (37 mg+113 mg sand) with synthetic flue gas containing 1 ppm HCl. Total Hg (solid circles) and elemental Hg (solid squares) in the effluent are presented as a per cent of the inlet Hg. "EOT" indicates the end of test (the later data points shown are for calibration checks).

FIG. 5 presents the comparative breakthrough curves for the corresponding nonhalogenated sorbents typically initiated at 5%-50% of inlet mercury, depending on the HCl concentration in the synthetic flue gas, thus indicating considerably lower reactivity for oxidation and capture of the mercury for the nonhalogenated sorbents. After breakthrough of either halogenated or nonhalogenated sorbent, most of the mercury in the effluent was oxidized mercury.

Example 2

Gas Phase Halogenation of Fluidized Carbon

A bed of activated carbon supported in a vertical tube by a plug of glass wool was fluidized by a nitrogen stream. The top of the fluidized bed tube was connected to a catching trap for carbon fines that blow out the top of the tube. The bromine gas generator as described in Example 1 was attached to the fluidized carbon bed and the desired amount of gaseous bromine was passed into the bed. The contents of the trap were then mixed with the material in the bed and weighed. The resulting brominated carbon exhibited properties similar to the brominated carbon of Example 1.

Example 3

Liquid Phase (Water) Halogenation

PAC ET AL. EXHIBIT 1019
Page 2312

A 5% solution of bromine in water was prepared by carefully adding 50 g of bromine to 1 liter of cold water. One kg of activated carbon was added to the bromine solution in a large metal can. The resulting slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon, as indicated by the disappearance of the red color. The slurry was then filtered using a Buchner funnel under vacuum. The moist carbon that was collected on the filter was dried in an oven at 110° C. for several hours to constant weight. As in Example 1, some moisture remains in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 4

Addition of the Optional Second Halide Component

Brominated carbon was produced by solution phase bromination similar to that described with reference to Example 3. However, before filtration, a solution of hydriodic acid (HI) was added to the slurry in an amount equal to 10% of the bromine amount. The slurry was stirred to complete the reaction and then filtered and dried as described in Example 3.

Example 5

Liquid Phase Phosphohalogenation

A solution of phosphorus tribromide (500 g) in ligroin (10 liters) was stirred in a large metal can and 10 kg of activated carbon was added. The resulting slurry was stirred with a large paddle at ambient temperature to complete the reaction. The slurry was filtered under vacuum on a large Buchner funnel in several batches. The wet filter cake was dried at 110° C. in an oven to constant weight. The dried product was fluffed in the rotating barrel as described in Example 3.

Example 6

Preparation and Sorption on Larger-Particle Carbon

PAC ET AL. EXHIBIT 1019
Page 2313

Tests were conducted on a pilot-scale combustor while firing a subbituminous coal, to evaluate mercury control by injecting larger-than-normal sized treated activated carbon. Standard AC sorbents generally are of fine size with a mean particle diameter of less than 20 micrometers, which is also typical of the flyash that is generated from pulverized coal combustion. Consequently, because the sizes of standard AC and flyash are similar, separation of the two is difficult. Injection of larger sized AC is generally not considered because the sorbent effectiveness decreases with size. In a scheme to recycle the injected carbon, the carbon is separated from the flyash. A separation based on size fractionation requires a treated larger particle sorbent. To test this concept, a treated larger sized (>60 μm) sorbent was developed, prepared, and tested.

Treatment—Gas Phase Halogenation

Granular activated carbon (Calgon F400) was ground and sieved through conventional mesh screens. The mesh size fraction −170 to +240 (corresponding to about 60 to about 88 micrometers) was collected and placed in a rotating vessel as described in Example 1 above. In a separate vessel, gas phase bromine was generated by passing a nitrogen stream over a weighed amount of liquid bromine that was warmed to about 40°-50° C., and the outlet from this gaseous bromine generator was connected via a ¼ inch (6.35 mm) plastic hose to a stationary metal tube inserted through a flange in the center of the lid and passing into the center of the rotating vessel, also as described in Example 1. The unit was operated until the desired amount of bromine had combined with the carbon, in this case 0.05 kg of bromine to 1 kg of carbon (5 wt. %). When the reaction was completed, the carbon was weighed. The treated carbon was odorless as has been described above.

PTC Apparatus

The pilot-scale combustor, known as the "Particulate Test Combustor" (hereinafter "PTC"), is a 550,000-Btu/hr (about 161 kW) pulverized coal ("PC")-fired unit, designed to generate combustion flue gas properties and fly ash that are representative of those produced in a full-scale utility boiler. The combustor is oriented vertically to minimize wall deposits. A refractory lining helps to ensure adequate flame temperature for complete combustion and prevents rapid quenching

PAC ET AL. EXHIBIT 1019
Page 2314

of the coalescing or condensing fly ash. Based on the superficial gas velocity, the mean residence time of a particle in the combustor is approximately 3 seconds. The coal nozzle of the PTC fires axially upward from the bottom of the combustor, and secondary air is introduced concentrically to the primary air with turbulent mixing. Coal is introduced to the primary air stream via a screw feeder and eductor. An electric air preheater is used for precise control of the combustion air temperature. Originally, the PTC used cold-water annular heat exchangers to provide flue gas temperature control to the baghouse (also referred to as a "fabric filter") or electrostatic precipitator (ESP). However, analysis of ash deposits collected from the heat exchangers indicated that some mercury was collected on the duct walls. To minimize this effect, the heat exchangers were modified to provide for higher duct wall temperatures.

The PTC instrumentation permits system temperatures, pressures, flow rates, flue gas constituent concentrations, and particulate control device (baghouse, Advanced Hybrid Particle Collector/AHPC™, and/or electrostatic precipitator/ESP) operating data to be monitored continuously and recorded on a data logger.

PTC Procedure

Flue gas samples were taken at combinations of two of the three available system sample points: the furnace exit, the particulate control device inlet, and the particulate control device outlet. After passing through sample conditioners to remove moisture, the flue gas was typically analyzed for O_2, CO, CO_2, SO_2, and NO_x. Each constituent was normally analyzed at both the furnace exit and the outlet of the particulate control device simultaneously, using two analyzers. The concentration values from all of the instruments were recorded continuously. In addition, data were manually recorded at set time intervals. NO_x was determined using a pair of Rosemount Analytical NO_x chemiluminescent analyzers. SO_2 was measured using a pair of Ametek Instruments photometric gas analyzers. The remaining gases were measured by a pair of Rosemount Analytical multi-gas continuous emissions monitors. Each of these analyzers was regularly calibrated and maintained to provide accurate flue gas concentration measurements.

PAC ET AL. EXHIBIT 1019
Page 2315

The baghouse vessel was a 20 inch (50.8 cm) (ID) chamber that is heat-traced and insulated, with the flue gas introduced near the bottom. The combustor produced about 200 ACFM (actual cubic feet per minute; about 5.7 actual m^3/min) of flue gas at 300° F. (about 150° C.), therefore three 13-ft by 5-inch (3.96 m by 12.7 cm) bags provided an air-to-cloth ratio of 4 ft/min (1.22 m/min). Each bag was cleaned separately in operation with its own diaphragm pulse valve. In order to quantify differences in pressure drop for different test conditions, the bags were cleaned on a time basis, rather than with the cleaning cycle initiated by pressure drop. Once bag cleaning was initiated, all three bags were pulsed in rapid succession on-line.

Tests were also conducted with a single-wire, tubular ESP replacing the fabric filter. The ESP unit was designed to provide a specific collection area of 125 at 300° F. (150° C.). Since the flue gas flow rate for the PTC is 130 SCFM (standard cubic feet per minute; about 3.7 NCMM (normal m^3/min)), the gas velocity through the ESP is 5 ft/min (about 1.52 m/min). The plate spacing for the ESP unit is 11 in (27.9 cm). The ESP was designed to facilitate thorough cleaning between tests so that all tests can begin on the same basis.

PTC Results

Results are illustrated in FIG. 6. As can be observed in FIG. 6, even though the tested sorbent particle size is significantly larger than normal sorbent particles, the treated larger-than-normal sized (that is, >60 micrometers) activated carbon sorbent was quite effective at capturing mercury. Approximately 75% of the mercury was captured when the larger-sized treated AC was injected ahead of the pilot-scale ESP, while approximately 85% of the mercury was captured when injected ahead of the pilot-scale fabric filter ("FF"). Note that in FIG. 6 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet (1 MACF is about 0.028 million actual cubic meters or "MACM").

Referring now to FIG. 7, it can be observed that the larger-sized treated AC when injected ahead of the pilot-scale ESP (diamond symbol(s)) performed better than the finer standard AC (triangles) under the same arrangement. In comparison, when injected ahead of the fabric filter (FF), the larger-sized treated AC (square)

PAC ET AL. EXHIBIT 1019
Page 2316

performed similarly to slightly worse. However, for this application, the larger-sized treated AC can be physically separated from the smaller flyash particles, and the sorbent can then be regenerated, recycled, and reused. This will substantially improve overall utilization and economics. These data thus show that a larger-than-normal sized sorbent can provide effective mercury control and ease flyash and AC separation, thereby also preserving the characteristics of the flyash for sale and beneficial use. Accordingly, because >60 μm sorbent particles have been successfully demonstrated, superior mercury control can be obtained with >40 μm particles, which may be preferred in some applications, depending on the sorbent particle/ash separation system used. Note that in FIG. 7 (and throughout) "Macf" (and "MACF") indicates million actual cubic feet.

Example 7

Liquid Phase (Organic Solvent) Halogenation

A 5% solution of bromine in ligroin was prepared by carefully adding 50 g of bromine to 1 liter of cold ligroin. One kg of activated carbon was added to the bromine solution in a large metal can. The slurry was stirred with a large paddle during the addition and for a short time afterwards until all the bromine had reacted with the carbon as indicated by the disappearance of the red color. The slurry was filtered using a Buchner funnel under vacuum. The carbon cake that was collected on the filter was dried in an oven at 110° C. for several hours until it appeared dry and a constant weight was obtained. As in Example 1, some moisture was left in the carbon, however. The dried carbon was then tumbled in the rotating barrel with metal pieces to break up and fluff the carbon.

Example 8

Promoted Activated Carbon Sorbents

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several promoted activated carbon sorbents using powdered carbon, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well

PAC ET AL. EXHIBIT 1019
Page 2317

as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100° C. in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. The results indicated that adding a second component to the solution improved the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu g/m^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM ("continuous emission monitor") (mfr. P S Analytical, Deerfield Beach, Fla., USA). The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer. A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it was treated with 0.1 N HBr, and the powder was collected by centrifugation and drying, revealed that the mercury capture activity increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicated that it not only captured mercury at the same level as before (100% capture) but its capacity was prolonged by several minutes, and thus enhanced. Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

Example 9

Fluidized/Ebullated Bed Preparation

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed or ebullated bed of the carbon. The amount of bromine taken up by the

PAC ET AL. EXHIBIT 1019
Page 2318

carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

Example 10

Full-Scale Testing

In this example, a baghouse (fabric filter) or ESP was used to collect particulates in the exhaust of a full-scale commercial pulverized coal-burning facility. A scrubber and sorbent bed were also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In this example, the halogen/halide promoted carbon sorbent was injected into the flue gas after the boiler. In general however, the inventive sorbent can be injected where desired (e.g., before, after, or within the boiler).

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu g/m^3$. The ash and injected carbon were collected in the baghouse at 350° F. to 375° F. (about 175-190° C.). Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/MACF ("MACF" and "Macf" represent one million actual cubic feet; 1.0 lb/MACF is about 16 kg/MACM (million actual cubic meters)) resulted in mercury effluent concentrations of 3.8-4.2 $\mu g/m^3$ (representing 62%-58% removal of the mercury from the gas, respectively), and at 2.0 lb/MACF (about 32 kg/MACM), gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/MACF resulted in 73%-69% removal and at 2.0 lb/MACF gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine promoted carbon sorbent of the present invention.

Example 11A

Addition of Optional Alkaline Component—Bench-Scale

The efficiency of the activated carbons for mercury capture can be improved considerably by employing a basic material co-injected with the activated carbon, in order to capture any oxidized mercury that may be released from the sorbent, or to

PAC ET AL. EXHIBIT 1019
Page 2319

capture some of the sulfur or selenium oxides in the flue gas that can have a detrimental effect on the sorbent capacity.

Bench-scale testing was conducted by preparing a filter composed of 37 mg of brominated activated carbon mixed with 113 mg of calcium oxide. The test was conducted as described in Example 1 and compared with the same carbon sorbent but with an inert diluent. The breakthrough curve for the mixture of brominated (2%) NORIT Darco FGD sorbent with inert sand is shown in FIG. 8, and the breakthrough curve for the mixture with CaO is shown in FIG. 9. It can be seen that the point of 50% breakthrough improves to 65 minutes with the mixture with CaO from only 48 min with the sand mixture.

