

US 20030206843A1

(19) **United States**

(12) **Patent Application Publication**
Nelson, JR.

(10) **Pub. No.: US 2003/0206843 A1**

(43) **Pub. Date: Nov. 6, 2003**

(54) **METHODS AND COMPOSITIONS TO
SEQUESTER COMBUSTION-GAS MERCURY
IN FLY ASH AND CONCRETE**

Publication Classification

(51) **Int. Cl.⁷ B01D 53/64**

(52) **U.S. Cl. 423/210; 423/460; 502/416**

(76) **Inventor: Sidney G. Nelson JR., Twinsburg, OH
(US)**

Correspondence Address:
HAHN LOESER & PARKS, LLP
TWIN OAKS ESTATE
1225 W. MARKET STREET
AKRON, OH 44313 (US)

(21) **Appl. No.: 10/430,721**

(22) **Filed: May 6, 2003**

Related U.S. Application Data

(60) **Provisional application No. 60/377,790, filed on May
6, 2002.**

(57) **ABSTRACT**

A method for removing mercury from a combustion gas in an exhaust gas system has the steps of providing a mercury sorbent; injecting the mercury sorbent into a stream of the mercury-containing combustion gas to enable mercury to adsorb onto the sorbent; and collecting and removing the sorbent from the combustion gas stream. The mercury sorbent is prepared by treating a carbonaceous substrate with an ozone-containing gas to increase the ability of the substrate to adsorb mercury. Concrete compositions with fly ash containing the mercury sorbents will have reduced interference with air-entraining-admixtures.

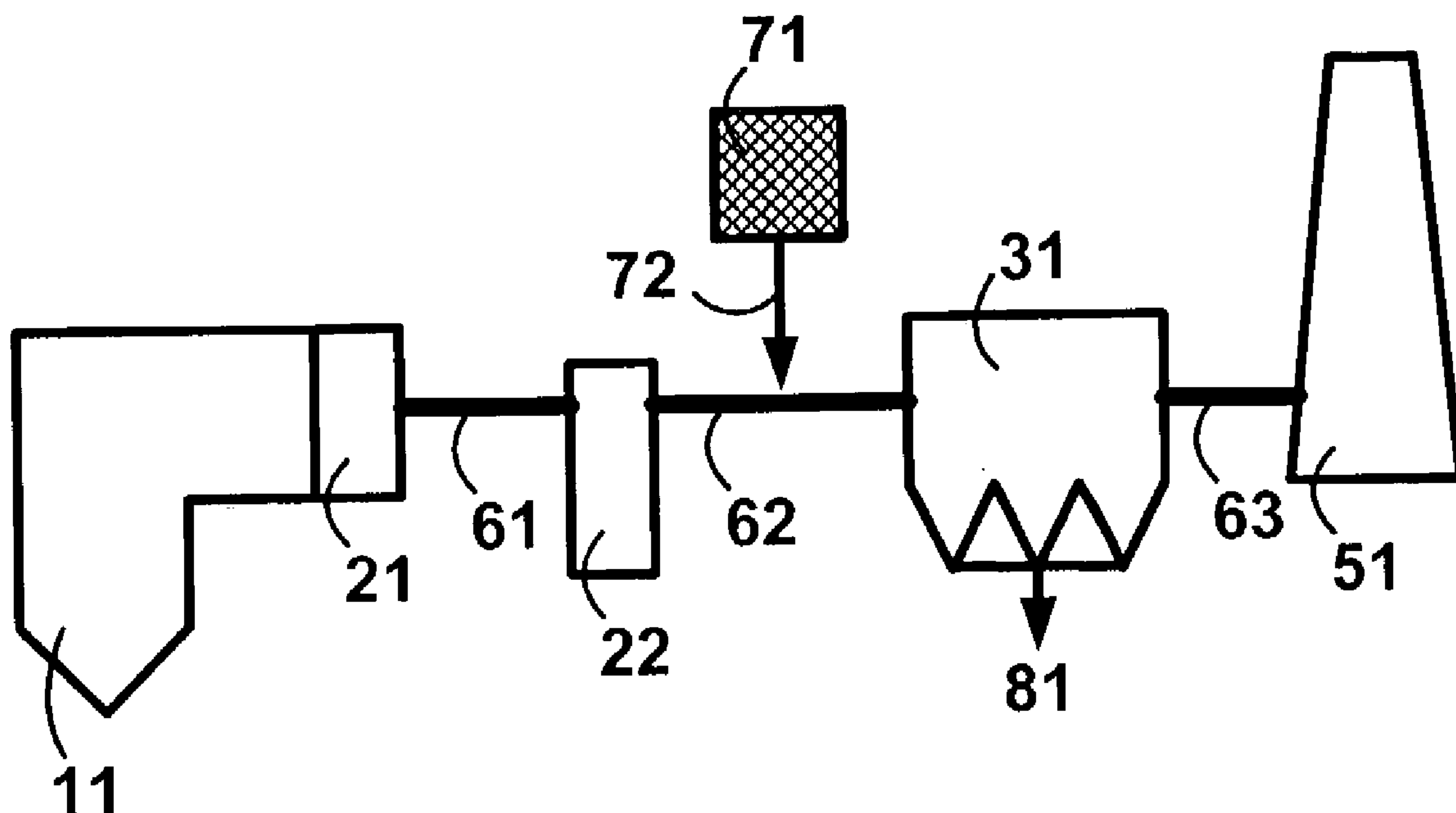


Figure 1.

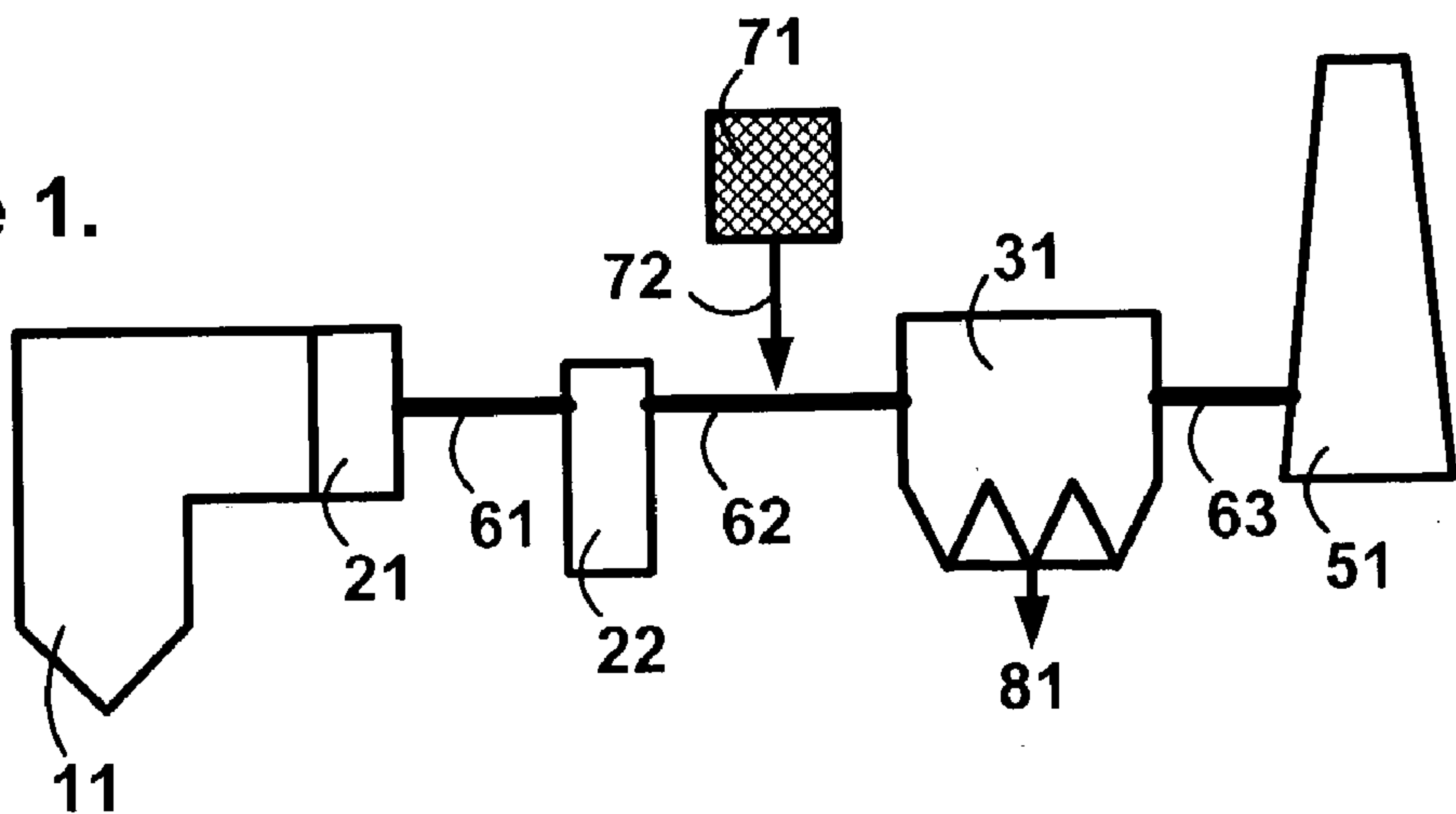


Figure 2.

