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Use of sulfide-containing gases and liquors for removing
mercury from flue gases

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ABSTRACT

A method and apparatus for reducing and removing mercury in industrial gases, such as a flue gas, produced by the combustion of fossil fuels, such as coal, adds hydrogen sulfide
5 and/or sulfide ions to the flue gas as it passes through a scrubber. The scrubber may be either a wet or dry scrubber for flue gas desulfurization systems.



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COMPLETE SPECIFICATION
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Applicant(s):

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COMPANY

Invention Title:

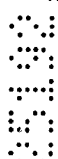
USE OF SULFIDE-CONTAINING GASES AND LIQUORS FOR
REMOVING MERCURY FROM FLUE GASES

The following statement is a full description of this
invention, including the best method of performing it known to
me/us:

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USE OF SULFIDE-CONTAINING GASES AND LIQUORS FOR REMOVING MERCURY FROM FLUE GASES

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FIELD AND BACKGROUND OF THE INVENTION



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The present invention relates generally to the field of combustion and flue gas cleanup methods and apparatus and, in particular, to a new and useful method and apparatus for removing mercury from the flue gases generated during the combustion of fossil fuels such as coal, or solid wastes, through the use of sulfide containing gases and liquors.

In recent years, the U.S. Department of Energy (DOE) and the U.S. Environmental Protection Agency (EPA) have supported research to measure and control the emissions of Hazardous Air Pollutants (HAPs) from coal-fired utility boilers and waste to energy plants. The initial results of several research projects showed that the emissions of heavy metals and volatile organic carbons (VOCs) are very low, except for mercury (Hg). Unlike most of the other metals, most of the mercury remains in the vapor phase and does not condense onto fly ash particles at temperatures typically used in electrostatic precipitators and fabric filters. Therefore, it cannot be collected and disposed of along with fly ash like the other metals. To complicate matters, mercury can exist in its oxidized (Hg^{+2}) form, principally as mercuric

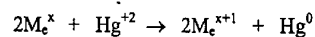
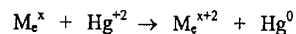
chloride, (HgCl₂), or in its elemental (Hg⁰) form as vaporous metallic mercury. The relative amount of each species appears to depend on several factors such as fuel type, boiler combustion efficiency, the type of particulate collector installed, and various other factors.

The search for industrially acceptable methods for the capture of mercury from industrial flue gases has included a significant effort to determine how much mercury can be removed by existing, conventional air pollution control equipment, such as wet or dry scrubbers.

Accordingly, tests have been performed on several commercial scale and pilot scale wet scrubbers, which are designed for the capture of sulfur oxides and other acid gases. In addition to being equally applicable to dry scrubber situations, these tests have produced some expected and some surprising results. It was generally expected that the oxidized mercury would be easily captured and the elemental mercury would be difficult to capture. These expectations were based on the high solubility of mercuric chloride in water and the very low solubility of elemental mercury in water. This expectation was generally fulfilled.

The surprising result concerned elemental mercury. Repeated tests during which the concentration of elemental mercury in the flue gas was measured revealed that more elemental mercury was leaving the wet scrubber than was entering.

One postulate proposed to explain the cause of the elemental mercury generation in the wet scrubber is described for example, by the following general reactions:



M_e is any number of transition metals such as Fe, Mn, Co, Sn, etc., that may be present in one of several possible oxidation states, x.

Transition metal ions are generally present in wet scrubber slurries as impurities in the industrial applications of concern. Thus, as the mercuric chloride is absorbed, a portion reacts with and becomes reduced by trace levels of transition metals and metal ions and because of its low solubility the elemental mercury is stripped from the liquid and returned to the flue gas.

Most of the recent efforts to capture and remove mercury from the flue gas produced by coal-fired units have concentrated on gas-phase reactions with introduced reagents such as activated carbon.

The subject of mercury emissions by the utility and waste to energy industries is a new area being investigated by both the DOE and EPA.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a method using a scrubber for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing oxidized mercury, the improvement comprising:

- providing the industrial gas containing oxidized mercury to the scrubber;
- providing means for generating hydrogen sulfide and providing said generated hydrogen sulfide into the industrial gas upstream of the scrubber, and/or providing an aqueous sulfide species to the scrubber;
- creating a gas-liquid interface within the scrubber and mixing the industrial gas with the sulfide from the hydrogen sulfide and/or from the aqueous sulfide species in order to rapidly precipitate the oxidized mercury at the gas-liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor; and
- subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.

In a second aspect, the present invention provides an apparatus using a scrubber for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing oxidized mercury, the improvement comprising:

- means for providing the industrial gas containing oxidized mercury to the scrubber;
- means for generating hydrogen sulfide and means for providing said generated hydrogen sulfide into the industrial gas upstream of the scrubber, and/or means for providing an aqueous sulfide species to the scrubber;
- means for creating a gas-liquid interface within the scrubber and mixing the industrial gas with the sulfide from the hydrogen sulfide and/or from the aqueous sulfide species in order to rapidly precipitate the oxidized mercury at the gas-liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor; and

means for subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.

In a third aspect, the present invention provides an apparatus for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing mercury, comprising:

5 means for providing the industrial gas containing oxidized mercury to the scrubber;

means for providing an aqueous sulfide species to the scrubber;

means for creating a gas-liquid interface within the scrubber and mixing the industrial gas with the aqueous sulfide species in order to rapidly precipitate the oxidized mercury at the gas-

10 liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor;

metering pump means for controlling the aqueous sulfide species directly to the scrubber liquor; and

15 means for subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.

In a fourth aspect, the present invention provides an apparatus for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing oxidized mercury, comprising:

20 means for providing the industrial gas containing oxidized mercury to the scrubber;

means for generating hydrogen sulfide and means for providing said generated hydrogen sulfide into the industrial gas upstream of the scrubber;

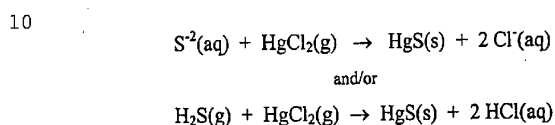
means for creating a gas-liquid interface within the scrubber and mixing the industrial gas with the sulfide from the hydrogen sulfide in order to rapidly precipitate the oxidized mercury at

25 the gas-liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor; and

means for subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.