Example 11B

Addition of Optional Alkaline Component—Pilot-Scale

Tests were conducted on the pilot-scale PTC combustor described above with reference to Example 6 while firing a Texas lignite to evaluate mercury control by co-injecting a standard activated carbon (also referred to herein as "AC") and an alkali material upstream of a fabric filter. Typical results are illustrated in FIG. 10. As shown in FIG. 10, co-injecting lime with activated carbon vastly improved mercury removal. Mercury removals of approximately 90% were achieved with the co-injected sorbents, whereas less than 60% removal was achieved with the use of standard AC alone, even at much higher injection rates. Data from similar tests show that injecting similar quantities of sodium carbonate and AC, and lime and AC, resulted in mercury removals of approximately 80%, and 87%, respectively. These data suggest that other alkali can also be co-injected with AC to improve mercury removal. Other data show that flue gas temperature may impact the effectiveness of the alkali addition. Further test data indicate that flue gas contaminants, flue gas constituents (SO_2, NO_x, HCl, etc.), operating temperature, mercury form, and mercury concentration may impact the effectiveness of the alkali addition. This indicates that it may be desirable to be able to adjust and tailor, onsite, the alkali-to-AC ratio in order to optimize removal for a given set of site conditions.

PAC ET AL. EXHIBIT 1019
Page 2320

Without wishing to be bound by any particular theory, the synergy observed in the improved performance when co-injecting the two materials can be explained as follows. First, tests indicate that binding sites on AC can be consumed by sulfur species and other contaminants. The alkali material interacts and reacts with these species thus minimizing their consumption of AC mercury binding sites. Second, other work has shown that standard AC will continue to oxidize mercury even though the binding sites are fully consumed. This oxidized mercury can then react with alkali material and subsequently be captured by the particulate control device. Thus, combining alkali with treated and/or non-treated AC synergistically takes advantage of these two mechanisms, resulting in improved mercury capture at reduced costs.

Example 12

Brominated Carbon Sorbent for Gasification Fuel Gas

Preparation of 5% Br2W-AC

Using a procedure similar to Example 3, a 2.5 wt/vol % solution of bromine in water was prepared. Granular Calgon F400 was added to the bromine solution to give a 5 wt/wt % brominated carbon product. The bromine solution was stirred with a large paddle during and after the addition until the red color in the water disappeared. The suspension was filtered by vacuum on a large Buchner funnel. The filter cake was dried in air, and then in an oven at 110° C. until a stable weight was obtained The moisture was reduced to 15%.

Preparation of 5% Br2D-AC

A brominated sorbent was prepared from Br_2 addition in solvent as described in Example 7, except that dichloromethane was used as the solvent instead of ligroin, and granular Calgon F400 was used.

Preparation of 5% PBr3-AC

A phosphohalogenated sorbent was prepared from PBr_3 using the method described in Example 5, except granular Calgon F400 was used.

Testing in Hydrogen Atmosphere—Procedure

PAC ET AL. EXHIBIT 1019
Page 2321

To simulate the capture of mercury from a heated fuel gas or syngas from coal gasification, tests were conducted employing a stream comprising 10% vol/vol hydrogen in nitrogen passing through the sorbent at 500 cc/min. The stream contained 26.9 micrograms/m^3 of elemental mercury from a commercial mercury permeation source.

In the tests, the sorbent (0.5 g) was placed in a 0.39 inch (1 cm, inside diameter) glass tube fitted with a medium frit sintered glass filter disc to hold the sorbent in the gas stream. The tube containing the sorbent bed was connected to a gas inlet tube for introducing the gas stream containing the mercury vapor and at the outlet to a tube connection to the detector. The detector was a Semtech 2000 continuous mercury emission monitor. The tube was equilibrated in a nitrogen flow (450 cc/min) for 5 minutes at ambient temperature to stabilize the system. The detector showed 0 concentration of mercury in the effluent from the sorbent bed. (The blank run with no sorbent read 26.9 micrograms/m^3). The tube was then placed in an oven at the selected temperature for the test (from 250° to 400° C.). Effluent mercury concentration data from the detector were collected until the detector showed a constant reading for 5 minutes. Hydrogen (50 cc/min) was then added to the gas stream and detector readings were taken every 5 min. Tests were conducted at several oven temperatures for various periods of time up to 3 hours, depending on the temperature and sorbent. The elemental mercury concentration data were plotted as a percent of inlet mercury concentration versus time as in Example 1. All the mercury in the effluent was elemental, so a single detector was sufficient, and no $SnCl_2$ trap was needed to convert to elemental mercury (as in Example 1). The time for 50% breakthrough (time to reach 50% capture) was then determined from the breakthrough curves.

Results

The results are shown in Table 1 (below) for the unbrominated sorbent (Calgon F-400), the brominated sorbents (5% Br2W-AC and 5% BrD-AC), and the phosphobrominated sorbent (5% PBr3-AC). The maximum mercury concentration obtained in the effluent in each run is also reported in Table 1 for the time period indicated in the last column.

PAC ET AL. EXHIBIT 1019
Page 2322

Under the reducing hydrogen conditions, the unbrominated sorbent broke through immediately and was exhausted after only 6.5 min. This complete failure occurred because the hydrogen reduces the captured mercury in the unbrominated sorbent at any temperature above 100° C. Both of the brominated sorbents exhibited excellent reactivity and good capacity at all temperatures, up to at least 400° C. The phosphobrominated sorbent exhibited superior reactivity and capacity at all temperatures, up to at least 400° C.

	Times for 50% Breakthrough Maximum Observed Hg Concentrations for Sorbents (10% Hydrogen Streams)			
Sorbent	Temp (° C.)	50% breakthrough (min)	Maximum [Hg] ($\mu g/m^3$)	Time (min)
F-400	250	6	20.3	6.5
5% Br2W-AC	250	>150	1.4	150
5% Br2W-AC	300	>180	4.3	180
5% Br2W-AC	350	160	15.1	180
5% Br2W-AC	400	60	13.9	65
5% PBr3-AC	250	>140	0.4	140
5% PBr3-AC	300	>150	0.5	150
5% PBr3-AC	350	>150	1.4	150
5% Br2D-AC	350	>180	2.1	180
5% Br2D-AC	400	>180	10.9	180

While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Accordingly, the scope of protection is not limited by the description set out above, but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims.

The examples provided in the disclosure are presented for illustration and explanation purposes only and are not intended to limit the claims or embodiment of this invention. While the preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without

PAC ET AL. EXHIBIT 1019
Page 2323

departing from the spirit and teachings of the invention. Process criteria, equipment, and the like for any given implementation of the invention will be readily ascertainable to one of skill in the art based upon the disclosure herein. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Use of the term "optionally" with respect to any element of the invention is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the invention.

The discussion of a reference in the Background is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated herein by reference in their entirety, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

Although the invention is described herein as a sorbent material and associated processes for its preparation and use, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

PROVISIONAL APPLICATION

A reactive sorbent material is described for capture of mercury in a vapor stream. The vapor stream includes flue gas from coal combustion or incineration, synthesis gas from gasification, as well as offgases from mineral processing, metal refining, retorting, cement manufacturing, chloralkali plants, dental facilities, and crematories. The sorbent is especially suited to, but not limited to, use in low-chlorine flue or exhaust gases where the mercury is mainly elemental. The sorbent comprises a bromide-modified carbon form containing a reactive compound produced by the reaction of bromine with the carbon. Other additional promoting substances can be added in smaller amounts to increase the reactivity with and

PAC ET AL. EXHIBIT 1019
Page 2324

sorption of elemental mercury. This combination results in a carbon bromide structure in the carbon lattice that can oxidize the mercury to a species that is strongly bonded to the carbon structure and, therefore, easily retained on the sorbent at higher temperatures in the presence of flue gas constituents. In some examples, the sorbent consists of a fine or coarse powdered material for injection into the gas stream or a granular or fibrous material for use in a fixed or moving bed. In some examples, the sorbent does not require in situ activation (an induction period) in a flue gas stream as do conventional activated carbon sorbents. Other additives of base chemistry (Ca, Na, and others) may be added to flue gas as a sorbent mixture, or co-injected to selectively sorb acid gases or other flue gas constituents to keep available reactive sites for mercury oxidation and subsequent capture. The sorbent can be regenerated by washing off contaminating components derived from flue gas that poison the spent sorbent. Novel methods for introduction of the sorbent dispersion into the mercury contaminated gas stream are described.

Following is an outline of examples of the invention. The invention may also take on various other examples or embodiments, as a person skilled in the art would understand.

1. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by applying a solution of molecular bromine in an organic solvent to the carbon, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon in air or nitrogen. The solution may also contain an additional promoting substance in small amounts. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30g per 100g of activated carbon, depending on the proportions used.

1A. (Dependent)

Same as 1, carbon is powdered activated carbon.

Carbon is granular activated carbon.

Carbon is very fine carbon black.

Carbon is very fine carbon fiber.

PAC ET AL. EXHIBIT 1019
Page 2325

Carbon is aerogel carbon film.

Carbon is char recovered from pyrolysis process.

Carbon is powdered activated carbon of size distribution larger than fly ash size distribution, so that it can be physically separated from the ash and regenerated for reuse.

Carbon is regenerated from previous usage cycle and recycled.

Other desired types of carbon may also be used.

1B. (Dependent)

Same as 1, Solvent is chlorinated hydrocarbon such as dichloromethane.

Same as 1, Solvent is hydrocarbon solvent such as petroleum ether or ligroin or pentane or hexane or toluene or benzene.

Same as 1, Solvent is water.

Same as 1, Solvent is carbon disulfide.

Same as 1, Solvent is a waste solvent.

Same as 1, Solvent is an ether.

Same as 1, Solvent is recycled from previous batch.

Same as 1, Solvent is supercritical solvent such as CO_2.

Other desired types of Solvents may also be used.

1C. (Dependent)

Same as 1, solution of bromine is applied by stirring the carbon in the bromine solution.

Same as 1, solution of bromine is applied by spraying a solution of molecular bromine in an organic solvent, followed by removal of solvent from the pores by drying the carbon in air or nitrogen.

The bromine may also be applied using other desired techniques.

1D. (Dependent)

Same as 1, removal of solvent is by filtration, centrifugation, settling, and decantation and drying in vacuum, air, or other gas.

PAC ET AL. EXHIBIT 1019
Page 2326

Same as 1, when sprayed or minimal volume, removal of solvent is by drying in air, vacuum, or other gas.

The solvent may also be removed using other desired techniques.

1E. (Dependent)

Same as 1, additional substance is iodine, at 1%-10% of the bromine concentration added.

Same as 1, additional substance is hydrohalide (HI, HBr, HCl), etc:, 1%-10 % of bromine.

Same as 1, additional substance is a compound comprised of a Group V or VI element or combination of Group V or VI with Group VII element, such as SCl_2, 1-10 wt % of bromine.

2. A modified carbon sorbent was prepared by reacting the carbon with molecular bromine by contacting the carbon with a gas containing molecular bromine. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100g of activated carbon, depending on the proportions used.

Contacting is by passing the Br_2 gas through a bed of the carbon.

Bed is ebullated or fluidized.

Bed is moving bed of granules or fibers.

Contacting is by admitting Br_2 gas to a duct through which the carbon is transported from a reservoir to the flue gas duct via an air-driven entrainment method, thus promoting the activity of the carbon in-flight.

Same additives as 1E, except these are added in the gas phase, and added in-flight as in 2 above.

3. A modified activated carbon sorbent was prepared by reacting the carbon with hydrogen bromide (HBr) by stirring the carbon in a solution of HBr in an organic solvent or in water, followed by removal of the modified carbon from the bulk of solvent and further removal of solvent from the pores by drying the carbon

PAC ET AL. EXHIBIT 1019
Page 2327

in air or nitrogen. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms. Same solutions and treatment as 1B,1C, 1D.

Same additives as 1E, added into the solution phase or later in the gas phase, and added in-flight as in 2 above.

4. An activated carbon sorbent was prepared by impregnating hydrogen bromide by passing a gas composition containing hydrogen bromide diluted with nitrogen or air through a fluidized bed or ebullated bed of the carbon. In one example, the amount of bromine taken up by the carbon ranges from <1 to about 30 g per 100g of activated carbon, depending on the proportions used.

Same dependent clauses as in 1A with regard to carbon forms.

Contacting options are similar to 2.

5. Sequential treatment of activated carbon with bromine or HBr, followed by another mercury stabilizing reagent to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H_2S, SO_2, H_2Se, Se, SeO_2, CS_2, P_2S_5.

6. Sequential treatment of activated carbon with mercury stabilizing reagent, followed by bromine or HBr to generate a highly reactive bifunctional sorbent, the reagent to include sulfur and selenium species, such as H_2S, SO_2, H_2Se, Se, SeO_2, CS_2, P_2S_5.

7. Treatment of a carbon with a Group V or VI element combined with Group VII element, such as PBr_3 or SCl_2. In one example, the amount of Group V or VI halide is 1-30 wt % of the carbon. The compound is added in vapor phase or in solution (solvent is hydrocarbon, chlorinated hydrocarbon, or other solvent as described in 1B, but not water, since the compound is destroyed in water solution).

PAC ET AL. EXHIBIT 1019
Page 2328

8. The process for preparing the bromine-containing activated carbon sorbent as described in Examples 1-6 and coupled with the injection of the bromine-containing fine-particle sorbent into the contaminated gas stream and subsequent removal of the fine particles of sorbent from the gas stream in a collection device, such as bag filtration of electrostatic precipitator (ESP).