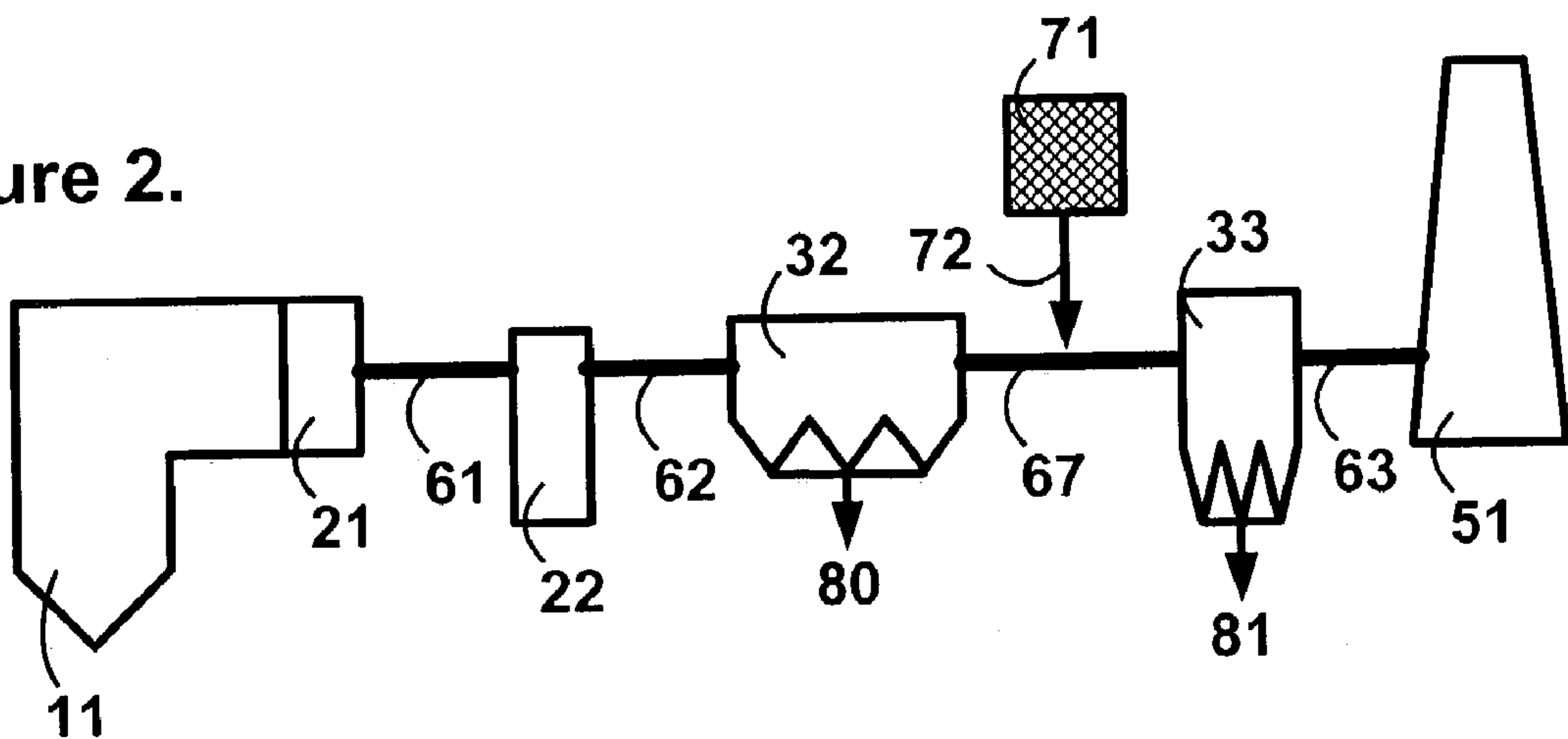


Figure 3.

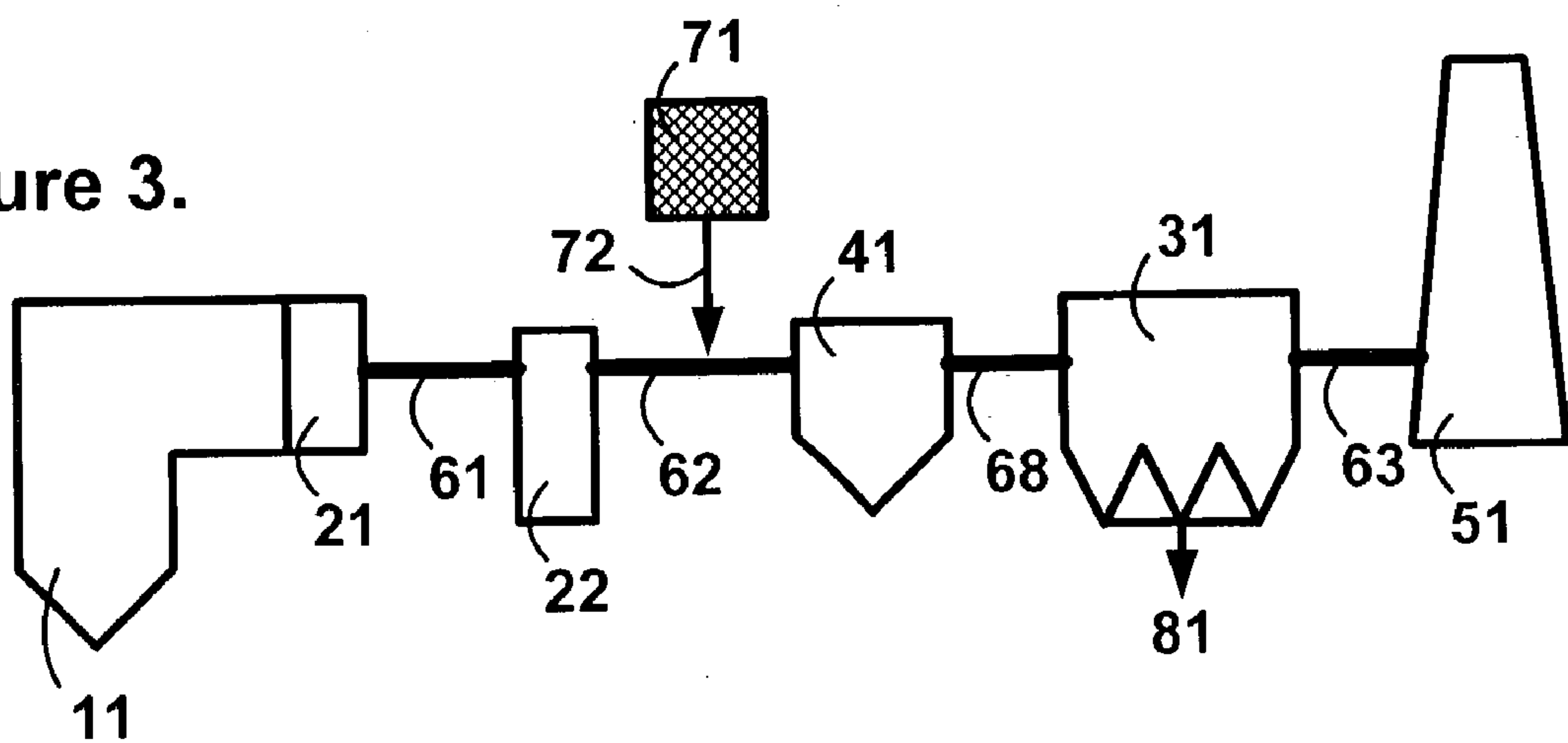


Figure 4.