30 Preferably, the aqueous sulfide species is selected from the group consisting of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, potassium sulfide, sodium sulfide, sodium hydrosulfide and potassium hydrosulfide.

The present invention provides a means in a wet or dry scrubber to rapidly precipitate the oxidized mercury at the gas/liquid interface in the scrubber before it can be reduced by the transition metals. One of the most insoluble forms of mercury is mercuric sulfide, which in mineral form is cinnabar. Means for supplying a source of sulfide to react with the oxidized mercury include use of hydrogen sulfide and/or aqueous sulfide species. Thus, at the gas/liquid interface in the scrubber, the following reactions are proposed for the absorption and precipitation of ionized (oxidized) mercury (depending upon whether the sulfide is derived from hydrogen sulfide gas, aqueous sulfide species, or some other sulfide species source):



15 HgS has a solubility product of 3×10^{-52} and therefore precipitates essentially completely. The aqueous sulfide species is added to the scrubbing liquor of the scrubber and comes into contact with the mercury in the flue gas, such that HgS is formed when the mercury is absorbed into the liquor. Likewise, in the case of hydrogen sulfide gas, there is good reason to expect that the precipitation reaction proceeds faster than the reduction reactions. Specifically, in the case of the precipitation reaction, both reactants are well mixed in the gas phase. Thus, as they diffuse from the gas to the gas/liquid interface, both reactants can react instantly at the interface. By contrast, the reduction reactions require that the reactants, i.e., the Hg⁺² and the transition metal ion, diffuse in the liquid phase to a reaction

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plane in the liquid. Liquid phase diffusion is orders of magnitude slower than gas phase diffusion.

Therefore, using gas and/or aqueous sulfide species, the oxidized mercury will rapidly precipitate as cinnabar in the scrubber and thereby prevent the reduction of that mercury back to vaporous elemental mercury. The precipitation of mercury as cinnabar has a distinct advantage over other mercury sequestering methods in that it converts mercury to a very insoluble form. In this way, the mercury should be inert and effectively removed from the food chain.

Accordingly, the present invention also contemplates the use of H_2S gas. Accordingly, a preferred embodiment of the present invention is drawn to an improvement in a method using a wet scrubber for receiving and scrubbing an industrial gas containing oxidized mercury with a wet scrubber slurry, the improvement comprising: providing means for generating hydrogen sulfide and providing said generated hydrogen sulfide into the industrial gas upstream of the scrubber. The method according to the present invention is particularly suited to the task of reducing mercury emissions in an industrial process which burns coal in a furnace to produce an exhaust flue gas, including conveying the exhaust flue gas through a dust collector and adding hydrogen sulfide to the flue gas prior to creating the gas-liquid interface in the wet scrubber.

Another preferred embodiment of the present invention is drawn to an apparatus using a wet scrubber for receiving and scrubbing an industrial gas containing oxidized mercury with a wet scrubber slurry, and particularly the improvement comprising: means for generating hydrogen sulfide; and means for providing said generated hydrogen sulfide into the industrial gas upstream of the wet scrubber. The present invention is again particularly suited to utility installations which burn fossil fuels such as coal, or solid wastes, and which use, in addition to the wet scrubber, an electrostatic precipitator or a fabric filter and other conventional components for reducing emissions to the atmosphere.

Particularly, the present invention contemplates provision of a hydrogen sulfide generating system which produces the hydrogen sulfide from a reaction of adding an acid to a solution of one of aqueous sodium sulfide and potassium sulfide to generate the hydrogen sulfide. Advantageously, the hydrogen sulfide generating system may use equipment and methods

wherein the acid is added to kraft green liquor from the Kraft pulping process to generate the hydrogen sulfide.

These particular hydrogen sulfide-related embodiments have an inherent safety advantage in that no gas phase H_2S is accumulated or stored. All H_2S that is generated is immediately injected.

5 Nevertheless, another preferred embodiment of the present invention is drawn to an improvement in a method using a scrubber for receiving and scrubbing an industrial gas containing oxidized mercury, the improvement comprising: adding an aqueous sulfide species selected from the group consisting of sulfidic waste water, kraft caustic liquor, kraft carbonate
10 liquor, potassium sulfide, sodium sulfide, sodium hydrosulfide and potassium hydrosulfide to the industrial gas and scrubbing the industrial gas in the scrubber. The method according to the present invention is particularly suited to the task of reducing mercury emissions in an industrial process which burns coal in a furnace to produce an exhaust flue gas, including conveying the exhaust flue gas through a dust collector, such as a fabric filter or electrostatic precipitator.

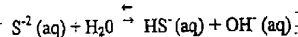
15 Another preferred embodiment of the present invention is drawn to an apparatus using a scrubber for receiving and scrubbing an industrial gas containing oxidized mercury with an aqueous alkali reagent, and particularly the improvement comprising: means for providing aqueous sulfide species and means for controlling the aqueous sulfide species provided to the industrial gas in the scrubber. The present invention is again particularly suited to utility
20 installations which burn fossil fuels such as coal, or solid wastes, and which use a dust collector (such as an electrostatic precipitator or a fabric filter), in addition to the scrubber, and/or other conventional components for reducing emissions to the atmosphere.

Also described herein is an apparatus for receiving and scrubbing an industrial gas containing mercury with an aqueous alkali reagent, comprising a scrubber, having a scrubber
25 liquor, for scrubbing the industrial gas with the aqueous alkali reagent; flue means for conveying the industrial gas to the scrubber; means for providing sulfide ions; and means for controlling the sulfide ions provided to the industrial gas.

This apparatus is again particularly suited to utility installations which burn fossil fuels, such as coal, and may be incorporated into a wet or dry scrubber.

30 These aqueous sulfide-related embodiments of the present invention contemplate means for providing sulfide ions, including but not limited to hydrosulfide (HS^-) ions.

Notably, such hydrosulfide ions (HS^-) provide sulfide ions (S^{2-}) by virtue of the equilibrium in aqueous solution:



This means can be accomplished through the addition of an aqueous sulfide species, such as sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, potassium sulfide and/or sodium sulfide to the scrubbing liquor in the scrubber. Alternatively, the hydrosulfide ions (HS^-) may be provided through the addition of an aqueous sulfide species such as sodium hydrosulfide and/or potassium hydrosulfide to the scrubbing liquor in the scrubber. Further, control means, such as a separate storage tank and metering pump, may be employed to selectively control the provision of sulfide to meet specific operational requirements.