9. The process of using additives (1-8) in conjunction with sorbents to capture acid gases and other flue gas constituents that block oxidation reactions or consume sorbent sites that would otherwise capture mercury. The additive is a compound comprised of Group I or II elements, such as Ca, Na, and others. These additives of base chemistry may be added to flue gas as a sorbent mixture or co-injected to selectively sorb acid gases or other gas constituents that compete for mercury reactive/sorption sites, thereby improving the effectiveness of activated carbon to capture mercury. In addition, the base additives can augment the treated activated carbon by helping to capture oxidized mercury forms in the flue gas, such as mercuric chloride, or that are produced on the carbon sorbent, such as mercuric bromide, but are released to the gas phase as the sorbent becomes saturated or capacity limited.

10. The process of preparing a larger-than-normal (>40 μm) sorbent particle size, promoting with the halogen treatment as described in 1-8, using the treated sorbent for capture of mercury by injecting in the flue gas, and finally separating and recovering the sorbent from the ash particles. The larger sorbent size thus will allow easy mechanical/physical separation so that sorbent can be regenerated, recycled, and reused, and the ash can be sold as a low-carbon cementatious byproduct for concrete. The separation can be effected by various methods, such as density (gravity), floatation, or sieving methods.

11. The process for preparing the bromine-containing activated carbon sorbent as described in Example 1-10, coupled with the direct injection of the slurry of the

PAC ET AL. EXHIBIT 1019
Page 2329

prepared fine-particle sorbent in the solvent or aqueous phase, so that the aerosol particles of the slurry achieve a high degree of dispersion in the gas stream and evaporation of the solvent in the hot gas occurs rapidly. The amount of slurry added is flow-controlled, and the concentration of particles in the slurry is monitored by optical density measurements prior to injection. Collection of particles is performed.

12. The process for preparing the bromine-containing activated carbon sorbent, as described in Examples 2 and 4, coupled where the fine-particle dispersion of brominated sorbent in the gas stream at the top of the ebullated bed is led to the flue gas or offgas duct where the said dispersion is contacted with mercury-contaminated flue gas or offgas stream. The amount of aerosol dispersion added is controlled by the gas flow to the ebullated bed, and the concentration of particles in the dispersion can be monitored by optical density measurements prior to injection. Collection of particles is performed by the existing particulate-collection equipment.

13. The process for preparing the bromine-containing activated carbon sorbent bed, coupled with contacting the bed with the mercury-contaminated flue gas or offgas.

14. The process for preparing the bromine-containing activated carbonBsorbent, as described in Examples 2 and 4, or untreated activated carbon, coated on a substrate or as activated carbon material. This material is placed in a moving system that geometrically allows for control of rate of exposure, sorption, and exchange of material in a continuous or semicontinuous manner.

15. In the sorbent and mercury removal process outlined in paragraphs above, the bromine reagents promote metal oxidation activity by creating cationic or radical character on the carbon edge structure that attracts mercury atoms and extracts electrons from said mercury atoms, resulting in oxidized mercury, which is more easily captured on a sorbent. A similar mechanism applies to oxidation and capture of reduced arsenic and other pollutant species.

PAC ET AL. EXHIBIT 1019
Page 2330

The invention relates to the process for the removal of mercury and other pollutant species from gas streams generated during the burning of fossil fuels, such as in a coal-fired utility or synthesis gas from gasification facilities. This removal process would utilize a sorbent and/or a combination of additives to remove pollutants from the gas stream, which are at the same time interacting with other gas components that result in poisoning or deactivating the sorbent and reducing its capacity or reaction rates with the targeted pollutant species. The present invention provides a cost-effective way to capture the pollutants by utilizing exceptionally active carbon sorbents and promoting mercury sorbent surface reactions, containing a bromide form of the carbon, that capture mercury with high kinetic chemisorption (oxidation) activity, so that capture can occur during contact times of seconds or less. The sorbent does not require in situ activation (induction period) in the gas stream to achieve high activity as do conventional activated carbon sorbents. The reactivity of the sorbent toward the pollutants and the sorption capacity can be regenerated, recycled, and reused.

Burning fossil fuels generates a flue gas that contains mercury (and other trace elements) that was in the coal, plus oxides of sulfur and nitrogen (acid gas emissions) and particulates whose release to the environment must be controlled by use of sorbents, scrubbers, filters, precipitators, and other removal technologies. While control of other elements and/or flue gas pollutants may apply, the discussion provided is focused on mercury. Initially, mercury is released in the elemental form during combustion/gasification, but downstream of the boiler, in the ducts and stack of the combustion system, part of the elemental mercury is oxidized. The amount oxidized depends on the amount of acid gases present in the flue gas and other factors. Amounts of mercury vary with the coal, but a typical concentration of mercury in the stream of combustion gas is about 5 parts per billion (ppb). A pound of mercury or more per day may be emitted in some utilities.

Discussion of Sorbent Technologies

PAC ET AL. EXHIBIT 1019
Page 2331

Several types of mercury control methods for flue gas have been investigated, including injection of fine sorbent particles into a flue gas duct and passing the flue gas through a sorbent bed. Fine-particle injection sorbents include activated carbon, metal oxide sorbent, sodium sulfide particles (for example, see U.S. Patent 6,214,304), and basic silicate or oxide sorbents (for example, see the Ghorishi reference (Ghorishi,B.; Gullet, B.K. Waste Manage Res. 1993, 16, 582). and Lancia references). When particle injection is employed, the mercury chemisorbed to the sorbent particle is removed from the gas stream in a bag house or ESP and collected along with ash particulates (for example, see U.S. Patents 4,889,698, 4,956,162, 5,672,323, 5,827,352, 6,027,551, and 5,505,766). The sulfide and basic silicate and oxide particles are effective only for the oxidized mercury, and the metal oxide sorbents exhibit slower capture kinetics than the carbon particles. Additionally, injection of fine carbon particles into the flue gas stream has been only partially successful in removing mercury, especially elemental mercury, where effective removal of approximately 60% was attained with a baghouse to collect carbon and ash. Even lower removal rates have been observed when using an ESP to collect the carbon, since the contact time of the carbon with the gas is very short.

A major problem with existing carbon injection systems is that the sorbent is initially unreactive, and only after exposure to the flue gas for about 20 minutes does the seasoned sorbent become effective and provide capture of 60% of the mercury in the gas. Consequently, these sorbents must be used in large amounts (high sorbent-to-mercury ratios) to effectively capture the mercury. These sorbents can be relatively expensive and cannot be easily separated from the ash, regenerated and reused. The collection of carbon in the ash also creates solid waste disposal problems, and the spent sorbent may contaminate the collected ash for use in various applications.

Use of Halogens in Mercury Capture

Methodologies for using halogens for the treatment of flue gas have not previously been effective. Halogen is defined as a member of the very active

PAC ET AL. EXHIBIT 1019
Page 2332

elements comprising Group VII-A of the periodic table. In the molecular elemental halogen form, including F_2, Cl_2, Br_2, and I_2, the reaction with elemental mercury is not fast enough to result in the formation of oxidized mercury in a coal combustion flue gas with conventional ash control technology. The atomic elemental halogen form, which includes F atom, Cl atom, Br atom, and I atom, is about a million times more reactive to mercury, but the concentrations of these forms are extremely low, and also, therefore, cannot result in oxidation of mercury in a utility flue gas.

A halide is a compound formed from reaction of a halogen with another element or radical. In general, the halide compounds are normally very much less reactive than the molecular halogens, having expended their high chemical potential in forming the low energy halide. The halide is considered a reduced form and cannot therefore oxidize anything by itself. It is for this reason that it is not obvious that a halide-halogen treated activated carbon would be effective at oxidizing elemental mercury and provide effective capture of elemental mercury. In fact, for tests with salts, analytical data show the addition of bromine to an activated carbon or carbon black or soot does form a compound by reacting with the unsaturated groups on the carbon. By applying x-ray photoelectron spectroscopy, it has been determined that bromine or HBr added to carbon black forms chemical compounds within a carbon structure.

A body of theory has been developed from scientific evidence to explain the nature of the promotion effect of the bromine compounds. This principle is illustrated in FIG. 2, which in step 1 shows the reaction of the hydrogen bromide with the unsaturated structure of the activated carbon. This may be a carbene species on the edge of the graphene sheets structures of the carbon. Molecular bromine or a bromine compound reacts to form a similar structure, with a positive carbon that is active for oxidizing the mercury.

We now teach that the formation of the new bromide compound with carbon increases the reactivity of the carbon forms toward mercury and other pollutants. The resulting bromide compound is uniquely suited to facilitate oxidation of the mercury. The effectiveness of the oxidation results from the promotion effect of the halide exerted on the developing positive charge on the mercury during the

PAC ET AL. EXHIBIT 1019
Page 2333

oxidation, known in the chemical art as a specific catalytic effect. Thus, as the mercury electrons are drawn toward the positive carbon, the halide anion electrons are pushing in from the other side, which stabilizes the positive charge developing on the mercury and lowers the energy requirement for the oxidation process. Bromide is especially reactive, owing to the highly polarizable electrons in the outer 4p orbitals of the ion. Thus, adding HBr or Br_2 to the carbon forms a similar carbon bromide, in which the positive carbon oxidizes the mercury with the assistance of the bromide ion.

Prior Art Publications

The earliest patents that relate to mercury capture on a sorbent are actually not for flue gas mercury control but for capture of mercury from air or other gas mixtures on a carbon or other sorbent. These patents were based on a model that recognized the affinity of halogens for mercury, rather than the formation of a reactive carbon. These patents are discussed below according to the type of halogen used for impregnation.

One patent that teaches a halogen impregnation (Stock, U.S. Patent 1,984,164, issued in 1934) describes the use of activated carbon or other solid impregnated with a halogen for removing Hg from air. The impregnation method is not specified. This seems to be the most general claim with respect to halogen impregnation. All the statements and claims appear to refer to halogen or iodine, but the patent does not appear to address bromides or other halides or bromide compounds or even specifically iodide or an iodine compound. The only example in the description is iodine impregnation. The patent also is restricted to air systems and did not pertain to flue gas systems with reactive acid gases. The description did not assume that the iodine formed a reactive carbon species.

Japanese Patent JP 49-43197 describes the treatment of Hg-contaminated electrolysis cell gas using a metal iodide salt on a support. A similar treatment using a resin impregnated with a metal iodide is described in JP 50-6438. These patents do not appear to represent a carbon bromide compound as specified in this patent application.

PAC ET AL. EXHIBIT 1019
Page 2334

Another early patent (Hilgen, U.S. Patent 3,849,267, issued in 1974) describes a method for Hg removal from a gas which claims mixing molecular chlorine (Cl_2) with the gas to be cleaned and passing it through a nonporous sorbent such as glass wool and NaCl (not carbon). This was evidently not an obvious extension of the Stock patent, since a halogen was introduced as part of the gas phase being cleaned.

A later patent (deJong, et al., U.S. Patent 4,196,173, issued in 1980) describes a method for Hg removal in air which claims using a bed of activated carbon impregnated with halogen-only Cl_2 is specified in the other claims and examples, and it is prepared by flowing the Cl_2 stream through a carbon bed.

An improved sorbent for mercury in air was patented by Revoir and Jones (U.S. Patent 3662523, issued in 1972), in which ICl and ICl_3 vapors were impregnated into the activated carbon. No explanation of the increased activity was provided. Since these compounds are interhalogen compounds, the patent did not infringe Stock.

U.S. Patent 5,891,324 describes an activated carbon containing an acid (HCl, H_2SO_4, or H_3PO_4) for the removal of mercury contained in a liquid phase, such as would occur in a process steam in the oil industry. In this case, the model presented was that mercury is adsorbed from the liquid into the solid carbon phase at relatively low temperatures.

In U.S. Patent Application 2004/0003716, a method is described for removing mercury from a combustion gas. This method employs an exposure of a finely powdered activated carbon to a molecular bromine gas at an elevated temperature or to HBr to produce a sorbent with good mercury removal ability when injected into the flue gas duct. The model for the efficacy of the Nelson sorbent is not clearly stated, so it can be presumed that the reasoning for using bromine is the simple premise that some bromine form will help capture the mercury, as does iodine and chlorine. The methods for incorporation of the bromine in the Nelson application are not the same as with the present invention, and the Nelson method will not produce the identical carbon bromide species that are obtained in the art described in this application. The Nelson method lacks many of the features

PAC ET AL. EXHIBIT 1019
Page 2335

described in this application that impart exceptional activity to the sorbent in a convenient way, for example, the addition of smaller amount of a second more powerful promoting agent, the use of facile solvent systems, including aqueous bromine, and the use of in-flight bromine treatment. Additionally, the patent application does not mention regeneration, recycling, or reuse, or the use of moving contactors or larger particle size to facilitate sorbent-ash separation.

Embodiments of the Invention.