Maximum Mercury Capacity as a Function of Ozonation Level
(Breakthrough Curves with Norit FGD PAC)

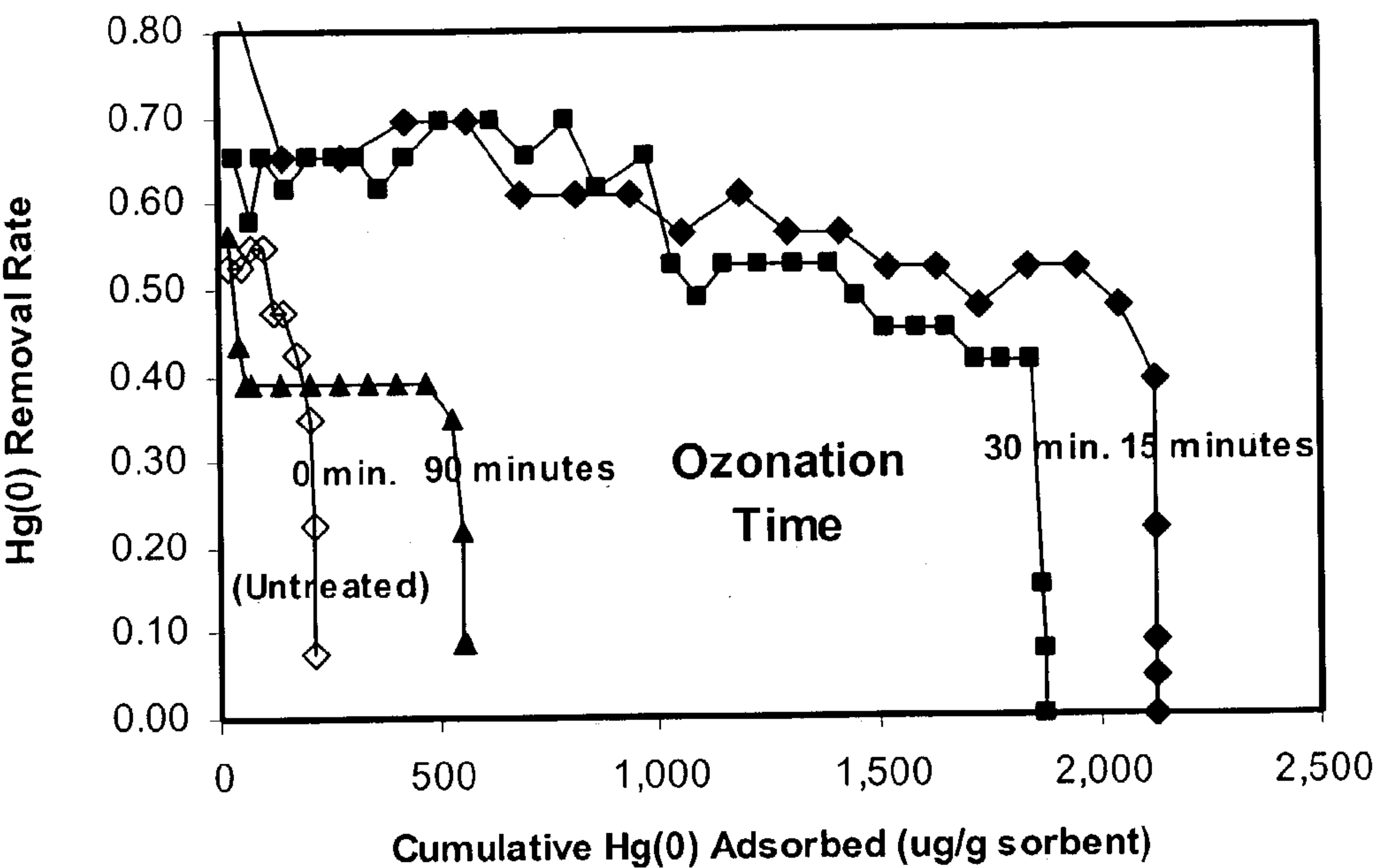


Figure 5.

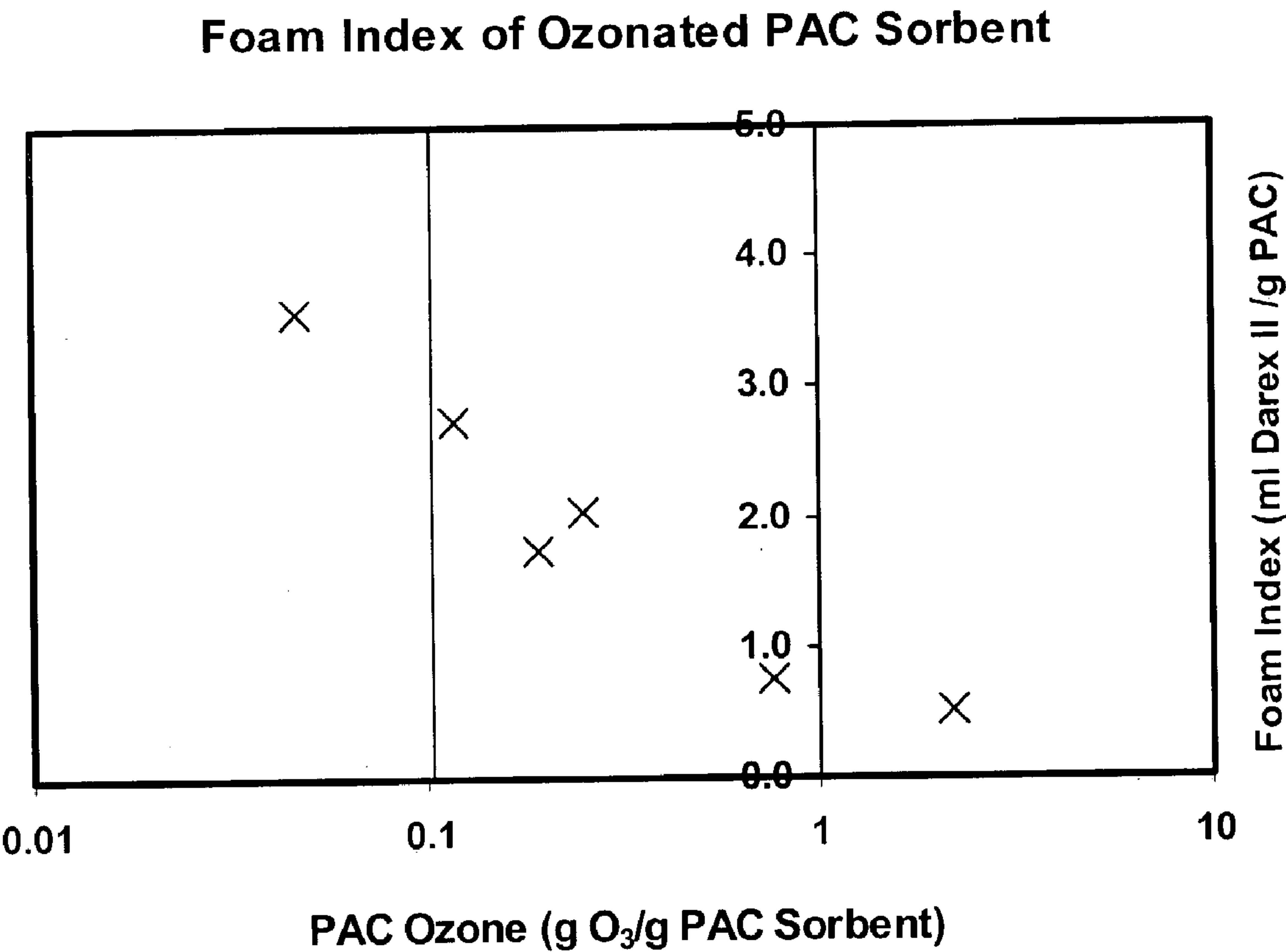


Figure 6.