This system has an inherent safety advantage in that no H_2S , which is odorous and toxic, is accumulated or stored. Further, the system is versatile in that it is equally applicable to wet or dry scrubbers and may be incorporated into current emissions control systems with minimal modifications or additions.

Features of the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating advantages and specific benefits attained by its uses, reference is made to the accompanying drawings and descriptive matter in which a preferred embodiment of the invention is illustrated.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

Fig. 1 is an illustration of the present invention as applied to a coal-fired utility boiler installation of the type used by utilities in the generation of electric power;

Fig. 2 is an illustration of a hydrogen sulfide H_2S generation system according to the present invention as particularly applied to a wet scrubber of Fig. 1;

Fig. 3 is an enlarged partial view of the circled area in Fig. 2, illustrating one embodiment of a system for injecting H_2S into flue gases for mercury control according to the present invention;

Fig. 4 is an enlarged partial view of the circled area in Fig. 2, illustrating another embodiment of a system for injecting H_2S into flue gases for mercury control according to the present invention;

Fig. 5 is a chart illustrating the results of tests comparing performance without H_2S injection to performance with H_2S injection;

Fig. 6 is an illustration of the present invention as applied to a coal-fired utility boiler installation of the type used by utilities in the generation of electric power which employs a dry scrubber flue gas desulfurization system;

Fig. 7 is a schematic illustration of a preferred embodiment of the aqueous sulfide embodiment of the wet scrubber for the present invention.

Fig. 8 is a schematic illustration of a preferred embodiment of the aqueous sulfide embodiment of the dry scrubber for the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawings generally, wherein like reference numerals designate the same or functionally similar elements throughout the several drawings, and to Fig. 1 in particular, Fig. 1 illustrates a coal-fired utility boiler installation of the type used by utilities in the generation of electric power, generally designated 10, and which represents one type of industrial process to which the present invention is applicable. In its broadest form, the present invention comprises a method for removing mercury from the flue gas generated during the combustion of fossil fuels or solid wastes through the use of hydrogen sulfide gas

and/or aqueous sulfide species selected from the group consisting of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, potassium sulfide, sodium sulfide, sodium hydrosulfide and potassium hydrosulfide. Of course, while the aforementioned coal-fired utility boiler installations are but one example, and the method of the present invention will likely first find commercial application to the removal of mercury from the flue gases produced by such utility boiler installations which combust such fossil fuels, any industrial process using a wet scrubber type of absorber module to purify such flue gases may benefit. Such processes could include incineration plants, waste to energy plants, or other industrial processes which generate gaseous products containing mercury. Thus for the sake of convenience, the terms industrial gas, flue gas, or simply gas will be used in the following discussion to refer to any

Page 7

gas from an industrial process and from which an objectionable component, such as mercury, is to be removed.

As will be described *infra*, an alternate embodiment of the present invention involves methods and apparatus for the addition of hydrogen sulfide gas and/or the aqueous sulfide species described above to industrial gases which are treated by dry scrubber flue gas desulfurization systems. Thus, while the majority of the following description is presented in the context of the present invention as being applied to wet scrubber systems, it will be appreciated that the present invention is not limited thereto. Further, since both wet and dry scrubbers remove sulfur species from the flue gas by introduction of an alkali sorbent, some common terminology may be used as appropriate for the sake of convenience. In the case of wet scrubbers, the alkali sorbent can be provided as an aqueous alkali solution or slurry; in dry scrubbers, the alkali sorbent is usually provided as an aqueous alkali slurry. Thus, for the sake of convenience in the following description, the term aqueous alkali reagent will be used to encompass both aqueous alkali solutions and/or aqueous alkali slurries as appropriate to the type of scrubber means being used.

As illustrated in Fig. 1, and proceeding in the direction of flue gas flow generated during the combustion process, the boiler installation 10 includes a furnace 12 having a gas outlet 14 which conveys flue gases, generally designated 16, to an air heater 18 used to preheat incoming air 20 for combustion. Pulverizers 22 grind a fossil fuel 24 (e.g., coal) to a desired fineness and the pulverized coal 24 is conveyed via burners 25 into the furnace 12 where it is burned to release heat used to generate steam for use by a steam turbine-electric generator (not shown). Flue gas 16 produced by the combustion process are conveyed through the gas outlet 14 to the air heater 18 and thence to various types of downstream flue gas cleanup equipment. The flue gas cleanup equipment may comprise a fabric filter or, as shown, an electrostatic precipitator (ESP) 26 which removes particulates from the flue gas 16. A flue 28 downstream of the ESP 26 conveys the flue gas 16 to a wet scrubber absorber module 30 which is used to remove sulfur dioxide and other contaminants from the flue gas 16. Flue gas 16 exiting from the wet scrubber absorber module or, simply, the wet scrubber 30, is conveyed to a stack 32 and exhausted to atmosphere. Forced draft fans 34 and induced draft fans 36 are used to propel the air 20, fuel 24, and flue gases 16 through the installation

10. For further details of various aspects of such installations 10, the reader is referred to STEAM its generation and use, 40th Ed., Stultz and Kitto, Eds., Copyright © 1992 The Babcock & Wilcox Company, particularly to Chapter 35 - Sulfur Dioxide Control, the text of which is hereby incorporated by reference as though fully set forth herein. While the
5 aforementioned STEAM reference contains a description of one form of wet scrubber 30 produced by The Babcock & Wilcox Company (B&W) and to which the present invention is applicable, the present invention is not limited to such B&W wet scrubber designs. Persons skilled in the art will appreciate that the principles of the present invention apply equally well to other types of wet (and, as below, dry) scrubber designs, available from other
10 manufacturers.

10 The wet scrubber 30 contains, in a lower portion thereof, an inventory of scrubber liquor 38. During operation of the wet scrubber 30, recirculation pumps 40 pump and recirculate the scrubber liquor 38 up through pipes 42 and into absorber spray headers 44 located in an upper portion of the wet scrubber 30. The scrubber liquor 38 is sprayed into the
15 flue gas 16 where it absorbs SO₂. The scrubber liquor 38 falls down through various devices and drains back into the lower portion of the wet scrubber 30. The scrubbed flue gas 16 then exits from a wet scrubber outlet 46 and is eventually conveyed to the stack 32.