A sorbent that is initially very reactive in oxidizing mercury can be used in very small amounts to achieve high capture efficiencies, thus lowering operation costs and lessening the disposal problem. In addition, further disposal reduction is made possible by recycling and reusing the sorbent that is produced using this technology. The time interval for the mercury and sorbent to interact in a flue gas duct and the subsequent collection of the mercury on the sorbent and ash may be very short- only seconds. This requires the sorbent to have high capacity and be very reactive toward mercury. A sorbent can be utilized in a very finely powdered form (e.g., 1-10 μm) to minimize mass transfer limitations. But, again, the reactivity should be very high to capture all of the mercury encountered by the fine particles. One feature of this invention is the process to prepare a sorbent containing a bromide compound formed on the carbon structure that provides a sorbent that is highly active on initial contact with the mercury contaminated gas stream, which allows for effective capture of the mercury.

One possible way to do this is to chemically combine molecular bromine from solution with activated carbon (edge sites). X-ray photoelectron spectroscopy established that the addition of bromine formed a chemical compound in the carbon structure. Thus, the sorbent does not represent a molecular bromine halogen form but a new chemically modified carbon structure. This may not occur with the less reactive iodine, where an I_2- molecular complex can exist on the carbon basal plane. In the bromine case, it is actually the carbon that oxidizes the mercury. Thus, an entirely new model is presented for the reactivity of the bromine-treated carbon with mercury. The reactive carbon form can be generated by the addition of bromine,

PAC ET AL. EXHIBIT 1019
Page 2336

hydrogen bromide, or combinations of bromine and other elements as described herein. Chlorine treatment resulted in lower-activity carbons because the chloride anion was less effective in promoting the oxidation by stabilizing the developing positive charge on the mercury in the transition state for oxidation. Based on this model, several innovative, inexpensive, activity-enhancing features have been developed.

It has been demonstrated that addition of an optional second component, in addition to the bromine, results in improved reactivity and capacity for the sorbent, exceeding that of both the untreated carbon and the brominated carbon. The second compound comprises either a second halogen or a compound from a second halogen, such as HBr. Thus, in addition to having a reactive carbon form present, the second component generates a Lewis base with greater ability to stabilize the developing positive charge on the mercury. Thus the second component is an element with more polarized electrons (4p and 5p).

Furthermore, we demonstrated that the sorbent can be readily treated with any combination of bromine and the second component in-flight using vapors of these components contacting the very fine carbon particles dispersed in air or other gas stream that conveys the particles to the flue gas duct. There is no particular temperature requirement for this contact. This technology is very simple to implement, so it will result in a great cost savings to the utility using this technology for mercury capture.

A unique, nonobvious technique for preparation of the treated carbon is through combining the treatment system with the carbon injection system at the end-use site. With this technique, the halogen is introduced to the carbon-air mixture in the transport line (or other part of the sorbent storage and injection system). Benefits over current concepts to treat sorbents off-site include the following:

- Capital equipment costs at a treatment facility are eliminated.
- Costs to operate the treatment facility are eliminated.
- There are no costs for transporting carbon and additive to a treatment facility.
- This process uses existing hardware and operation procedures.

PAC ET AL. EXHIBIT 1019
Page 2337

- This technology ensures that the sorbent is always fresh, and thus, more reactive.
- No new handling concerns are introduced.
- There are no costs for removing carbon from treatment system.
- This process allows rapid on-site tailoring of additive-sorbent ratios in order to match the requirements of flue gas changes, such as needed when changing fuels or reducing loads, thus further optimizing the economics.
- This technology reduces the amount of spent sorbents that are disposed.

With the foregoing and other features in view, there is provided, in accordance with the invention, a process for preparing and regenerating carbon sorbents whose activity for mercury capture is promoted by the addition of bromine to the carbon structure.

The invention applies to use of a sorbent in a powdered form that has been injected into a flue gas stream before or after ash particulates have been removed. Examples of the composition of the sorbent are a powdered modified activated carbon prepared by adding Br_2 or HBr plus a second optional component. Alternatively, the sorbent is on a moving contactor consisting of particles or fibers containing the compositions listed in the previous sentence. Either type can be regenerated; the poisoning contaminants from the flue gas are removed and an inexpensive promoting agent added to restore mercury sorption activity. This process of promoting the activity of the carbon itself contrasts with the earlier, more expensive art of adding a reagent (such as peroxide, gold, triiodide, etc.) to the sorbent. The activated carbon sorbent treated with bromine and/or the other components is noncorrosive.

Detailed examples of sorbent regeneration techniques are described in co-pending, commonly-owned PCT patent application No. PCT/US04/12828, titled "PROCESS FOR REGENERATING A SPENT SORBENT", which is incorporated by reference herein.

Although the invention is described herein as a sorbent material, it is nevertheless not intended to be limited to the details described, since various modifications and structural changes may be made therein without departing from

PAC ET AL. EXHIBIT 1019
Page 2338

the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific exemplary embodiments.

FIG. 11 is a block diagram illustrating the use of the invention in a coal fueled facility. Of course, the invention can also be used in any other desired type of facility. FIG. 11 shows a boiler for burning pulverized coal. The facility utilizes various devices to clean the exhaust of the boiler. In this example, a baghouse or ESP is used to collect particulates in the exhaust. A scrubber and sorbent bed are also used to remove undesired constituents from the flue gas stream, before being fed to the stack. In the example shown, the sorbent is injected into the flue gas after the boiler. The additive can be injected where desired (e.g., before, after, or within the boiler).

Another advantage of the present invention relates to the use of a feedback system to more efficiently utilize the invention. Where possible, the mercury control technology of the present invention will utilize measurement of mercury emissions as feedback to assist in control of the sorbent injection rate. Tighter control on the sorbent levels in this way will ensure mercury removal requirements are met with the minimal sorbent requirements and therefore the associated costs will be minimized. In one example, the emissions are measured at the stack.

Carbon Sorbent

Reactions of halogens and acidic species with the basic binding sites on the activated carbon sorbent create sites for oxidizing mercury. Other metal ions, such as boron, tin, arsenic, galium, Sb, Pb, Bi, Cd, Ag, Cu, Zn, or other contaminants, will also react with the oxidation sites generated on the carbon.

According to our model, adding the bromine from the bromine reagent or a proton from a hydrogen halide acid to a basic carbene site on the carbon edge structure forms a carbocation that accept electrons from the neutral mercury atom forming the oxidized mercury species that is bound to the sorbent surface. The

PAC ET AL. EXHIBIT 1019
Page 2339

reactive site may also generate reactive bromine radicals or carbon radicals at the active sites on the carbon. Thus, the activated carbon serves to stabilize the bromine, yet provides a highly reactive bromine- containing reagent that can oxidize the mercury and promote its capture on the activated carbon. The sorbent that contains bromine is expected to be more reactive than the corresponding sorbent containing chlorine and much less expensive than the sorbent containing iodine.

A bench-scale procedure based on the above description was used to test the initial activities and capacities of several powdered carbon sorbents, including the bromine-containing activated carbons prepared from a commercially available sorbent and an aerogel carbon film sorbent, as well as the original precursor carbons for comparison. Bromine-treated carbons were prepared by impregnation of the powdered activated carbon precursors in a stirred solution of bromine in carbon tetrachloride or methylene chloride, or alternatively, in an aqueous solution of HBr, followed by drying in air at ambient temperature and drying in an oven at 100°C in air or nitrogen. Bromine-treated carbons were also prepared by impregnating bromine from the gas phase by passing the gas through a rotating dry bed of the activated carbon precursor. Adding a second component to the solution was demonstrated to improve the capacity of the sorbent.

The carbons were initially tested in a heated bed, where a synthetic flue gas stream containing elemental mercury (11 $\mu g/m^3$) was passed through the bed. Concentrations of total and elemental Hg in the effluent gas were determined using a Sir Galahad mercury CEM. The powdered sorbent was supported on a quartz filter during the test, and the other sorbents were tested as a triple layer.

A comparison of the original commercial-grade powdered carbon sorbent with the sorbent after it has been treated with 0.1 N HBr, collecting the powder by centrifugation and drying, revealed that the mercury capture activity is increased from an initial capture efficiency of about 50% of the Hg in the inlet to 100% capture. A comparison of the sorbent after subsequent regeneration with HBr indicates that it not only captures mercury at the same level as before (100% capture) but is enhanced such that its capacity is prolonged by several minutes.

PAC ET AL. EXHIBIT 1019
Page 2340

Similar results were obtained with the carbon film and carbon fiber sorbents by treatment with molecular bromine in solution or in dry beds as described above.

An activated carbon sorbent was prepared by treating the carbon by impregnating molecular bromine from a gas composition containing molecular bromine by flowing the gas through a liquid bromine reservoir in series with a fluidized bed of ebullated bed of the carbon. The amount of bromine taken up by the carbon ranges (in one example) from <1 to about 30 g per 100 g of activated carbon, depending on the proportions used.

In one exemplary test conducted at a facility fired with lignite coal, the flue gas phase mercury (elemental) concentration was between 10 and 11 $\mu g/m^3$. The ash and injected carbons were collected in the baghouse at 350E to 375EF. Injection of commercial-grade activated carbon powder (untreated) at a rate of 1.0 lb/Macf resulted in mercury effluent concentrations of 3.8-4.2 $\mu g/m^3$ (representing 62%-58% removal of the mercury from the gas), and at 2.0 lb/Macf, gave 74%-71% removal. Injection of the bromine-treated carbon at 1.0 lb/Macf resulted in 73%-69% removal and at 2.0 lb/Macf gave 86%-84% removal. Thus, a significant increase in the mercury capture was exhibited during use of the bromine-treated carbon.

Addendum: Other References to Hg Sorption

Sorbent Beds with Particulate Removal

Carbon beds have also been utilized for mercury capture in flue gas. The German Patent 34 26 059 describes the use of a very thick carbon bed for treatment of flue gases containing polyhalogenated compounds. Although the system employed at Dusseldorf would also have the potential for Hg removal (for example, see the Streng reference), it is not very practical to use such a thick bed. Spent sorbent is burned and not regenerated. The carbons are not pretreated.

The GE-Mitsui-BF system (Tsuji, K.; Shiraishi, I.; Dague, R.F. Proceedings, Sixth International Symposium, Air & Water Management Assoc., New Orleans, LA, March 10-12, I993) employs a recirculating carbon bed, where mercury is removed along with acid gases (as ammonium salts) and the carbon is regenerated at high temperatures where ammonium sulfate is decomposed to SO_2 and N_2 and

PAC ET AL. EXHIBIT 1019
Page 2341

mercury is converted to the elemental form, which desorbs from the sorbent. Attrition of the sorbent results in a significant sorbent cost. The carbons are not pretreated.

Sorbent Injection After Particulate Removal

A process of injecting manganese oxide sorbent particles is described in U.S. Patent Application 2002/0150516. Regeneration is claimed by removal of spent oxide particles from the reaction zone and rinsing with dilute aqueous acid.

Sorbent Beds After Particulate Removal

Of particular interest in designing a mercury control process is to use the sorbent downstream of a particulate control device so the sorbent is not highly diluted with the ash particles. The sorbent could then be more easily regenerated and recycled. The prior art teaches several examples of this type of configuration and sorbent processing.

U.S. Patent 5,607,496 teaches the oxidation of mercury on a metal oxide sorbent bed and subsequent absorption to sorbent. The sorbent bed follows the particulate-removal equipment and, thus, the gas still contains the SO_x and NO_x, which react with the metal oxide sorbent to form the metal sulfates, which poison the bed. High temperatures are proposed to regenerate the bed. However, Hg is only partially removed from the sorbent at temperatures up to 500°C. The sorbents do not work effectively after regeneration using this technique; the problem may be that manganese sulfate formed during the sorption cycle does not completely decompose back to an active manganese oxide form.

U.S. Patent 6,383,981 describes a fixed MnO_2 or Fe_2O_3 bed for removal of Hg from a hydrocarbon stream. No regeneration method appears to be included.

A recent U.S. Patent application (2001/0003116) describes the regeneration of a plate or honeycomb material composed of transition metal oxides that was used for sorption of mercury in flue gas. The claimed process involves heating the sorbent in a reducing gas stream to remove poisons, followed by impregnation with a polyfunctional complex-forming reagent containing the catalyst active component

PAC ET AL. EXHIBIT 1019
Page 2342

to restore mercury capture capacity. The first of these steps can remove the mercury, but it is unclear whether it actually removes the sulfate poison. The second of these steps is rather expensive, because one is actually reconstituting the reagent on the sorbent

Porous beds containing a mercury oxidizing reagent on a solid support are described in several patents for removal of mercury from gas streams. These include peroxomonosulfate (for example, see U.S. Patent 4,786,483), triiodide or other mixed halogens (for example, see U.S. Patents 3,194,629; 3,662,523), or sulfur (for example, see U.S. Patents 3,194,629, 4,101,631, 4,708,853, 6,258,334). The reagent material is destroyed either by reaction with the flue gas during sorption or by attempts to regenerate the sorbent; there is no way to regenerate these sorbents, except by reimpregnation of the expensive reagent.

Amalgamating noble metals (gold, silver) on a suitable support can be regenerated by microwave heating (for example, see U.S. Patent 6,136,072), but they are expensive and not especially active for sorption in flue gas.

Hg Sorbents for Air or Natural Gas Treatment

Melkersson (U.S Patent 3786619) described a Hg sorbent comprising SeO_2 or SeS_2 for air treatment. This method did not appear to employ a carbon support or halide.