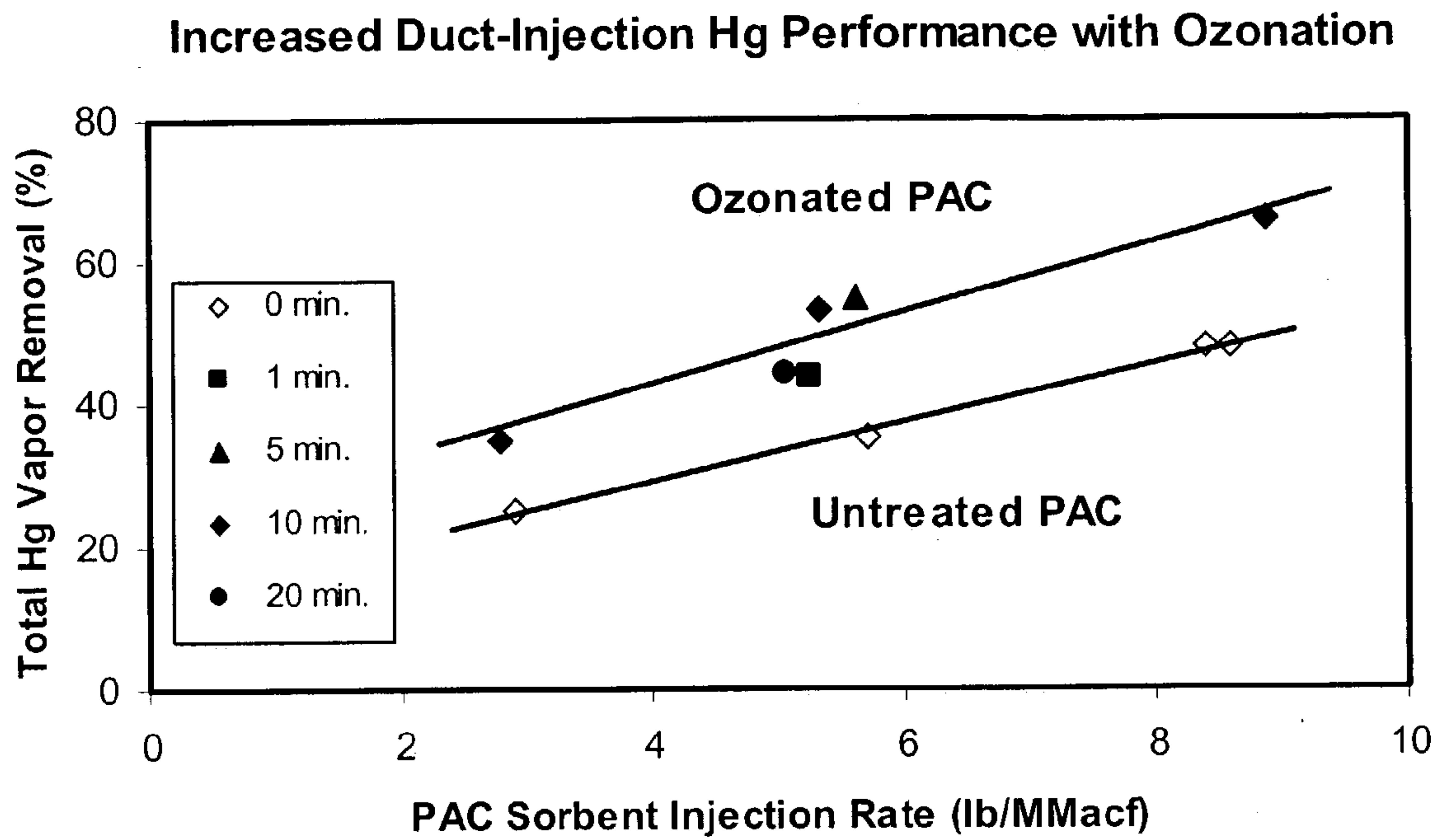
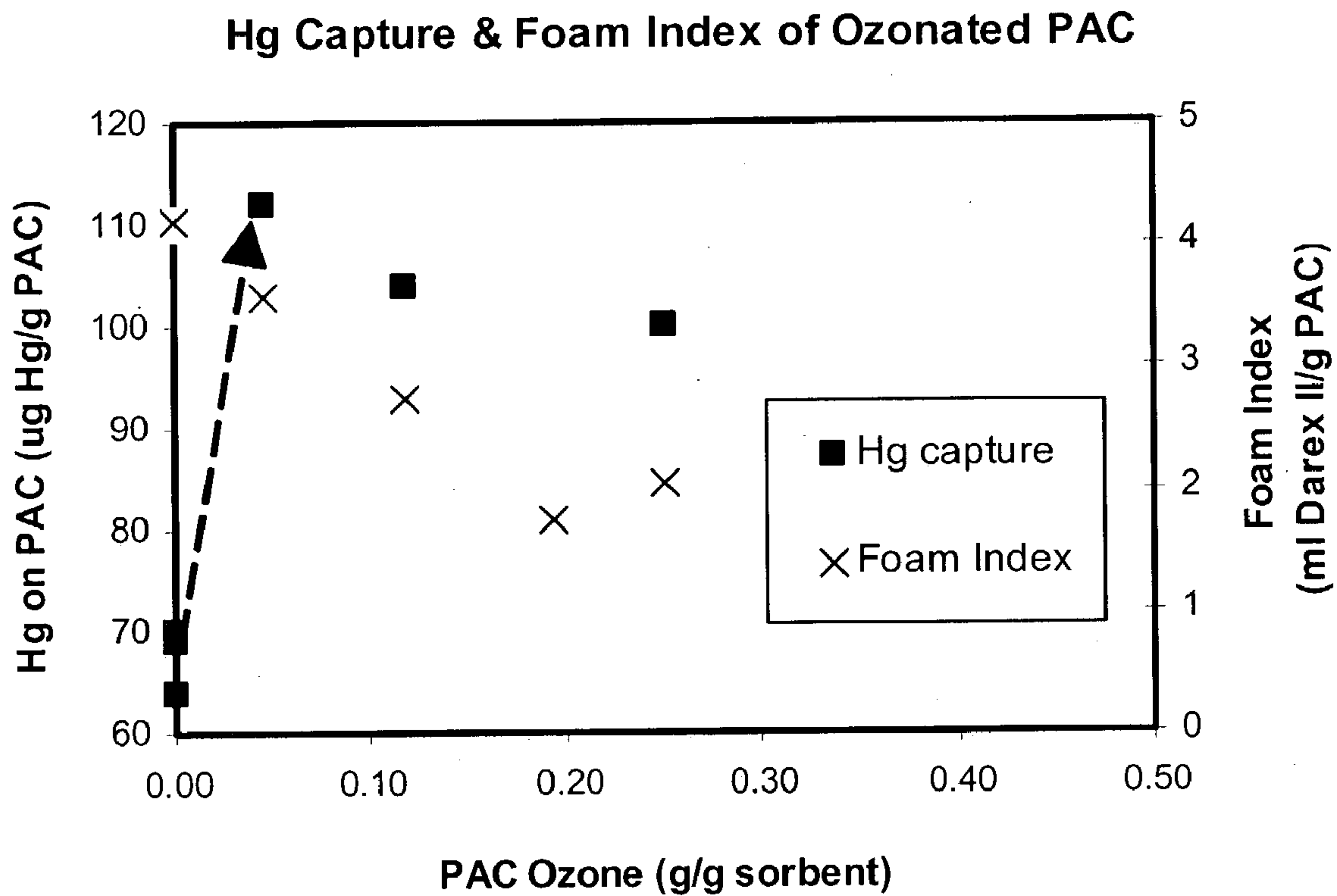


Figure 7.



METHODS AND COMPOSITIONS TO SEQUESTER COMBUSTION-GAS MERCURY IN FLY ASH AND CONCRETE

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims the priority of U.S. Provisional Application No. 60/377,790, filed May 6, 2002, entitled "Methods to Remove Mercury from Combustion Gases," which is hereby incorporated by reference as if fully recited herein.