20 Referring now to Fig. 2 in particular, there is shown an embodiment of a system for accomplishing the method of injecting small amounts of H₂S into flue gas for mercury removal according to the present invention. An H₂S generation system, generally referred to as 50, is provided and includes a well-stirred tank containing a liquid section 54 comprising sodium and/or potassium sulfide and a gas section 52 where air and H₂S are mixed and the mixture 74 of air and H₂S is transferred to an injection apparatus 76, described *infra*. The H₂S vapor pressure in the tank 51 is controlled by pH. The pH in the tank 51 liquid solution
25 54 is controlled by the addition of a strong mineral acid 56, such as hydrochloric or sulfuric acid (HCl or H₂SO₄) from a tank or container 58, or by the addition of an alkali solution 57 such as sodium carbonate or sodium hydroxide (NaOH or Na₂CO₃) from a tank or container 85. The acid is added to lower the pH and increase the H₂S vapor pressure in tank 51. The alkali is added to raise the pH and lower the H₂S vapor pressure in tank 51. The H₂S
30 produced is immediately transported to the injection system 76. This is an inherent safety

feature since no gaseous H_2S is allowed to accumulate. Stirring or mixing means, advantageously comprising a motor 64 and driven stirring shaft with two paddles 66, keep the tank sections 52 and 54 well stirred. As a result, the constituents in the liquid zone 54 are well mixed to yield the H_2S at the desired vapor pressure and the air 68 and generated H_2S are well mixed in the gas section 52. Pumping means 60 conveys the mineral acid 56 to the tank 51 via line 62; pumping means 61 conveys the alkali solution 57 to the tank 51 via line 63. Suitable control valves in lines 62 and 63 would be used as needed to control the flow of acid 56 and alkali 57.

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conditions of the elemental mercury content of the flue gas 16 at the wet scrubber inlet and outlet, without H₂S addition. The large increase in elemental mercury at the wet scrubber outlet is due to the chemical reduction of oxidized mercury within the wet scrubber 30 according to the reactions previously noted. The right two bars represent the improved performance achieved when H₂S was injected at a concentration of about two parts per million (2 ppm). As shown, the chemical reduction of oxidized mercury to elemental mercury was completely prevented.

Fig. 7 depicts a detailed schematic of a preferred embodiment of the wet scrubber 30 for use with sulfide containing liquors. Wet scrubber 30 comprises a main chamber 300 with scrubber inlet 45 and scrubber outlet 46. As above, main chamber 300 has a lower portion containing an inventory of scrubber liquor 38 which recirculates from the main chamber 300 into absorber spray headers 44 by means of general recirculation line 302. General recirculation line 302 may comprise pipes 42 and recirculation pumps 40. Frequently, the lower portion of main chamber 300 containing scrubber liquor 38 will include means for injecting air, such as air sparger 41, into the scrubber liquor 38. The use of air sparger 41 oxidizes the products of SO₂ absorption in scrubbing liquor 38. Finally, scrubber liquor 38 may be contained in a bulk storage vessel which forms the lower portion of main chamber 300 (as pictured), or it may comprise a separate holding tank connected to a drain in the main chamber 300 and recirculation line 302.

A sulfide containing salt may be added directly to scrubber liquor 38 and mixed with the flue gas 16 via spray headers 44. Further, by injecting an aqueous sulfide species solution directly into recirculation pump 40 and/or general recirculation line 302, the added sulfide solution will not be prematurely oxidized before contacting and scrubbing flue gas 16 in the

main chamber 300. Aqueous sulfide species can be provided by means of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, or an aqueous solution containing potassium sulfide, sodium sulfide, sodium hydrosulfide and/or potassium hydrosulfide.

Alternatively, aqueous sulfide species may be added to an isolated sulfide storage tank 310 which is connected to recirculation line 302 upstream of recirculation pump 40. Further, a metering pump 312 may be employed to control the flow of sulfide species into the wet scrubber 30 and, more particularly, into and/or through recirculation line 302 (a system

employing metering pump 312 for control of sulfide into recirculation line 302 only is shown). The concentration of sulfide species and/or rate of flow into and/or through the recirculation line 302 permits the selective control of the scrubber's overall mercury removing ability. Thus, a coordinated control system, such as using storage tank 310 and/or metering pump 312, is a preferred embodiment of the present invention. The rate of sulfide addition must be proportional to the flue gas flow rate through the scrubber. Most of the sulfide added to the scrubber will be immediately stripped from solution as H_2S in the gas-liquid contact zone. If too much sulfide is added at any one instant, an objectionable odor will emanate from the flue gas at the exit of the stack. It is therefore desirable to limit H_2S concentrations leaving the stack to less than about 2 parts per million (ppm).

To limit the H_2S concentration in flue gas 16 exiting the scrubber to no more than about 2 ppm, the maximum rate of sulfide addition must be less than about 8×10^{-5} gm moles per M^3 of treated flue gas. A typical 100 megawatt scrubber module treats about $8 \times 10^3 M^3$ per minute of flue gas. For such a module, the maximum sulfide addition rate would be $(8 \times 10^{-5}) \times (8 \times 10^3)$, or 0.64 gm moles/min. If a 2 molar solution of sodium sulfide were used, the feed rate would be 0.32 liters per minute. It is understood that these figures are merely illustrative, and do not represent any sort of limitation of the principles disclosed in this application.

In operation, flue gas 16 flows from inlet 45 into main chamber 300. Sulfide species added to recirculation line 302 allow spray header 44 to mix the sulfide species and scrubber liquor 38 with the flue gas 16. This contact initiates the chemical reaction, *supra*, which removes mercury. The flue gas then flows through outlet 46 and into the stack 32. The precipitated mercury remains in scrubber liquor 38 and can be subsequently removed and disposed of by various methods known to those skilled in the art.

As described earlier and as illustrated in Fig. 6, the present invention is also applicable to combustion systems employing dry scrubbers for flue gas desulfurization. Again, like reference numerals designate the same or functionally similar parts. Flue gas 16 produced by the combustion process are conveyed through the gas outlet 14 to the air heater 18 and thence to various types of downstream flue gas cleanup equipment. A flue 28 conveys the flue gas 16 to a dry scrubber absorber module 150 which is used to remove

sulfur dioxide and other contaminants from the flue gas 16. Flue gas 16 exiting from the dry scrubber 150 is conveyed to a fabric filter or, as shown, an electrostatic precipitator (ESP) 26 which removes particulates from the flue gas 16 and then the flue gas 16 is conveyed to a stack 32 and exhausted to atmosphere. As in Fig. 1, forced draft fans 34 and induced draft fans 36 (not shown in Fig. 6) are used to propel the air 20, fuel 24, and flue gases 16 through the installation 10 as before.