Yan (U.S. Patent 4814152) described a Hg sorbent comprising elemental sulfur and a metal catalyst on a carbon support. This method did not appear to employ a halide.

Attia (U.S. Patent 65080281) described a sorbent for mercury and a variety of other contaminants comprising an inorganic aerogel composition. This method did not appear to employ a carbon support or halide.

Following is a List of Various Background References:

Lancia, A.; Musmarra, D.; Pepe, F.; Volpicelli, G. *Combust. Sci. & Technol.* **1993,** *93,* 277.

Streng, S.; Kassebohm, B. *Fuel Proc. Technol.* **1994,** *39,431.*

PAC ET AL. EXHIBIT 1019
Page 2343

U.S. Patent 6,214,304 Rosenthal

U.S. Patent 4,889,698 Moller

U.S. Patent 4,956,162 Smith

U.S. Patent 5,672,323 Bhat.

U.S. Patent 5,827,352 Altman

U.S. Patent 6,027,551 Hwang

U.S. Patent 5,505,766 Chang

U.S. Patent 5,607,496 Brooks

U.S. Patent 6,383,981 Blankenship

U.S. Patent 4,786,483 Audeh

U.S. Patent 3,194,629 Dreibelbis, et al

U.S. Patent 4,101,631 Ambrsini, et al

U.S. Patent 3,662,523 Revoir

U.S. Patent 4,708,853 Matviya

U.S. Patent 6,258,334 Gadkaree

U.S. Patent 6,136,072 Sjostrom

U.S. Patent Application 2002/0150516

U.S. Patent Application 2001/0003116 Neufert

CLAIMS

1. A method for separating mercury from a mercury-containing gas, the method comprising:

combusting a mixture of coal and an additive, to form the mercury-containing gas, wherein the additive is chosen from halides, halogens, salts thereof, and combinations thereof;

adding a particulate sorbent material comprising activated carbon into the mercury-containing gas;

promoting at least a portion of the sorbent material by chemically reacting the sorbent material with the additive in the mercury-containing gas, to form a promoted sorbent material;

chemically reacting mercury in the mercury-containing gas with the promoted sorbent material, to form a mercury-sorbent; and

separating the mercury-sorbent from the mercury-containing gas.

2. The method of claim 1, further comprising mixing the additive and the coal before combusting the coal.

3. The method of claim 2, wherein the additive mixed with the coal is in a liquid.

4. The method of claim 3, wherein the liquid is a hydrocarbon, a chlorinated hydrocarbon, supercritical carbon dioxide, water, salt solution, or a combination thereof.

5. The method of claim 1, wherein the promoted sorbent material comprises active sites, wherein the active sites comprise halide anions bound to the activated carbon.

6. The method of claim 1, wherein the promoted sorbent material comprises active sites, wherein the active sites comprise carbocations bound to halide anions.

7. The method of claim 1, wherein chemically reacting the sorbent material with the additive in the mercury-containing gas comprises chemically reacting carbene species edge sites in the activated carbon with the additive.

8. The method of claim 1, wherein carbocations in the activated carbon of the mercury-sorbent accept electrons from mercury atoms of the mercury-sorbent.

9. The method of claim 1, wherein the additive is substantially in vapor form in the mercury-containing gas.

10. The method of claim 1, wherein the additive is chosen from Cl_2, HCl, sodium chloride, calcium chloride, and a combination thereof.

11. The method of claim 1, wherein the additive is chosen from Br_2, HBr, sodium bromide, calcium bromide, and a combination thereof.

12. The method of claim 1, wherein the additive is chosen from PBr_3, SCl_2, and a combination thereof.

13. The method of claim 1, wherein the additive is chosen from I_2, HI, sodium iodide, calcium iodide, potassium iodide, and combinations thereof.

14. The method of claim 1, wherein the activated carbon is chosen from powdered activated carbon, granular activated carbon, carbon black, carbon fiber, aerogel carbon, pyrolysis char, and combinations thereof.

15. The method of claim 1, further comprising adding an alkaline component to the mercury-containing gas, the alkaline component chosen from alkali elements, alkaline earth elements, alkali salts, alkaline earth salts, and combinations thereof.

PAC ET AL. EXHIBIT 1019
Page 2346

16. The method of claim 1, further comprising contacting at least one of the sorbent material and the promoted sorbent material with a mercury-stabilizing reagent chosen from S, Se, H_2S, SO_2, H_2Se, SeO_2, CS_2, P_2S_5, and combinations thereof.

17. The method of claim 1, further comprising contacting at least one of the sorbent material and the promoted sorbent material with a secondary component chosen from halogens, hydrogen halides, Group V halides, Group VI halides, and combinations thereof.

18. The method of claim 17, wherein the secondary component is chosen from halogens, halide salts, HI, HBr, HCl, and combinations thereof.

19. The method of claim 17, wherein the secondary component is chosen from I_2, HI, and combinations thereof.

20. A method for separating mercury from a mercury-containing gas, the method comprising:

combusting coal mixed with an additive, wherein the additive is chosen from halides, halogens, salts thereof, and combinations thereof, to form the mercury-containing gas;

injecting a sorbent material comprising activated carbon into the mercury-containing gas;

promoting at least a portion of the sorbent material by chemically reacting the sorbent material with the additive in the mercury-containing gas, to form a promoted sorbent material;

chemically reacting mercury in the mercury-containing gas with the promoted sorbent material, to form a mercury-sorbent; and

separating the mercury-sorbent from the mercury-containing gas;

wherein the coal and promoter are mixed at a location upstream of a combustion furnace where combustion occurs.

PAC ET AL. EXHIBIT 1019
Page 2347

Abstract

A promoted activated carbon sorbent is described that is highly effective for the removal of mercury from flue gas streams. The sorbent comprises a new modified carbon form containing reactive forms of halogen and halides. Optional components may be added to increase reactivity and mercury capacity. These may be added directly with the sorbent, or to the flue gas to enhance sorbent performance and/or mercury capture. Mercury removal efficiencies obtained exceed conventional methods. The sorbent can be regenerated and reused. Sorbent treatment and preparation methods are also described. New methods for in-flight preparation, introduction, and control of the active sorbent into the mercury contaminated gas stream are described.

PAC ET AL. EXHIBIT 1019
Page 2348

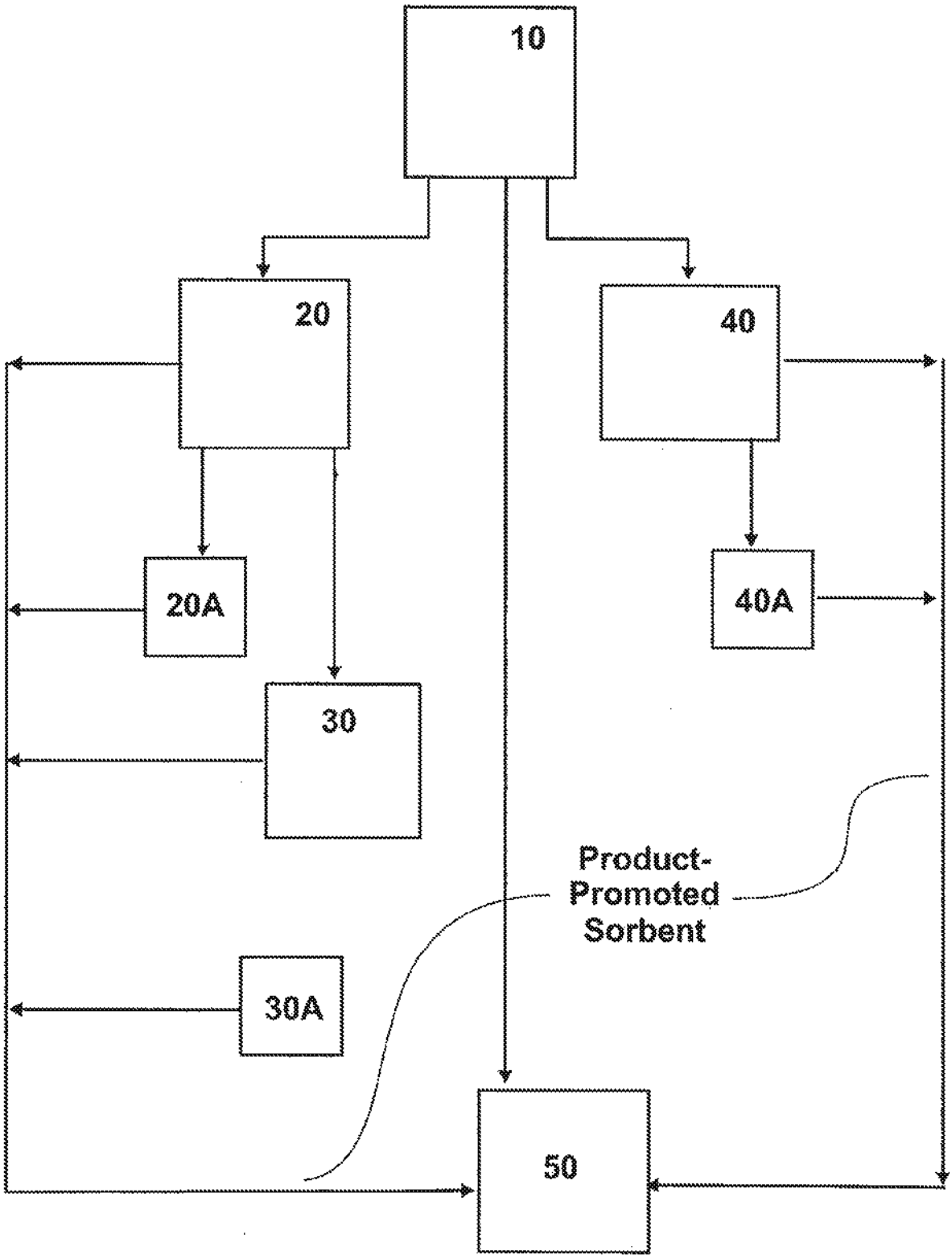


FIG. 1

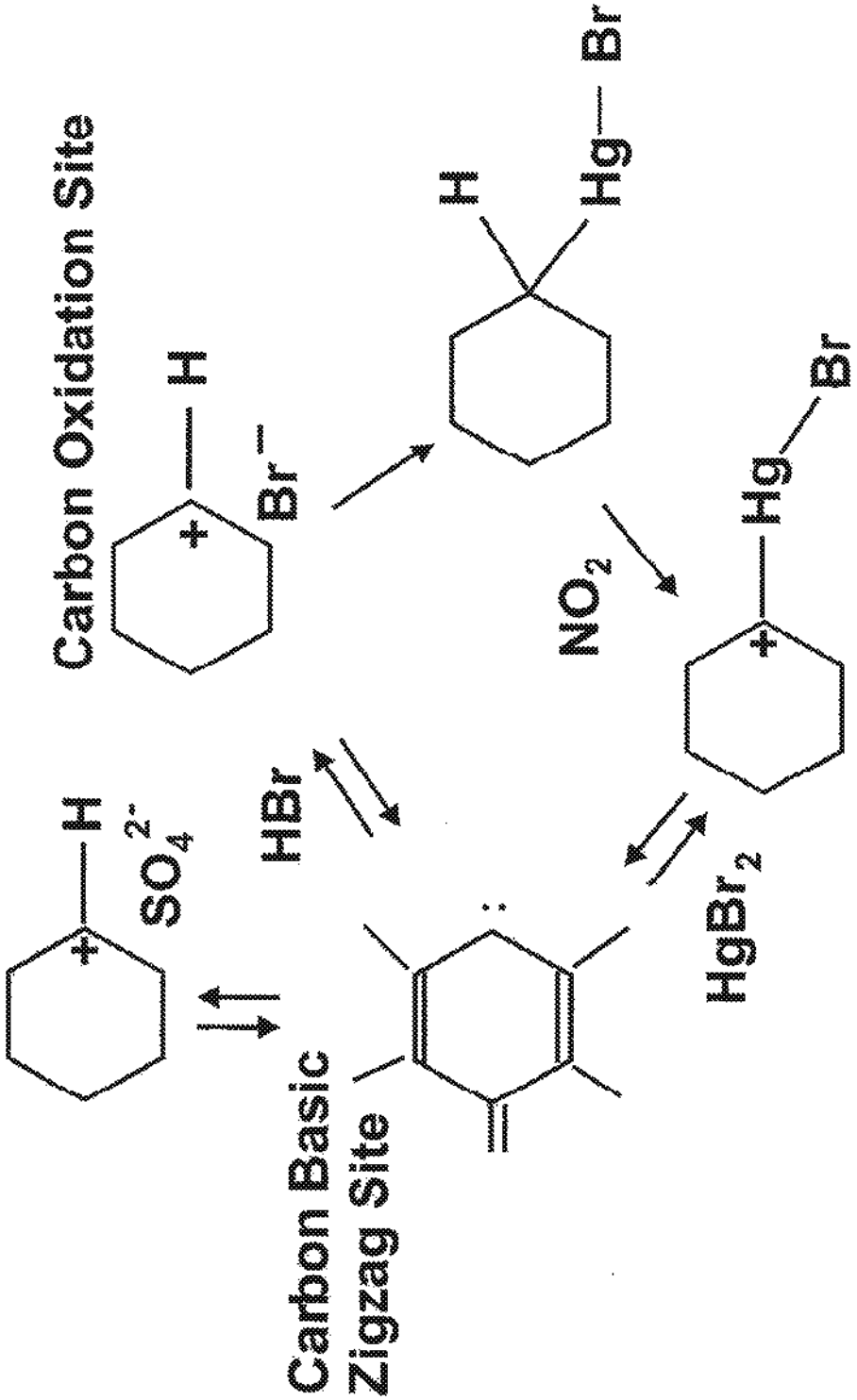

Carbon Oxidation Site
H
Br⁻
+
H
Hg—Br
NO₂
Hg—Br
+
HBr
HgBr₂
H
SO₄²⁻
+
Carbon Basic
Zigzag Site