STATEMENT REGARDING FEDERALLY SUPPORTED RESEARCH OR DEVELOPMENT

[0002] The United States Government may own certain rights to present invention pursuant to U.S. Environmental Protection Agency Contract No. 68-D-01-075 and National Science Foundation Award No. DMI-0232735, to Sorbent Technologies Corporation.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention

[0004] This invention relates to the injection of carbon sorbent materials into the combustion gas streams of coal-fired power plants to remove mercury and to the use in concretes of the mixture of fly ash and sorbents recovered from the combustion-gas particulate-collector.

[0005] 2. Description of the Related Art

[0006] It is well known that mercury is both hazardous and poisonous. Consequently, there is frequently a need to remove it from, for example, the air streams around industrial processes, such as at chlor-alkali plants, or from the air in dental offices using amalgams, where people may be directly exposed to mercury vapor. Similarly, there is a need to sequester mercury from natural gas and hydrocarbon streams, where it corrodes processing equipment; from wastewater streams, where its discharge can contaminate ecosystems; and from the hot combustion-gas emissions of waste incinerators, where it is emitted to the environment to methylate and bio-concentrate up the food chain. Each of these gas or liquid streams has different characteristics that make some mercury removal methods effective and appropriate, but others, ineffective and inappropriate. Consequently, over the years, a multitude of approaches have had to be developed for effectively removing mercury species from various streams. These overall approaches include, among others: liquid scrubbing technologies, homogenous gas-phase technologies, metal amalgamation techniques, and processes utilizing various sorbent materials in different application schemes, with adsorbents optionally impregnated with various reaction aids.

[0007] A recent concern is the mercury emitted from coal-fired power plants. It has been estimated, for example, that about 100,000 pounds of mercury are being emitted into the atmosphere annually in the United States from coal-fired power plants. Capturing and isolating this mercury is a very difficult technical problem because the gas volumes to be processed are great, the concentrations of the mercury in the gases are low, and the gas temperatures are high. Also, many other complicating compounds are present in the flue gas and multiple mercury species have to be sequestered. Even

though many mercury control techniques have already been developed, new means for effectively and economically controlling utility mercury emissions are still needed. After a thorough investigation of the prior art on mercury removal from power-plant gas streams, the U.S. Environmental Protection Agency (EPA) concluded in the Executive Summary to its 1998 Utility Hazardous Air Pollutants (HAPs) Report to Congress that:

[0008] "Regarding potential methods for reducing mercury emissions, the EPA has not identified any demonstrated add-on control technologies currently in use in the U.S. that effectively remove mercury from utility emissions." [Page ES-18].

[0009] In the past, activated carbons have demonstrated utility for sequestering mercury vapors in some applications. Moreover, when treated with other compounds, the mercury sequestration performance of activated carbons can be improved. Manes and Grant U.S. Pat. No. 3,193,987, for example, propose use of an activated carbon impregnated with an amalgamating metal, such as copper or silver. Stock U.S. Pat. No. 1,984,164 teaches the advantages of loading activated carbon with halogens, particularly iodine, to remove mercury from various gases. In U.S. Pat. No. 6,533,842 Maes et al., a cupric-chloride-impregnated carbon in combination with calcium hydroxide is shown to improve mercury reductions from a gas stream. Dreibelbis and Joyce U.S. Pat. No. 3,194,629 teach the use of activated carbon impregnated with either an iodine-potassium iodide mixture or sulfur dissolved in carbon disulfide. And in U.S. Pat. No. 3,876,393, Kasai et al. recommend impregnating activated carbon with sulfuric acid for mercury removal.

[0010] In most of the prior art teachings, a solution is used to transfer the various adsorption aids to the carbons, requiring additional processing steps to wet and dry the materials, which can be especially problematical if the sorbents are very fine powers. Commercial iodine-impregnated carbons, for example, are produced using a solution into which potassium iodide has been dissolved. Sometimes other post-processing is required to delump the sorbents or change the state of the added chemicals. And the contaminated solvents must be disposed of. Morrell and Tobiasson U.S. Pat. No. 2,511,288 provide a discussion of the various complications involved in activated carbon impregnation using solvents.

[0011] Consequently, the production of activated carbons from dissolved metals, halide salts, and sulfur compounds is laborious and difficult to perform on a large scale. So while sorbent made from solvent-dissolved species may perform well, they end up being very expensive. In the recent Utility HAPs Report to Congress, which included a detailed evaluation of control technologies available for power plant mercury control, the U.S. EPA reported that:

[0012] "Sulfur-, iodide-, chloride salt-, and $\text{Ca}(\text{OH})_2$ -impregnated activated carbons show promise for increasing the mercury removal efficiency, but further testing is needed. [However, t]he cost of these modified carbons can be as much as 20 times higher than that of unmodified AC." [Page 13-42.]

[0013] These high costs, due to the chemical impregnates involved and the solution-based manufacture, make them uneconomic for duct-injection use at power plants with electrostatic precipitators (ESPs), because large volumes of sorbents are required and they are ultimately thrown away with the fly ash.

[0014] Moreover, problems may result from the vaporization of the impregnates if they are used at elevated temperatures, such as the case with corrosive iodine or sulfur oxides. And upon disposal of the sorbents, problems can occur with leaching of the cations involved, such as copper, or of any captured mercury put into a soluble form.

[0015] Recently, a number of inventive methods have been developed to apply mercury sorbent technologies to the large-scale gas streams of coal combustion for power generation. The U.S. patents of Moller et al. U.S. Pat. No. 4,889,698 and Chang, U.S. Pat. No. 5,505,766, for example, describe the injection of very finely powdered activated carbon (PAC) into hot combustion flue gases at various points along their journey through pollution-control equipment trains. However, to practice the art of Moller et al., an expensive spray dryer is required and to practice Chang, the construction of second large particulate collector is required.

[0016] A handful of full-scale power-plant sorbent-injection trials have recently taken place at coal-fired units with just an electrostatic precipitator (ESP) for pollution control. About 65% of U.S. coal-fired utility boilers have this configuration, without fabric filters or flue gas desulfurization systems that offer easier and less-expensive options for mercury control. The ESP-only configuration requires in-flight mercury removal, with some amount of sorbent time on the ESP plates parallel to the gas flow. Mercury removal at plants with only an ESP is a most difficult mercury-sequestration situation and an application especially targeted by the current invention.

[0017] Contamination of the fly ash by the mercury sorbent further complicates the problem of mercury control at coal-fired power plants. Almost 20% of U.S. power-plant fly ash is beneficially used as a cement substitute in concrete. Power plants that can sell their fly ash not only receive income for their waste product, but save even more in avoided landfill costs. This great industrial recycling success story, however, is now threatened by PAC injection for mercury control.

[0018] PAC duct-injection trials at We Energy/Wisconsin Electric's Pleasant Prairie power plant in Wisconsin were the first large-scale mercury sorbent tests at a representative, ESP-equipped U.S. power plant. The Pleasant Prairie plant burns a subbituminous coal and, at the time, sold all of its fly ash as a cement replacement in concretes. Mercury-removal performance in the trials was modest, with over 40% removal when a Norit Darco FGD® PAC was injected at 1 lb/MMacf, but leveling off at about 70% removal when the injection rate was greater than 10 lb/MMacf. However, it was also discovered that the suitability of their fly ash in concretes became severely compromised with PAC injection.

[0019] Even at the lowest injection levels tested, when the PAC became incorporated in the plant's fly ash in the ESP, the fly ash failed the required specification tests for concrete use. The problem is that the PAC that was designed to be such an efficient adsorbent material for mercury is, by its nature, also an excellent adsorbent for the organic air-entraining-admixtures (AEAs) added to concretes to produce and stabilize fine air bubbles in the matrix, which provides workability, strength, and freeze/thaw capabilities. The economic implications of this PAC interference with AEAs could be huge. At Pleasant Prairie, for example, the

loss in fly ash revenues and added land-disposal costs would be a few times greater than the total mercury-control costs.

[0020] A common measure of the degree to which a fly ash interferes with AEAs is known as its "Foam Index." A fly ash sample, in this case incorporating 1 or 2 wt % PAC, is placed in a small closed container with water, shaken, and then the liquid surface is observed for a stable foam. Drops of a standard AEA solution are sequentially added until a stable foam results, with the amount of AEA added representing the foam index. The lower the foam index, the less the fly ash interferes with the AEA.