Advantages of the present invention as used with hydrogen sulfide gas include the fact that the cost of control of mercury emissions according to the present invention is relatively insignificant compared to the costs for control of other hazardous air pollutants. Further, the amount of H₂S required should be below the threshold odor level. The cost and operating expenses of a system as depicted in Fig. 2 should be substantially less compared to any other system proposed to date. According to a preferred embodiment of the present invention, one source of the sodium sulfide used to generate the H₂S can comprise green liquor, an intermediate chemical used in the Kraft pulp and paper industry and which is readily available from pulp and paper companies. As is known to those skilled in the art, green liquor consists of an aqueous mixture of sodium sulfide and sodium carbonate. Green liquor is relatively easy and safe to handle and should be widely available.

According to the present invention as used with hydrogen sulfide gas, the mercury in the flue gas 16 ends up as mercuric sulfide (also known as cinnabar). This is the chemical form that mercury is most often found in nature and is probably the most desirable chemical form to sequester mercury. Much of the mercury in this form is present as a fine particulate in the scrubber slurry and for that reason, it is possible to separate much of the mercury from the gypsum crystals.

Fig. 8 depicts a detailed schematic of a preferred embodiment of the dry scrubber 150 for use with sulfide containing liquors. Dry scrubber 150 comprises a main chamber 400 with spray header 44, scrubber inlet 445, and scrubber outlet 446. Notably, scrubber liquor 38 may be contained in a bulk storage vessel 401 and provided to main chamber 400 by means of first feed line 402a. Feed line 402a may contain a scrubber liquor feed pump 440.

A sulfide containing salt may be added directly to scrubber liquor 38 in vessel 401, pumped to main chamber 400 via first feed line 402a, and mixed with flue gas 16 via spray

headers 44. Aqueous sulfide species can be provided by means of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, or an aqueous solution containing potassium sulfide, sodium sulfide, sodium hydrosulfide and/or potassium hydrosulfide.

Alternatively, aqueous sulfide species may be added to an isolated sulfide storage tank 410 and introduced into the main chamber 400 via spray header 44. Tank 410 is connected to second feed line 402b. Further or in the alternative, a metering pump 412 may be employed to control the flow of sulfide species into the dry scrubber 150 and, more particularly, into feed line(s) 402a and/or bulk storage vessel 401 (a system employing metering pump 412 for control of feed line 402a only is pictured). The concentration of sulfide species and/or rate of flow into and/or through the feed line(s) 402a and/or 402b permits the selective control of the scrubber's overall mercury removing ability. Thus, a coordinated control system, such as using storage tank 410 and/or metering pump 412, is a preferred embodiment of the present invention. However, control of sulfide species provided to the gas may also be achieved by periodic and/or manual addition of the aqueous sulfide species into the scrubber system by way of a valve, port, or other injection device or by means of a separate system (i.e., chamber, storage means, spray headers, and/or recirculation line).

In operation, flue gas 16 flows from inlet 445 into main chamber 400. Sulfide species added to feed line 402a and/or bulk storage vessel 401 allow spray header 44 to mix the sulfide species and scrubber liquor 38 with the flue gas 16. This contact initiates the chemical reaction, *supra*, which removes mercury. The flue gas then flows through outlet 446 and into the stack 32. The precipitated mercury remains in the dried solid product of scrubber 150 and can be subsequently removed and disposed of by various methods known to those skilled in the art.

Advantages of the present invention as used with sulfide containing liquors include the fact that the cost of control of mercury emissions according to the present invention is relatively low compared to the costs for control of other hazardous air pollutants. Further, the use of aqueous sulfide species can be incorporated with minimal modifications or additions to current emissions control systems. Most significantly, use of aqueous sulfide species eliminates the need to produce or have available toxic gases, such as hydrogen sulfide gas, which, when mixed with flue gas containing mercury oxidized by an aqueous alkali reagent

may be another method for removing mercury from flue gas. Also, aqueous sulfide species can be easily metered into the main scrubbing liquor inventory at a specific, desired rate in order to enhance efficiency of the scrubber or to achieve specific results.

According to the present invention as used with sulfide containing liquors, the
5 mercury in the flue gas 16 ends up as mercuric sulfide (also known as cinnabar). This is the chemical form that mercury is most often found in nature and is probably the most desirable chemical form to sequester mercury.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the
10 invention may be embodied otherwise without departing from such principles. By way of example and not limitation, while the principles of the present invention were described as being particularly applicable to fossil-fired boiler installations, it will be appreciated by those skilled in the art that the present invention can be used to remove mercury from industrial gases produced by refuse incinerators, refuse boilers, hazardous waste incinerators, or ore
15 roasters.

It is to be understood that a reference herein to a prior art document does not constitute an admission that the document forms part of the common general knowledge in the art in Australia or in any other country.

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In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. In a method using a scrubber for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing oxidized mercury, the improvement comprising:
 - providing the industrial gas containing oxidized mercury to the scrubber;
 - providing means for generating hydrogen sulfide and providing said generated hydrogen sulfide into the industrial gas upstream of the scrubber, and/or providing an aqueous sulfide species to the scrubber;
 - creating a gas-liquid interface within the scrubber and mixing the industrial gas with the sulfide from the hydrogen sulfide and/or from the aqueous sulfide species in order to rapidly precipitate the oxidized mercury at the gas-liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor; and
 - subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.
2. The method according to claim 1, wherein the aqueous sulfide species is selected from the group consisting of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, potassium sulfide, sodium sulfide, sodium hydrosulfide and potassium hydrosulfide.
3. The method according to claim 1 or claim 2, further comprising the step of adding the aqueous sulfide species directly to the scrubber liquor.
4. The method according to claim 1 or claim 2, wherein the scrubber is a wet scrubber and further comprising the step of: conveying the industrial gas through a dust collector to remove particulates from the industrial gas prior to creating the gas-liquid interface in the wet scrubber.
5. The method according to claim 4, wherein the dust collector is one of a fabric filter and an electrostatic precipitator.
6. The method according to claim 1 or claim 2, wherein the scrubber is a dry scrubber and further comprising the step of: conveying the industrial gas which is substantially free of oxidized mercury to a dust collector in order to remove other non-mercuric particulates from industrial gas which is substantially free of oxidized mercury.