FIG. 2

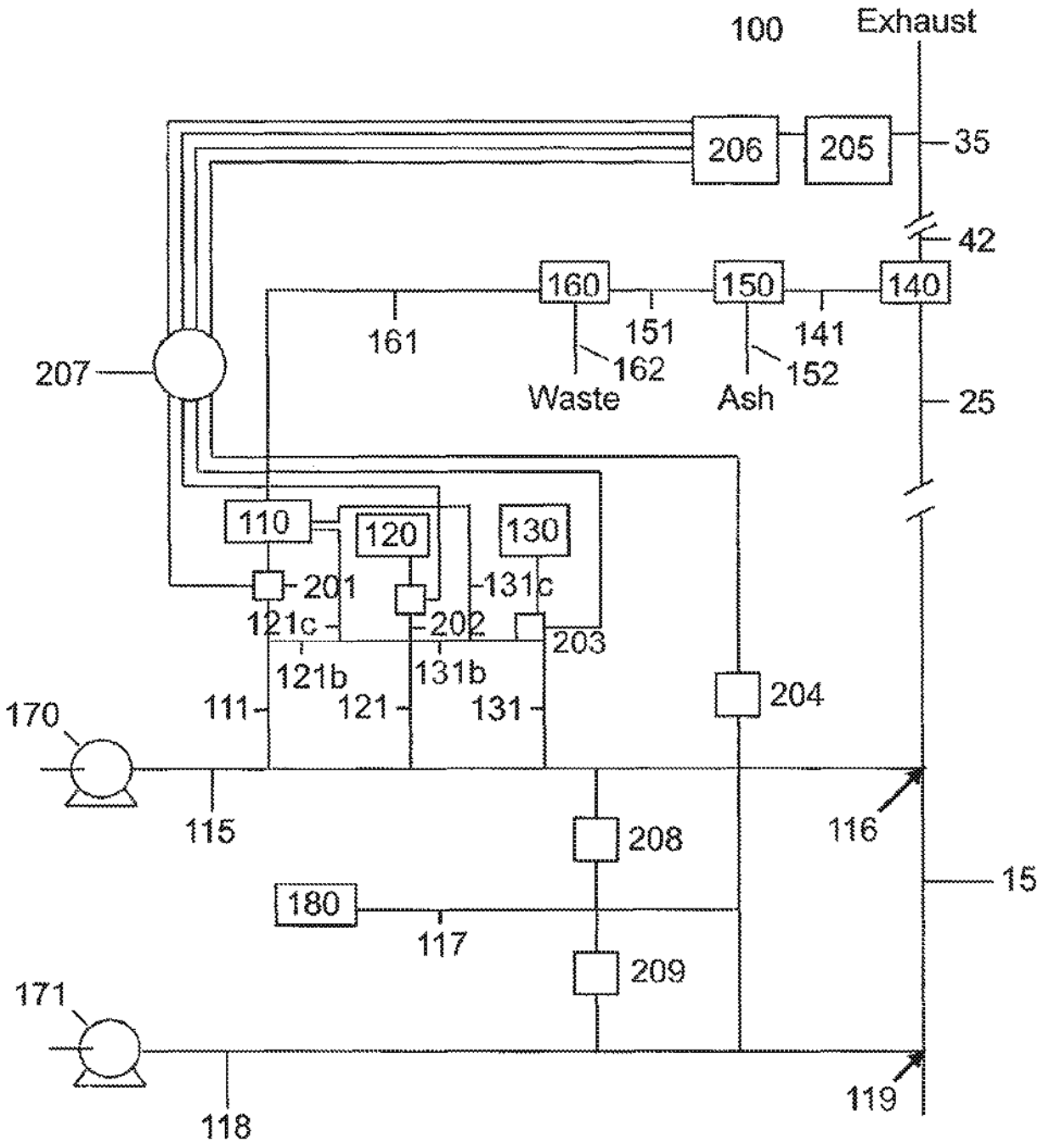

100
Exhaust
206
205
35
42
160
150
140
161
151
141
162
152
Waste
Ash
207
25
110
120
130
201
131c
121c
202
203
121b
131b
111
121
131
204
170
115
208
116
15
180
117
209
171
118
119