[0021] Fly ash usually already contains some unburned carbon particles from incomplete fuel combustion. These, too, interfere with AEAs. Because over two-thirds of concrete in the U.S. is air-entrained, a number of methods have been developed to decrease the foam indexes of carbon-containing fly ashes. Tsukada et al. U.S. Pat. No. 5,286,292, for example, found that treating carbon-containing fly ashes with gaseous halogens, particularly chlorine or fluorine, significantly lowers their foam indexes, enabling it to be used in concrete. Hurt et al. U.S. Pat. No. 6,136,089 duplicated this approach using ozone gas. If power plants are to add highly-adsorbent PACs to their flue gas streams for mercury control, methods are needed to reduce the sorbent impact on AEA in concrete.

[0022] 3. Objects of the Invention

[0023] Accordingly, it is an object of the present invention to provide a sorbent material that may be injected into a hot mercury-containing flue gas, so that a significant portion of the mercury is sequestered onto the sorbent and removed from the flue gas with its fly ash.

[0024] In addition, it is an object of the present invention to provide a sorbent material that has a reduced interference with air-entraining-admixtures when a fly ash incorporating the saturated sorbents is used in concretes, sequestering the power-plant mercury from the environment.

[0025] Moreover, it is an object of the present invention to provide methods for inexpensively manufacturing and applying these improved mercury sorbent materials.

SUMMARY OF THE INVENTION

[0026] These and other objects of the invention are achieved by a method for removing mercury and mercury-containing compounds from a combustion gas in an exhaust gas system. The method has the steps of providing a mercury sorbent; injecting the mercury sorbent into a stream of the mercury-containing combustion gas for a sufficient time to allow at least an effective amount of the mercury and mercury-containing compounds in the combustion gas to adsorb onto the mercury sorbent and collecting and removing the mercury sorbent from the combustion gas stream. The mercury sorbent is prepared by treating a carbonaceous substrate with an effective amount of an ozone-containing gas for a sufficient time to increase the ability of the carbonaceous substrate to adsorb mercury and mercury-containing compounds and to decrease the degree of interference of the substrate on air-entraining-admixtures used with the substrates as a component of a concrete composition.

[0027] In some aspects of the invention, the carbonaceous substrate comprises activated carbon. The carbonaceous

substrate is reduced to a particle size distribution fluidizable in the combustion gas stream prior to the injecting step. The points of injecting and collecting and removing the mercury sorbent may be varied, depending upon the exact configuration of the exhaust gas system.

[0028] In other aspects of the invention, a method for manufacturing a mercury sorbent is provided. The manufacturing method has the steps of: providing a carbonaceous substrate; providing an ozone-containing gas; and contacting the carbonaceous substrate with the ozone-containing gas for a sufficient time to increase the mercury adsorbing ability of the carbonaceous substrate and to decrease the degree of interference of the substrate on air-entraining-admixtures used with the substrates as a component of a concrete composition. In some aspects of this manufacture, the carbonaceous substrate is activated carbon.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The present invention will be best understood when reference is made to the accompanying drawings, wherein identical objects are identified by identical reference numerals and wherein:

[0030] **FIGS. 1 through 3** are schematic diagrams describing possible methods for utilizing the improved sorbent compositions to remove and isolate mercury species from hot combustion flue gases;

[0031] **FIG. 4** is a plot of sorbent breakthrough curves indicating improvements in mercury capture and capacity with the sorbent materials of the invention;

[0032] **FIG. 5** is a graph indicating the degree to which the foam index of sorbents processed according to this invention are lowered with increasing contact with ozone;

[0033] **FIG. 6** is a graph indicating the improved mercury capture levels, in a simulated coal-fired, duct-injection, ESP application, of sorbents processed according to this invention, compared to those not so processed; and

[0034] **FIG. 7** is a graph indicating the improved mercury utilization, in a simulated coal-fired, duct-injection, ESP application, of sorbents processed according to this invention, along with these sorbents' improved foam indexes.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0035] There are five essential elements to the mercury sequestration claims of the present invention. The first three are that (1) a carbonaceous adsorbent, such as powdered activated carbon (PAC), is used (2) to capture and concentrate vaporous mercury species from (3) a hot, flowing gas stream of combustion products. The fourth requirement is that the adsorbent material be (4) injected into the flowing gas, intimately mix with it, and be separated from the gas in a particulate collector along with fly ash. The fifth and final essential element of the invention is that at some time before it is mixed with the mercury-containing combustion gas, the carbon material must (5) be exposed to an ozone-containing treatment gas, producing a sorbent material that is both particularly reactive to gaseous mercury species and that has a decreased adsorption of air-entraining-admixtures (AEAs) if mixed with fly ash in a concrete composition.

[0036] I have discovered that the simple act of exposing a carbonaceous material, preferably powdered activated carbon (PAC), to gaseous ozone, $O_3(g)$, significantly increases the material's ability to adsorb vaporous mercury species when injected into high-temperature coal-fired flue-gas compositions. Reaction of the carbon with ozone produces an inexpensive sorbent material that can be simply injected into the ductwork of a power plant ahead of an existing particulate collector, without the need for large volumes of sorbent, retrofitted flue-gas cooling, or extended sorption time on an additional fabric filter. When the carbon particles are removed from the flue gas along with the fly ash by an electrostatic precipitator (ESP) or fabric filter, for example, the mercury is removed with them. The mercury sorbents are then disposed of with the fly ash. The captured mercury appears to be very stable. The toxic mercury is thus sequestered from environmental interactions.

[0037] If the fly ash from an application of the process is to be used as a cement substitute in concretes, the ozone treatment of the mercury sorbent has the additional beneficial effect of decreasing the resulting foam index of the fly ash. Lowering the sorbent's interference with AEAs can enable some fly ashes to be used in concretes, completely sequestering the power-plant mercury in a cementitious matrix.

[0038] Production of the new mercury sorbent materials is simple. The carbon material and the ozone gas need simply be contacted with each other, a process herein referred to as "ozonation." Ozone is a gas at ambient temperature. Using a gas-phase carbon reactant considerably simplifies the production of the sorbent. Any common mixing method and equipment can be used to contact the ozone with the carbon-based substrates.

[0039] Manufacture of the improved mercury sorbent of this invention begins with a carbonaceous substrate material for the mercury sorbent. Many different materials can perform this role. By way of example, but not intending to be limiting, possible carbonaceous materials include: activated carbon, activated charcoal, activated coke, char, and unburned or partially-burned carbon from a combustion process. The important features of the sorbent substrate material are that it contain significant elemental carbon and that it has an adequate degree of porosity or surface area to provide mercury removal in the process. The size of the carbonaceous particles during ozonation is not critical as long as their mass is uniformly exposed to and reacted with the ozone. The material can be fine enough already so that it can be mixed with and carried by the mercury-containing flue-gas stream, or it can be large and granular, to be comminuted after ozonation, but prior to being injected into the mercury-containing gas stream.

[0040] A preferred carbonaceous substrate material is activated carbon. If the manufacturing process of this invention is integrated into the manufacture of the activated carbon material itself, the carbonaceous substrate could be, for example, the carbon material after it has undergone a steam activation procedure. Alternately, the activated carbon entering the treatment process can be an existing commercial product. Preferably the activated carbon is in a very fine state, which allows for a more uniform ozonation. An example would be a powdered activated carbon (PAC). Such a material would already have some gas-phase mercury

adsorption capability which the treatment process of this invention will greatly amplify.

[0041] If the carbonaceous substrate material is at ambient temperature, preferably it is heated to a temperature of above about 100° C. to drive off any physically-adsorbed moisture that can block the material's pores or interfere with the ozonation step. A separate vessel may optionally be utilized for this preheating step or it can be integrated into the larger processing scheme. Higher temperatures will clean off other heteroatom complexes.

[0042] The key step in the sorbent manufacturing process is exposing the dried carbonaceous materials to the ozone-containing gas. When the gas contacts the solids, it quickly reacts with the materials, modifying the distribution of heteroatom surface-complexes on the carbon surface. Surprisingly, treatment with only a very small initial amount of ozone leads to a very large increase in mercury sequestration performance of carbonaceous materials. Modest amounts of additional ozone appear to have relatively little marginal effect on mercury performance. Higher degrees of ozone treatment actually decrease the mercury capabilities of such a sorbent, as structural carbon is oxidized to CO and CO₂ and the porous structure of the material breaks down.