7. The method according to claim 6, wherein the dust collector is one of a fabric filter and an electrostatic precipitator.
8. The method according to claim 1 or claim 2, comprising the step of adding the hydrogen sulfide to the industrial gas in the scrubber.
9. The method according to claim 1 or claim 2, comprising the step of supplying the hydrogen sulfide to the industrial gas at a rate sufficient to produce a concentration of hydrogen sulfide in the industrial gas of about 0.05 to 10 ppm.
10. The method according to claim 1 or claim 2, comprising the steps of providing the means for generating hydrogen sulfide with a tank containing a liquid section containing a solution of one of aqueous sodium sulfide and potassium sulfide, and a gas section where air and hydrogen sulfide are mixed, and adding an acid to said solution to generate the hydrogen sulfide.
11. The method according to claim 10, comprising the step of adding an alkali to said solution.
12. The method according to claim 10, comprising the step of controlling a pH of said solution to control a vapor pressure of the generated hydrogen sulfide.
13. The method according to claim 12, comprising the step of adding acid to said solution to lower the pH thereof and increase the vapor pressure of the generated hydrogen sulfide.
14. The method according to claim 12, comprising the step of adding alkali to said solution to raise the pH thereof and decrease the vapor pressure of the generated hydrogen sulfide.
15. The method according to claim 10, comprising the steps of mixing the hydrogen sulfide with air in the gas section of said tank and supplying the mixture of air and hydrogen sulfide into the industrial gas.
16. The method according to claim 1 or claim 2, comprising the steps of providing the means for generating hydrogen sulfide with tank means for providing a supply of kraft green liquor, providing a supply of acid to said kraft green liquor to generate the hydrogen sulfide, and providing a supply of air to said tank means to convey a mixture of air and hydrogen sulfide

from said tank means to said industrial gas.

17. The method according to claim 16, comprising the step of controlling a pH of the kraft green liquor to control a vapour pressure of the generated hydrogen sulfide.

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18. The method according to claim 17, comprising the step of adding acid to said kraft green liquor to lower the pH thereof and increase the vapor pressure of the generated hydrogen sulfide.

10 19. The method according to claim 17, comprising the step of adding alkali to said kraft green liquor to raise the pH thereof and decrease the vapor pressure of the generated hydrogen sulfide.

15 20. In an apparatus using a scrubber for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing oxidized mercury, the improvement comprising:

20 means for providing the industrial gas containing oxidized mercury to the scrubber;
means for generating hydrogen sulfide and means for providing said generated hydrogen sulfide into the industrial gas upstream of the scrubber, and/or means for providing an aqueous sulfide species to the scrubber;
means for creating a gas-liquid interface within the scrubber and mixing the industrial gas with the sulfide from the hydrogen sulfide and/or from the aqueous sulfide species in order to rapidly precipitate the oxidized mercury at the gas-liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor; and
25 means for subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.

30 21. The method according to claim 20, wherein the aqueous sulfide species is selected from the group consisting of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, potassium sulfide, sodium sulfide, sodium hydrosulfide and potassium hydrosulfide.

35 22. The apparatus according to claim 20 or claim 21, wherein the scrubber is one of a dry scrubber and a wet scrubber.

23. The apparatus according to claim 20 or claim 21, comprising means for providing

sulfide ions directly to the scrubber liquor.

24. The apparatus according to claim 20 or claim 21, comprising a controlled metering pump connected to an isolated sulfide ion storage tank for providing the sulfide ions directly to the scrubber liquor.

25. The apparatus according to claim 20 or claim 21, wherein the means for generating hydrogen sulfide comprises a hydrogen sulfide generating system including tank means for providing a solution of one of aqueous sodium sulfide and potassium sulfide, acid supply means for providing a supply of acid to said solution to generate the hydrogen sulfide, and means for supplying air to said tank means to convey a mixture of air and hydrogen sulfide from said tank means.

26. The apparatus according to claim 25, comprising means for conveying the mixture of hydrogen sulfide and air from said tank means to a flue conveying said industrial gas.

27. The apparatus according to claim 26, comprising a hydrogen sulfide/air injection system for introducing the mixture of hydrogen sulfide and air into the industrial gas.

28. The apparatus according to claim 27, wherein the hydrogen sulfide/air injection system comprises a plurality of pipes having apertures therein for discharging the mixture into the industrial gas.

29. The apparatus according to claim 27, wherein the hydrogen sulfide/air injection system comprises a plurality of air foils having apertures therein for discharging the mixture into the industrial gas.

30. The apparatus according to claim 20 or claim 21, wherein the means for generating hydrogen sulfide comprises a hydrogen sulfide generating system including tank means for providing a supply of kraft green liquor, acid supply means for providing a supply of acid to said kraft green liquor to generate the hydrogen sulfide, and means for supplying air to said tanks means to convey a mixture of air and hydrogen sulfide from said tank means to said industrial gas.

31. The apparatus according to claim 30, comprising means for conveying the mixture of hydrogen sulfide and air from said tank means to a flue conveying said industrial gas.

32. The apparatus according to claim 20 or claim 21, comprising a hydrogen sulfide/air injection system for introducing the mixture of hydrogen sulfide and air into the industrial gas.

33. The apparatus according to claim 32, wherein the hydrogen sulfide/air injection system comprises a plurality of pipes having apertures therein for discharging the mixture into the industrial gas.

34. The apparatus according to claim 32, wherein the hydrogen sulfide air/injection system comprises a plurality of air foils having apertures therein for discharging the mixture into the industrial gas.

35. An apparatus for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing mercury, comprising:

means for providing the industrial gas containing oxidized mercury to the scrubber;

means for providing an aqueous sulfide species to the scrubber;

means for creating a gas-liquid interface within the scrubber and mixing the industrial gas with the aqueous sulfide species in order to rapidly precipitate the oxidized mercury at the gas-liquid interface, thereby producing an industrial gas which is substantially free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the scrubber liquor;

metering pump means for controlling the aqueous sulfide species directly to the scrubber liquor; and

means for subsequently removing the industrial gas which is substantially free of oxidized mercury from the scrubber.