FIG. 3

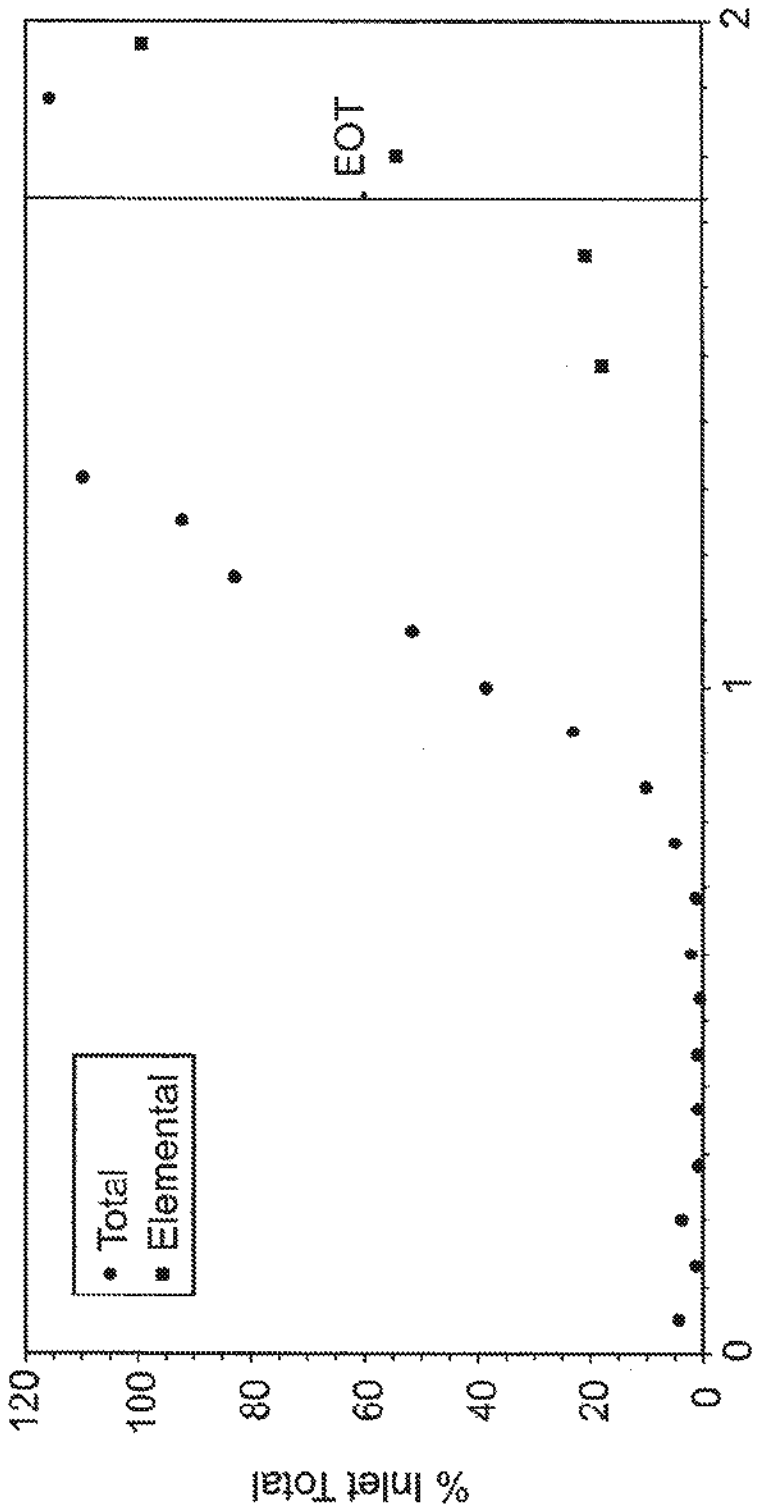

% Inlet Total
120
100
80
60
40
20
0
0
1
2
Time, hr
EOT
Total
Elemental

FIG. 4

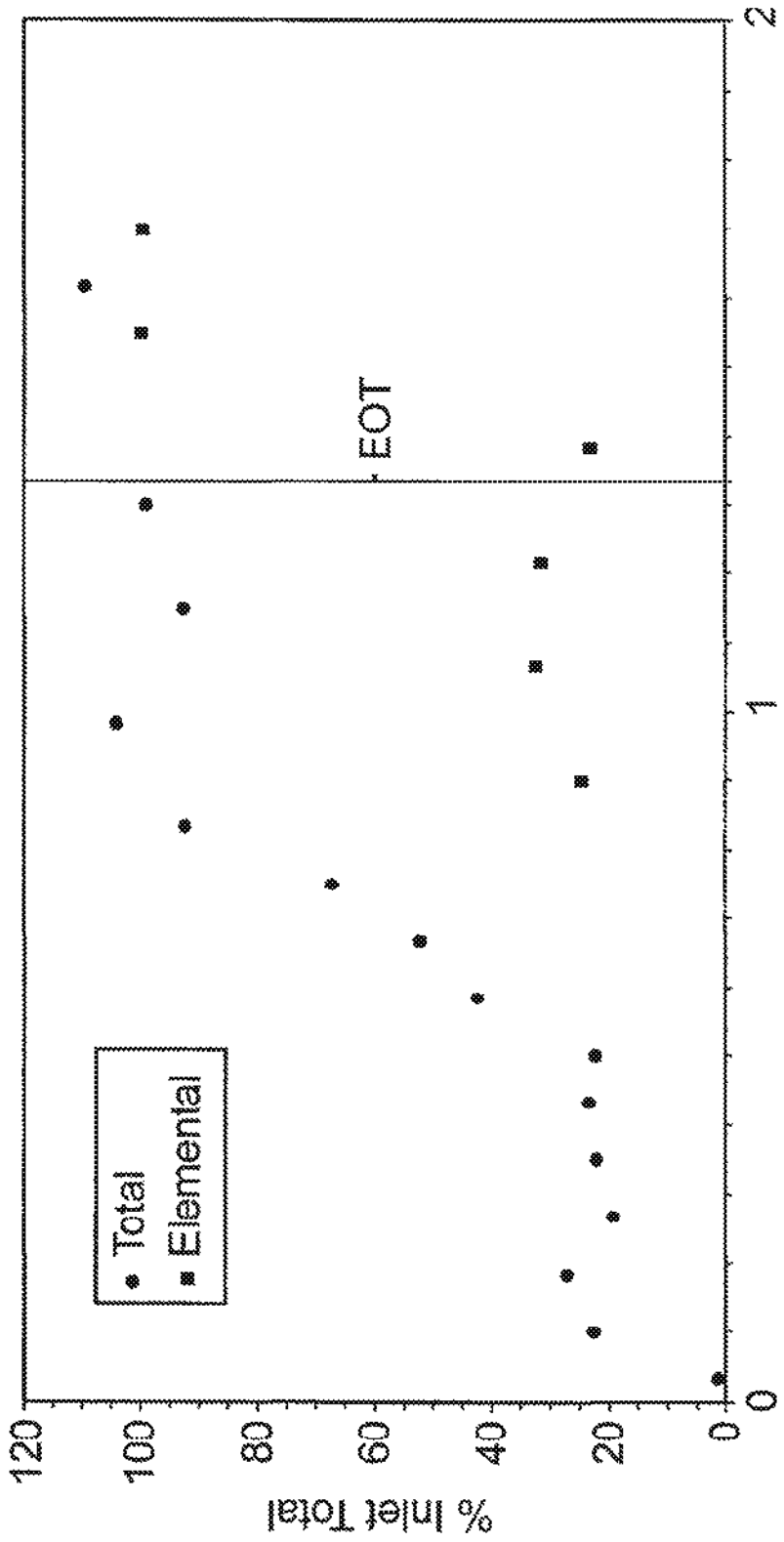

% Inlet Total
120
100
80
60
40
20
0
0
1
2
Time, hr
EOT
Total
Elemental

FIG. 5

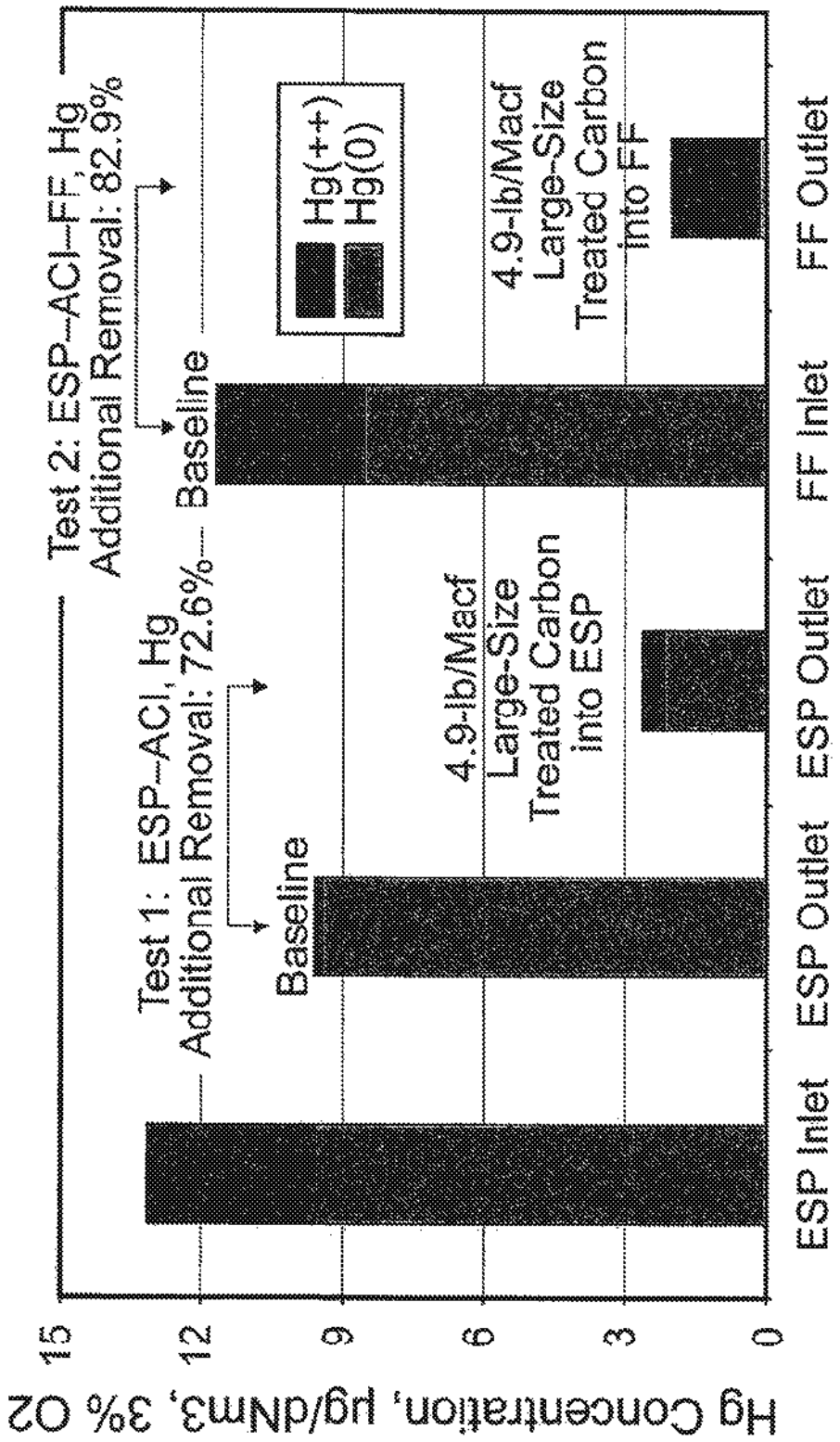

Hg Concentration, µg/dNm3, 3% O2
15
12
9
6
3
0
Test 2: ESP–ACI–FF, Hg
Additional Removal: 82.9%
Baseline
Test 1: ESP–ACI, Hg
Additional Removal: 72.6%
Baseline
Hg(++)
Hg(0)
4.9-lb/Macf
Large-Size
Treated Carbon
into ESP
4.9-lb/Macf
Large-Size
Treated Carbon
into FF
ESP Inlet
ESP Outlet
ESP Outlet
FF Inlet
FF Outlet

FIG. 6

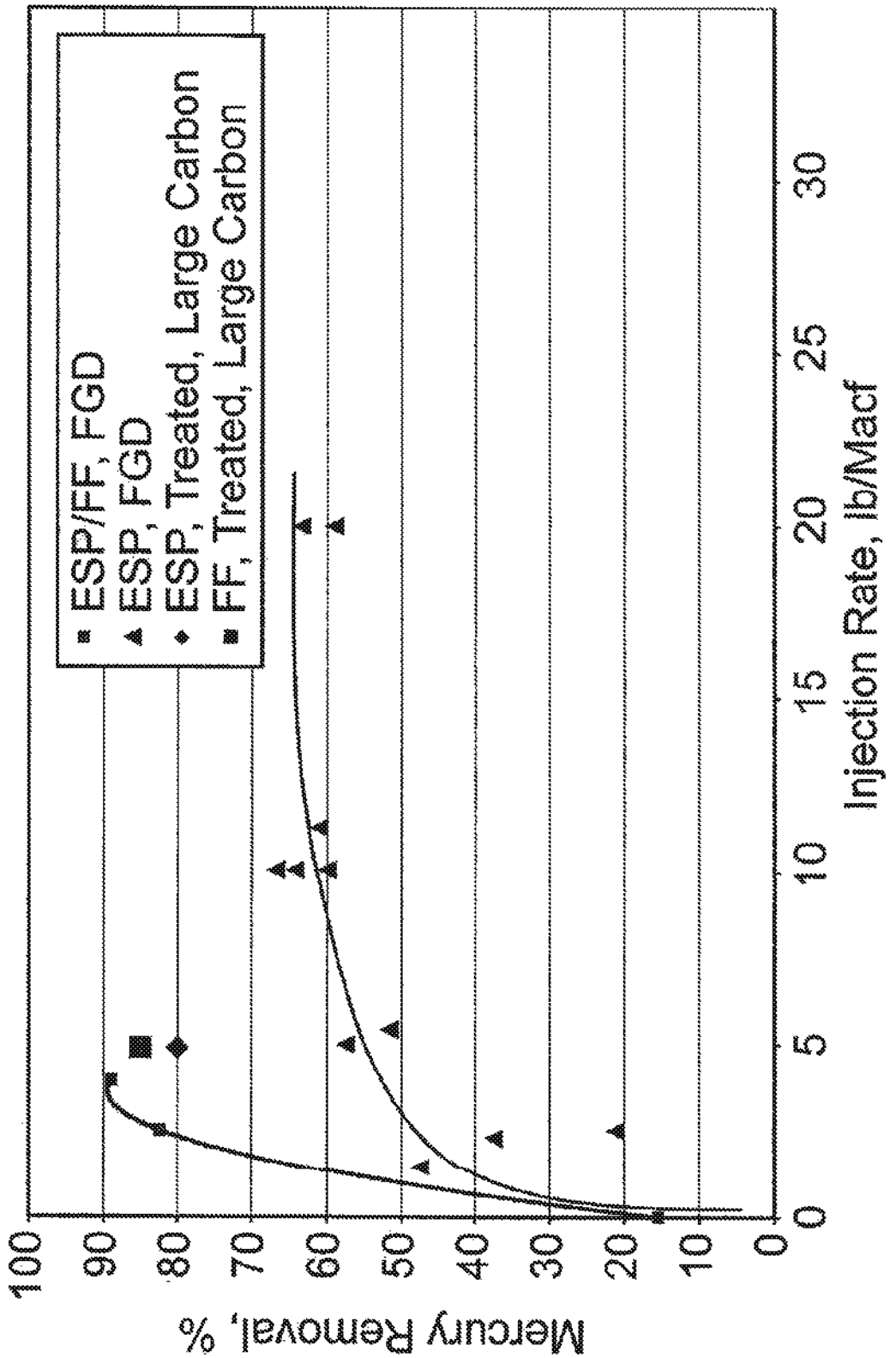

ESP/FF, FGD
ESP, FGD
ESP, Treated, Large Carbon
FF, Treated, Large Carbon
Mercury Removal, %
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
Injection Rate, lb/Macf