[0043] In contrast, any level of ozonation of the carbonaceous substrates appears to lower its foam index value and the deleterious effect it can have on AEAs in concretes. The greater the contact with ozone, the lower the foam index of the material and the less it interferes with AEAs.

[0044] So the optimum level of ozone to combine with the carbonaceous material will vary with the particular situation. Obviously, mercury sorbents treated to higher ozone levels will take longer to produce and cost more. If the fly ash containing the carbonaceous sorbents is to be sold for use in concrete, then it can be advantageous to ozonate to a higher level, for example, using 300 grams of ozone per kilogram of powdered activated carbon. If the fly ash is not to be sold for concrete use, on the other hand, a more economic level of 10 g O₃/kg PAC or even less might be preferred. If the surface area of a PAC is 200 m²/g, these ozonation levels would translate to 50 and 1 μmole of ozone per square meter of total carbon surface area, respectively.

[0045] Note that the ozonation step can occur in any number of possible reactors. The particular equipment used to contact the carbonaceous substrates with the ozone-containing gas can be, for example, a stationary mixer, a rotating drum, a structure with a vertically-moving bed, a fluidized-bed or bubbling-bed unit, a transport reactor, or any other contactor known in the art. The contactor units of Hurt et al. U.S. Pat. No. 6,521,037, for example, would suit this purpose. So would applying the scheme of Altman U.S. Pat. No. 6,395,145. However, the mercury sorbent manufacturing process is not limited by the type of process equipment used. Any equipment or method that quickly and evenly distributes the ozone-containing gas to intimately contact the carbonaceous particles will satisfy the requirements of the invention.

[0046] In one preferred embodiment of the process, any ozone remaining in gas streams exiting the contactor can be transported to unsaturated carbon materials upstream in the process, eliminating the need to decompose ozone from the off-gas stream.

[0047] Reference will now be made in detail to the preferred embodiments of the invention which are illustrated in the accompanying figures.

[0048] **FIGS. 1 through 3** are schematic diagrams describing possible methods, among others, for utilizing the sorbents of the invention to remove and sequester mercury from hot combustion gases.

[0049] **FIG. 1** applies the sorbents to a combustion gas stream where a particulate collector is utilized to collect the fly ash generated during combustion. In this invention, this device can be used to collect the injected mercury sorbents as well, concentrating the mercury species in a sequesterable stream. The particulate collector may be a fabric filter or baghouse, an electrostatic precipitator (ESP), a cyclone, a venture scrubber, or any other device capable of removing the combustor fly ash or injected mercury sorbents from the gas stream. In the application described in **FIG. 1**, coal or wastes or other fuels are combusted in a boiler 11 generating mercury-containing flue gas which is cooled by steam tubes and an economizer 21. The gas typically flows through ductwork 61 to an air preheater 22, which drops the gas temperature from about 300-to-400° C. down to about 150-to-200° C. in the ductwork 62 exiting the air preheater.

[0050] In such an arrangement, the mercury sorbent of this invention, stored in a container such as a bin 71, is fed to and through an injection line 72 to the ductwork 62 and injected through a multitude of lances to widely disperse in the hot combustion flue gas. Mixing with the flue gas, the sorbent adsorbs a fraction of its elemental mercury and oxidized mercury species. The sorbent then flows with flue gas to the particulate collector 31. If the collector is a fabric filter, the mercury sorbent is deposited on the filter bags in a filter cake along with the fly ash and other gas-stream particulates. In a fabric filter the flue gas is forced through the filter cake and through the bag fabric. This causes intimate contact between the sorbents and the remaining mercury in the flue gas and will result in a high degree of mercury capture with a high degree of utilization of the sorbents. Cleansed of its mercury content and particulates, the flue gas exits the particulate collector to ductwork 63, the smokestack 51, and then to the atmosphere. Upon cleaning of the fabric filter bags or the ESP collection plates, the mercury sorbents fall into hoppers and are eventually emptied 81 from the particulate collector and are disposed of along with the collected fly ash and unburned carbon. The mercury sorbents of this invention will generally make up on the order of 1 or 2 wt % of the collected particulates in pulverized coal power-plant applications.

[0051] If the particulate collector in **FIG. 1** is an electrostatic precipitator (ESP) instead of a fabric filter, it becomes a more difficult situation for mercury removal because the flue gas is not forced through the sorbent in a filter cake layer of a collection bag. Because of the poorer mass transfer of mercury to sorbent within an ESP, in this case it is particularly important to inject at 72 as far ahead of any turning vanes, flow distributors, ductwork, and exposed surface-area in the ducts as possible. This not only provides more residence time for the sorbents to mix with and remove mercury from the flowing gas, but provides more mass transfer area for the sorbent to collect on, increasing overall mercury removal. In the ESP 31, the sorbents are collected on plates with the fly ash and upon rapping of the plates are

eventually discharged from the ESP **81** for disposal along with the rest of the particulates.

[0052] The method for removing mercury from combustion gas streams of this invention is not limited to the particular arrangements described in the figures. These have been provided simply to illustrate common examples and many other variations are possible. For example, a wet scrubber for flue gas desulfurization could appear at **63** in **FIG. 1**. Similarly, a selective catalytic reduction (SCR) unit for NO_x reduction or a flue gas conditioning system to improve particulate removal could be placed in the equipment arrangements. The utility of the disclosed mercury-removal method would be unaffected, however.

[0053] Similarly, the mercury sorbents of this invention could be injected while mixed in with sorbents for other flue gas components, such as calcium or magnesium hydroxide or oxide for flue gas SO₃, HCl, or SO₂, rather than injected alone. Alternately, the mercury sorbents could be injected in a liquid slurry, which would quickly evaporate in the hot flue gas. Other variations of the methods of applying this invention can be formulated by those familiar with art and they should be considered within the scope of this disclosure and the included claims.

[0054] Two such arrangements bear particular mention. **FIG. 2** applies the sorbents in a "TOXECON®" arrangement. Here the mercury sorbents **71** are injected after an ESP **32** into the almost particulate-free ductwork **67** before a small, high-velocity fabric filter **33**. In this manner the fly ash **80** does not become mixed with the carbonaceous sorbents, allowing the fly ash to be sold directly for concrete use. Moreover, the filter cake of fabric filter **33** would predominantly be mercury sorbent, allowing a longer residence time, higher utilization levels, and the possibility of recovering and reinjecting the sorbent to lower costs. The superior reactivity and capacities of the mercury sorbents of this invention make them prime candidates for use in such an arrangement.

[0055] **FIG. 3** illustrates sorbent usage at plants that have spray dryers for acid rain control. The mercury sorbent could be injected before the spray dryer **62**, into the spray dryer **41**, into the ductwork **68**, between the spray dryer and the particulate collector **31**, or mixed in with the scrubber slurry itself.

[0056] Other possible alternatives within the scope of the invention would be to ozonate carbonaceous "thief" particles withdrawn from the combustor **11** before their complete combustion and to inject them at lower temperatures downstream. Alternately, unburned carbon and unsaturated mercury sorbents could be physically separated from fly ash, ozonated, and injected back into the gas stream.

[0057] Now the present invention will be further described in detail by way of examples.

EXAMPLE 1

[0058] The ozone-gas treatment of this invention was found to markedly increase the mercury sequestration performance of carbonaceous materials. **FIG. 4** presents the fixed-bed mercury breakthrough-curve of a common untreated commercial PAC and the breakthrough curves of three similar samples that had been treated with varying amounts of ozone gas. Laboratory fixed-bed maximum-

capacity tests like this roughly simulate the conditions of a sorbent in a filter cake on a bag in a fabric filter. While they do not simulate the kinetics and mass transfer of duct-injection into an ESP, they do provide measures of the maximum mercury capacity of the material and the slope of the breakthrough curve provides some idea of the kinetics.