36. The method according to claim 35, wherein the aqueous sulfide species is selected from the group consisting of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, potassium sulfide, sodium sulfide, sodium hydrosulfide and potassium hydrosulfide.

37. The apparatus according to claim 35 or claim 36, wherein the scrubber is one of a dry scrubber and a wet scrubber.

38. An apparatus for receiving and scrubbing an industrial gas with a scrubber liquor containing an aqueous alkali reagent to remove sulfur species from the industrial gas, the industrial gas also containing mercury, comprising:

means for providing the industrial gas containing oxidized mercury to the scrubber;
means for generating hydrogen sulfide and means for providing said generated
hydrogen sulfide into the industrial gas upstream of the scrubber;
means for creating a gas-liquid interface within the scrubber and mixing the industrial
5 gas with the sulfide from the hydrogen sulfide in order to rapidly precipitate the oxidized
mercury at the gas-liquid interface, thereby producing an industrial gas which is substantially
free of oxidized mercury within the scrubber wherein the precipitated mercury remains in the
scrubber liquor; and
means for subsequently removing the industrial gas which is substantially free of
10 oxidized mercury from the scrubber.

39. The method according to claim 38, wherein the hydrogen sulfide generating means
comprises tank means for providing a solution of one of aqueous sodium sulfide and potassium
sulfide, acid supply means for providing a supply of acid to said solution to generate the
15 hydrogen sulfide; and alkali supply means for providing a supply of alkali to said solution.

40. The apparatus according to claim 39, comprising means for controlling at least one of
the supply of acid and alkali to said solution to adjust the pH of said solution and thereby
control a vapor pressure of the generated hydrogen sulfide within the tank means.

41. The apparatus according to claim 39, wherein the means for supplying the hydrogen
sulfide into the industrial gas comprises: means for supplying air to said tank means to convey a
mixture of air and hydrogen sulfide from said tank means; and at least one of a plurality of pipes
and a plurality of air foils, each having apertures therein, for discharging the mixture of
25 hydrogen sulfide and air into the flue conveying the industrial gas.

42. The apparatus according to claim 38, wherein the hydrogen sulfide generating means
comprises tank means for providing kraft green liquor, acid supply means for providing a
supply of acid to said kraft green liquor to generate the hydrogen sulfide; and alkali supply
30 means for providing a supply of alkali to said kraft green liquor.

43. The apparatus according to claim 42, comprising means for controlling at least one of
the supply of acid and alkali to said kraft green liquor to adjust the pH of the kraft green liquor
and thereby control a vapor pressure of the generated hydrogen sulfide within the tank means.

44. The apparatus according to claim 38, wherein the scrubber is one of a dry scrubber
and a wet scrubber.

46. An apparatus for receiving and scrubbing an industrial gas substantially as herein
5 described with reference to the accompanying drawings.

10 Dated this 10th day of December 2003
MC DERMOTT TECHNOLOGY, INC. and
THE BARCOCK & WILCOX COMPANY
 By their Patent Attorneys
 GRIFFITH HACK

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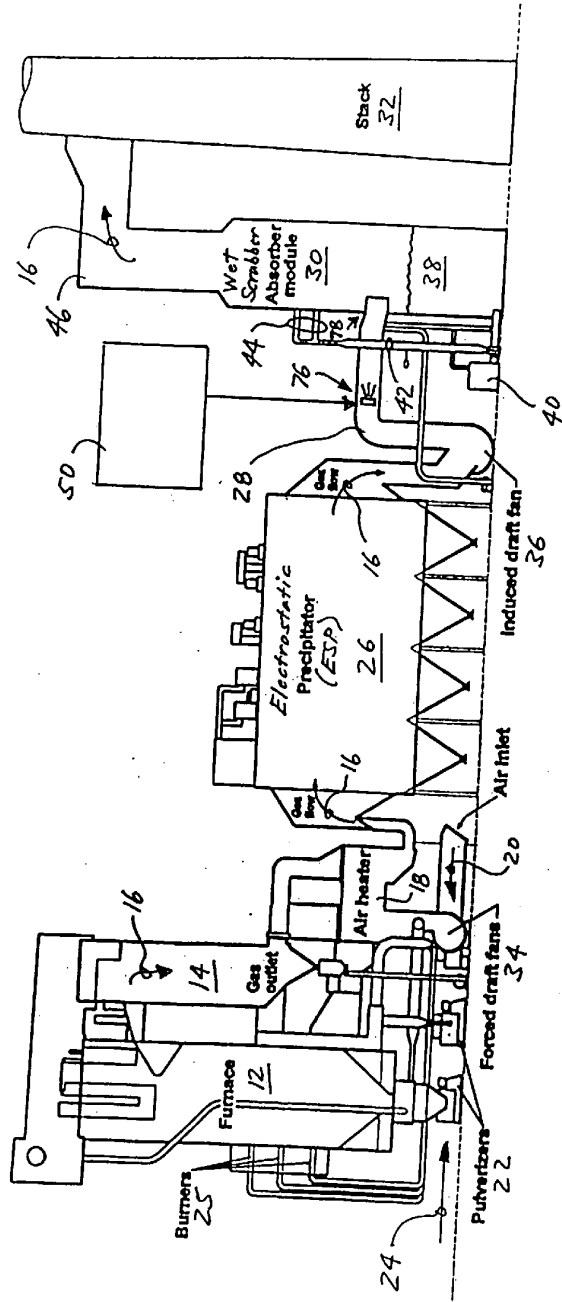