FIG. 7

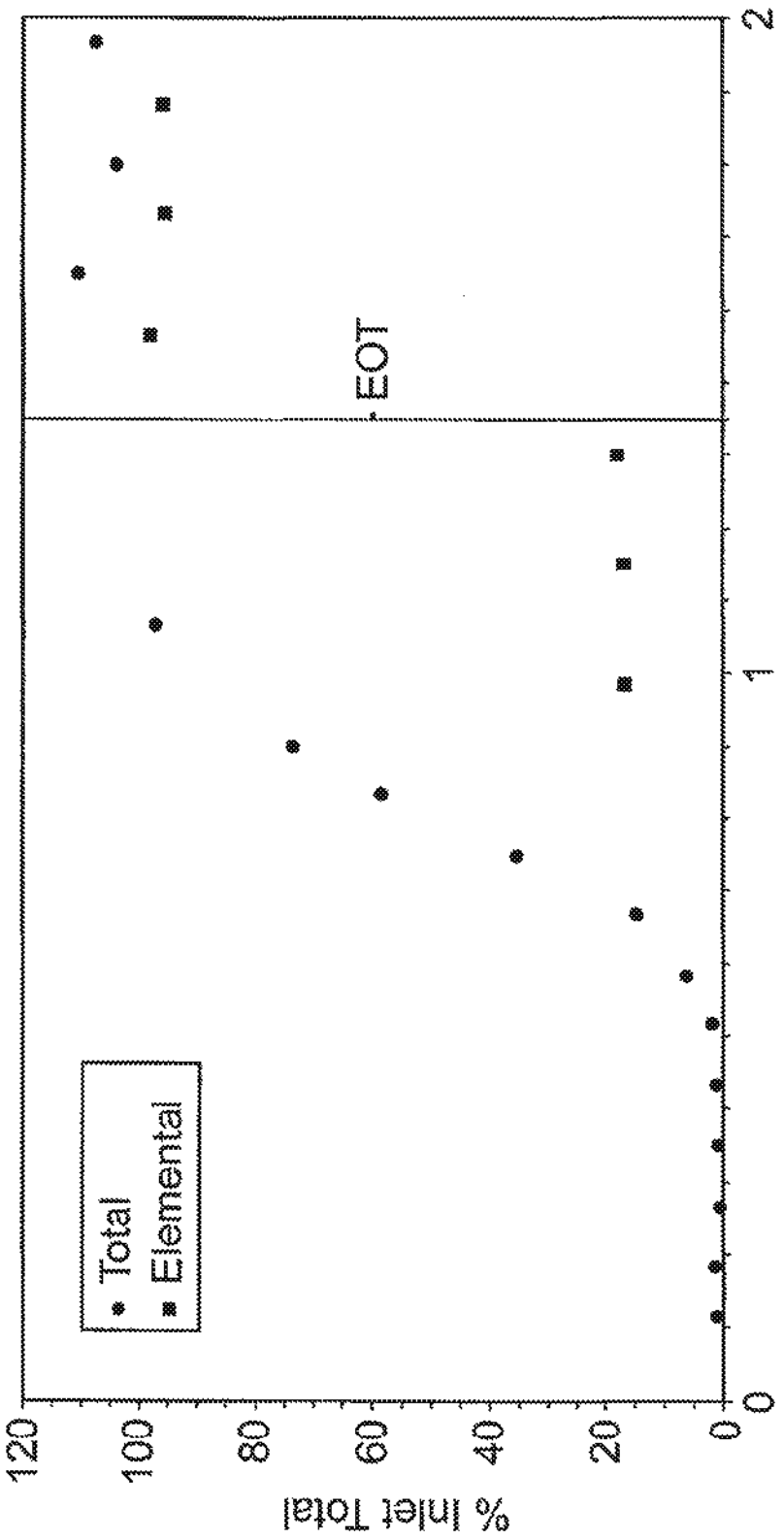

% Inlet Total
120
100
80
60
40
20
0
0
1
2
Time, hr
EOT
Total
Elemental

FIG. 8

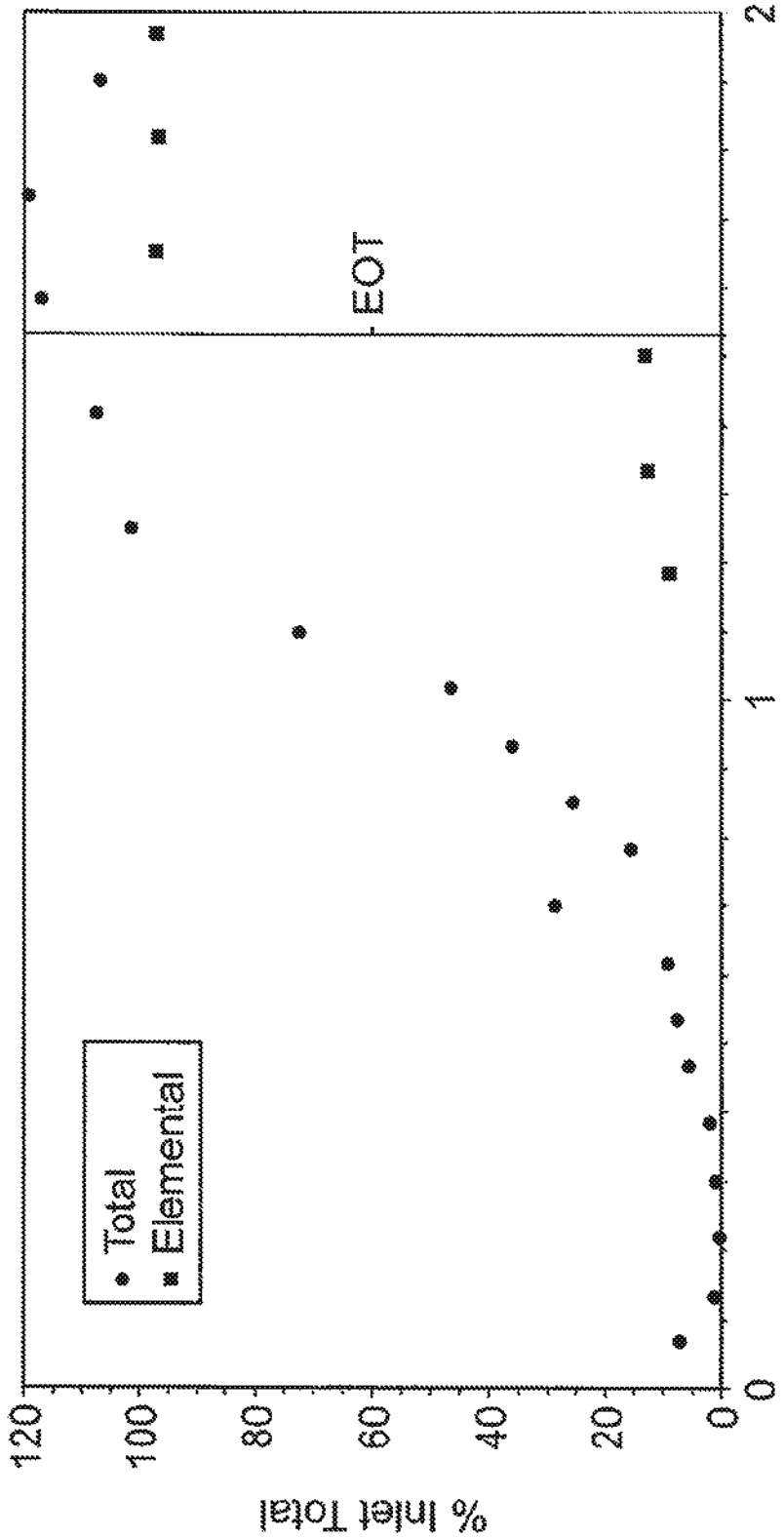

% Inlet Total
120
100
80
60
40
20
0
0
1
2
Time, hr
EOT
Total
Elemental

FIG. 9

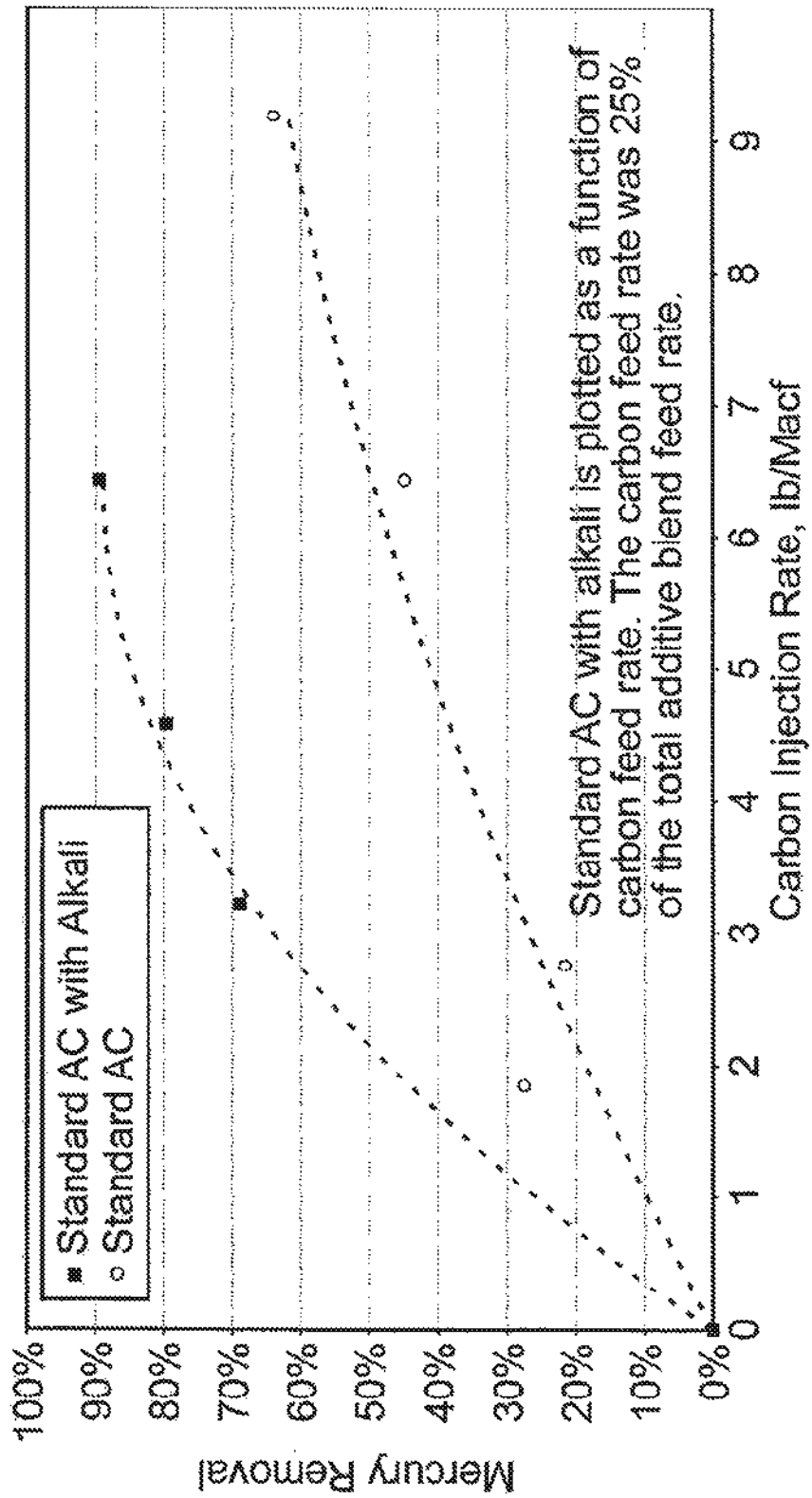

Standard AC with Alkali
Standard AC
Mercury Removal
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
0
1
2
3
4
5
6
7
8
9
Carbon Injection Rate, lb/Macf
Standard AC with alkali is plotted as a function of carbon feed rate. The carbon feed rate was 25% of the total additive blend feed rate.

FIG. 10

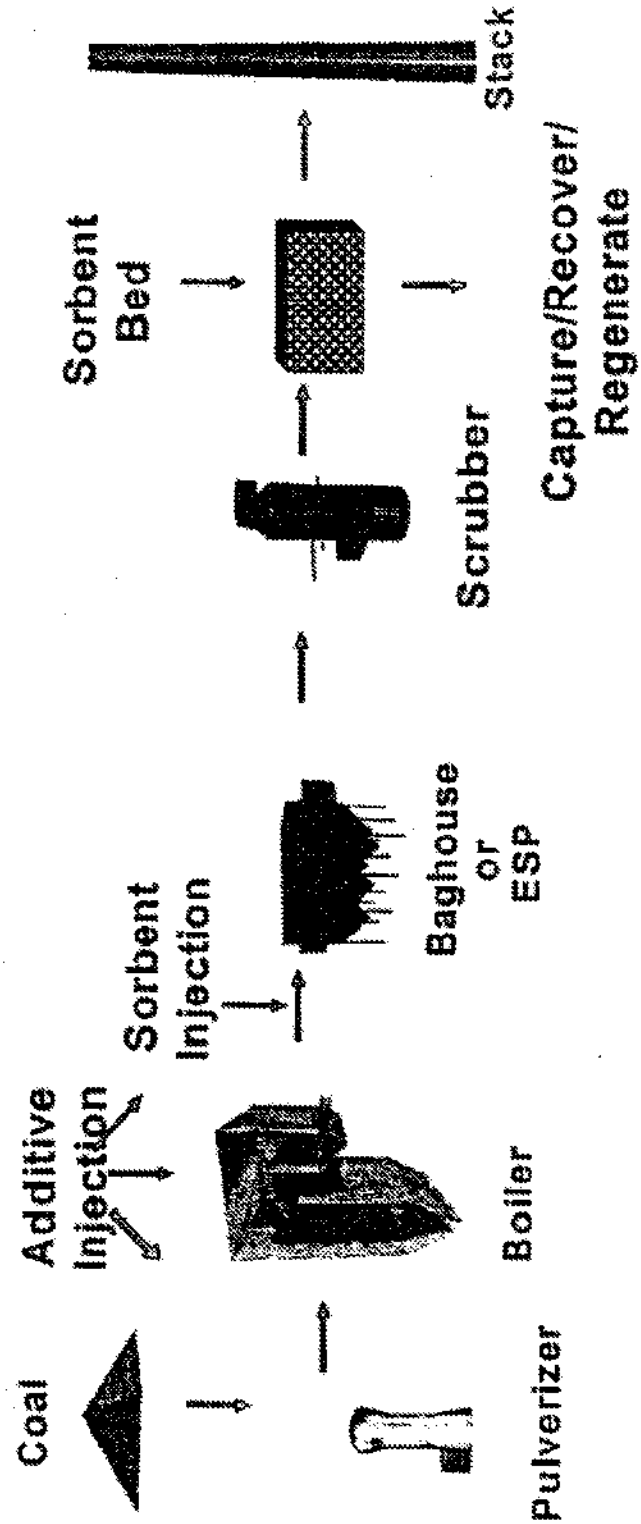

Coal
Pulverizer
Additive Injection
Boiler
Sorbent Injection
Baghouse or ESP
Scrubber
Capture/Recover/ Regenerate
Sorbent Bed
Stack

FIG. 11

Amended PTO/AIA/01 (06-12)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

As the below named inventor, I hereby declare that:

This declaration:

Is directed to: ☐ The attached application, or

☑ United States application or PCT international application number 13/966,758, filed on August 14, 2013.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR:

Inventor: Edwin S. Olson Date (Optional): _____

Signature: Edwin S. Olson

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 3 minutes to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

8338.095US5

Approved for use through 07/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

As the below named inventor, I hereby declare that:

This declaration is directed to: ☐ The attached application, or

☒ United States application or PCT international application number 13/966,768, filed on August 14, 2013.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR:

Inventor: Michael J. Holmes Date (Optional): Dec 26 2013

Signature:

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing this form, call 1-800-PTO-9199 and select option 2.

3334.005US1

Approved for use through 07/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☒ United States application or PCT international application number 13/966,768, filed on August 14, 2013.

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: John Henry Pavlish Date (Optional): _____

Signature: _____

Note: An application data sheet (PTO/SB/14 or equivalent), including either the entire inventive entity, must accompany this form. Use an additional PTO/AIA/01 form for each additional inventor.

This collection of information is required by 35 U.S.C. 115 and 37 CFR 1.63. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 1 minute to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

3338 0ESUSS

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Filer:	Jose M. Nunez/Megan Reed
Attorney Docket Number:	4820.001US9

Filed as Large Entity

Filing Fees for Track I Prioritized Examination - Nonprovisional Application under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY APPLICATION FILING	1011	1	300	300
UTILITY SEARCH FEE	1111	1	660	660
UTILITY EXAMINATION FEE	1311	1	760	760
REQUEST FOR PRIORITIZED EXAMINATION	1817	1	4000	4000
Pages:				
Claims:				
Miscellaneous-Filing:				
PROCESSING FEE, EXCEPT PROV. APPLS.	1830	1	140	140

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**5860**

Electronic Acknowledgement Receipt

EFS ID:	32568544
Application Number:	15974343
International Application Number:	
Confirmation Number:	1072
Title of Invention:	SORBENTS FOR THE OXIDATION AND REMOVAL OF MERCURY
First Named Inventor/Applicant Name:	Edwin S. Olson
Customer Number:	21186
Filer:	Jose M. Nunez/Megan Reed
Filer Authorized By:	Jose M. Nunez
Attorney Docket Number:	4820.001US9
Receipt Date:	08-MAY-2018
Filing Date:	
Time Stamp:	17:13:48
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$5860
RAM confirmation Number	050918INTEFSW00004554190743
Deposit Account	
Authorized User	

The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		SIGNED_4820_001US9_ApplicationPriorExam.pdf	4777424 646d47241e55720d3d973a32ee07c7f3be155a07	yes	85

Multipart Description/PDF files in .zip description

Document Description	Start	End
Transmittal of New Application	1	1
TrackOne Request	2	2
Application Data Sheet	3	10
Specification	11	67
Claims	68	70
Abstract	71	71
Drawings-only black and white line drawings	72	82
Oath or Declaration filed	83	85

Warnings:

Information:

2	Fee Worksheet (SB06)	fee-info.pdf	38494 73fb0830b92bf209b8e149810929eb5c7df58cb6	no	2

Warnings:

Information:

Total Files Size (in bytes):	4815918

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.