[0059] The standard laboratory fixed-bed testing procedure that was used in this example is similar to that of other researchers and generates a traditional breakthrough curve. In the standard procedure used in these experiments, thin fixed-beds of Norit's Darco FGD® PAC of about 5-mg were vacuum-applied to filters and placed in a filter-holder in a laboratory oven at 175° C., the temperature commonly available before particulate collection devices at combustor facilities. The treated samples had been earlier exposed to gaseous ozone by passing air containing about 0.4% ozone through the materials at about 10 g O₃/min/kg of PAC.

[0060] In the examples of **FIG. 4 a** mercury challenge gas was sent through heated lines to each of the materials at 6.7 lpm that contained an average of about 13 $\mu\text{g}/\text{Nm}^3$ of elemental Hg from permeation tubes in an oil bath. To simulate a coal-combustion gas stream, 1400 ppm SO₂ and 600 ppm NO from bottled gases and 4 wt % of water from a peristaltic pump were also spiked into the gas with the balance being 11.5% O₂ and the rest, N₂. Mercury levels both into and out from the materials were measured with a gas-phase elemental-mercury analyzer.

[0061] As described in the figures, the ozone treatments of this invention increased the elemental mercury capacity of these PACs by from 300% to 1000%. A relatively small amount of ozone, from 15 minutes of treatment, produced a large gain in mercury capacity. Longer ozone treatments, like to 90 minutes, however, degraded the material's performance.

EXAMPLE 2

[0062] In the next example, a series of FGD PAC samples were prepared by treating them according to the procedures of Example 1 with significantly different amounts of total ozone gas. Foam index tests using the common AEA Darex II® were then performed multiple times from each sample and the values were averaged. The results are plotted logarithmically in **FIG. 5**. Clearly, increasing the amount of ozone contacting the PAC decreases its foam index and allows bubbles to stabilize with less AEA.

EXAMPLE 3

[0063] In the next example, a large series of actual duct-injection runs were performed with a simulated coal-fired flue-gas stream on a 50-acfm pilot-scale test system. The mercury mass transfer to fluidized sorbent and adsorption kinetics in this system are similar to that in a full-scale utility application. The fully-instrumented duct-injection test system included a propane burner unit to generate the hot flue gas; a humidification drum to add an appropriate degree of moisture to the gas; a mercury spiking subsystem with elemental-mercury permeation tubes; a flue gas spiking subsystem with mass flow controllers for SO₂, NO_x, and HCl; a small sorbent feeder and fluidizing injection subsystem to lessen sorbent pulsing; 10 meters of insulated, 10-cm-diameter ducting circling the ceiling; thermocouples; an electrostatic filter with an effective specific collection

area of about 500 ft²/Kacf; a back-up fabric filter; a safety filter; an orifice plate to measure flow; and a variable-speed I.D. fan. The gas temperature at injection was about 175° C. and at the ESP was about 145° C. and the spiked flue gas concentrations were about 24 µg/Nm³ Hg(0), 1400 ppm SO₂, 600 ppm NO_x, and 5 ppm HCl, typical values for coal-fired power plants.

[0064] Both an untreated PAC, Norit Darco FGD®, and ozonated samples were injected at various rates into the hot gas with a ductwork residence time of about 3.5 seconds before the small ESP. The ozonated PACs were treated with about 10 g of O₃ per minute per kg of PAC. Mercury measurements before and during injection were taken using a SnCl₂ oxidized-mercury conversion system and a cold-vapor atomic adsorption analyzer outfitted for continuous, gas-phase use.

[0065] The results of the various duct-injection runs appear in **FIG. 6**. At every ozonation level and every injection level tested, the ozonated samples removed more mercury from the flue gas than did the untreated samples. There was not much difference in the performance between the various ozonated samples, with the sample treated for one minute removing about the same amount of mercury from the hot flowing gas as the sample ozonated for twenty minutes. In general, however, the ozonated samples performed about twice as well at sequestering mercury as the untreated samples. To achieve 40% mercury removal, for example, required about 8 lb of untreated PAC per million actual cubic feet of gas flow, but required only about 4 lb of ozonated PAC.

EXAMPLE 4

[0066] The foam index values of the PAC samples from Example 3 with Darex II®, a commonly-used air-entraining-admixture, were measured. These are plotted in **FIG. 7** against the ozonation level of the sample. Also plotted are the resulting mercury utilization levels of the sorbents, measured in terms of micrograms of captured mercury per gram of PAC. Again, a surprisingly-large increase in mercury performance occurred with just a small exposure of the carbonaceous substrate to ozone, with essentially no gain thereafter. However, the foam index of the materials continued to beneficially drop upon increasing exposure.

What is claimed is:

1. A method for removing mercury and mercury-containing compounds from a combustion gas in an exhaust gas system, comprising the steps of:

providing a mercury sorbent that has been prepared by treating a carbonaceous substrate with an effective amount of an ozone-containing gas for a time sufficient to increase the ability of the carbonaceous substrate to adsorb mercury and to reduce the degree of possible interference of the sorbent with air-entraining-admixtures used with the substrates as a component of a concrete composition;

injecting the mercury sorbent into a stream of the mercury-containing combustion gas for a sufficient time to allow an effective amount of the mercury and mercury-containing compounds in the combustion gas to adsorb onto the mercury sorbent; and

collecting and removing the mercury sorbent from the combustion gas stream.

2. The method of claim 1 wherein:

the carbonaceous substrate comprises activated carbon.

3. The method of claim 1, wherein:

the carbonaceous substrate or mercury sorbent is reduced to a particle size distribution fluidizable in the combustion gas stream.

4. The method of claim 2, wherein:

the carbonaceous substrate or mercury sorbent is reduced to a particle size distribution fluidizable in the combustion gas stream.

5. A process for manufacturing a mercury sorbent, comprising:

providing a carbonaceous substrate;

providing a ozone-containing gas; and

contacting the carbonaceous substrate with the ozone-containing gas for a time sufficient to increase the mercury adsorbing ability of the carbonaceous substrate and to reduce the degree of interference of the substrate with air-entraining-admixtures used with the sorbent as a component of a concrete composition.

6. The process of claim 5, wherein:

the carbonaceous substrate is activated carbon.

7. The process of claim 5, further comprising the step of:

reducing the particle size distribution of the carbonaceous substrate or mercury sorbent to a distribution that is fluidizable in the ductwork of a combustion gas stream.

8. The process of claim 6, further comprising the step of:

reducing the particle size distribution of the carbonaceous substrate or mercury sorbent to a distribution that is fluidizable in the ductwork of a combustion gas stream.

9. A mercury sorbent prepared according the process of claim 5.

10. A mercury sorbent prepared according the process of claim 8.

11. A process in which ozone is used to pacify the surface of a carbon source material extrinsic to ash comprising applying ozone to said carbon source material extrinsic to ash to produce a product which reduces the undesirable affect on air entrainment when said carbon source material is incorporated into concrete.

12. The process of claim 11 wherein the amount of ozone added to the carbon is 10-300 g-ozone/kg-carbon.

13. The process of claim 11 wherein the amount of ozone added to the carbon is 1-50 µmoles-ozone/m²-total-carbon-surface area.

14. The process of claim 11 in which the carbon source material is treated separately with ozone and then added to the ash stream.

15. A process comprising oxidizing activated carbon-based sorbents which are used to capture metal vapors, said oxidizing reducing the undesirable affect on air entrainment when said activated carbon-based sorbents are to be incorporated into ash and the ash subsequently used in concrete.

16. The process of claim 15 where the metal vapor is either oxidized or elemental mercury.

17. The process of claim 15 in which the oxidant is ozone.

- 18.** The process of claim 15 in which the activated carbon is treated prior to its use as a mercury sorbent, so that the final ash is not degraded in its concrete performance.
- 19.** A process of surface oxidation used to pacify the surface of a carbon containing source material extrinsic to carbon containing ash comprising the step of surface oxidation of said carbon containing source material to prepare a material useful for incorporation into concrete.
- 20.** The process of claim 19 wherein the surface oxidation is performed with ozone.

- 21.** The process of claim 19 wherein the oxidation is performed with a member selected from the group of air, oxygen, nitric acid, chromic acid, persulfate, permanganate, and hydrogen peroxide.
- 22.** A concrete composition comprising concrete and an ozone treated carbon source material extrinsic to ash wherein the undesirable affect on air entrainment is reduced.

* * * * *