Fig. 1

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Fig. 3

Fig. 2

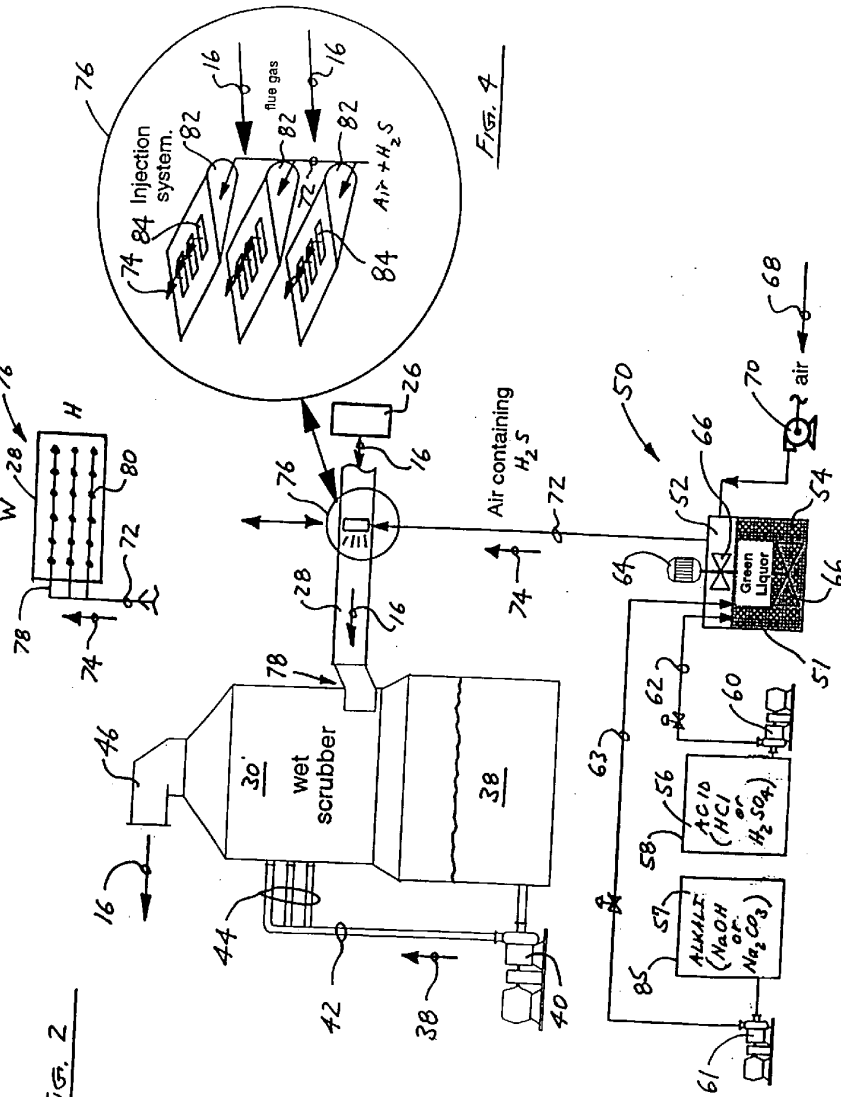
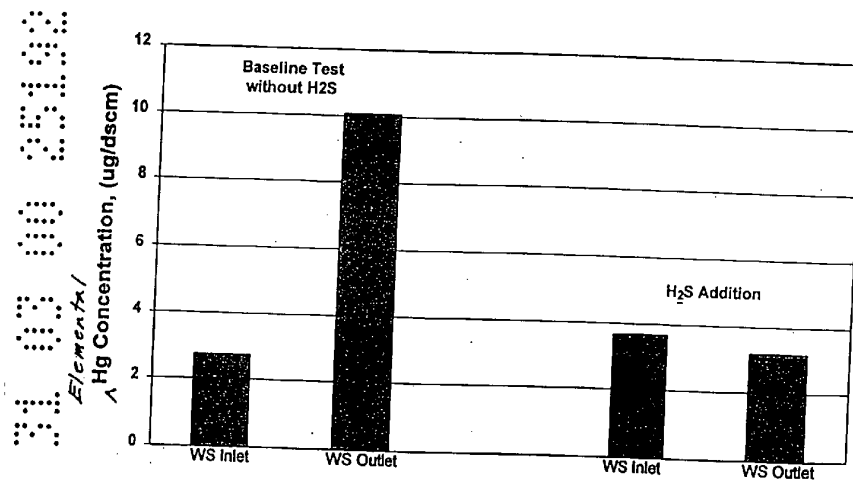


Fig. 4

Fig. 5

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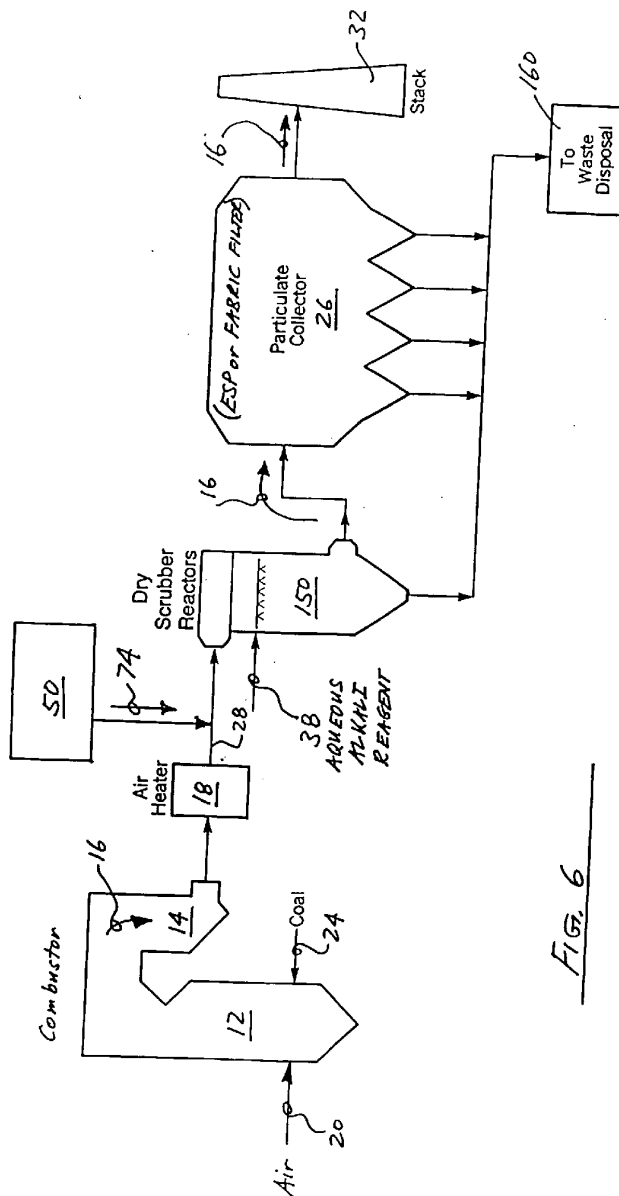


FIG. 6

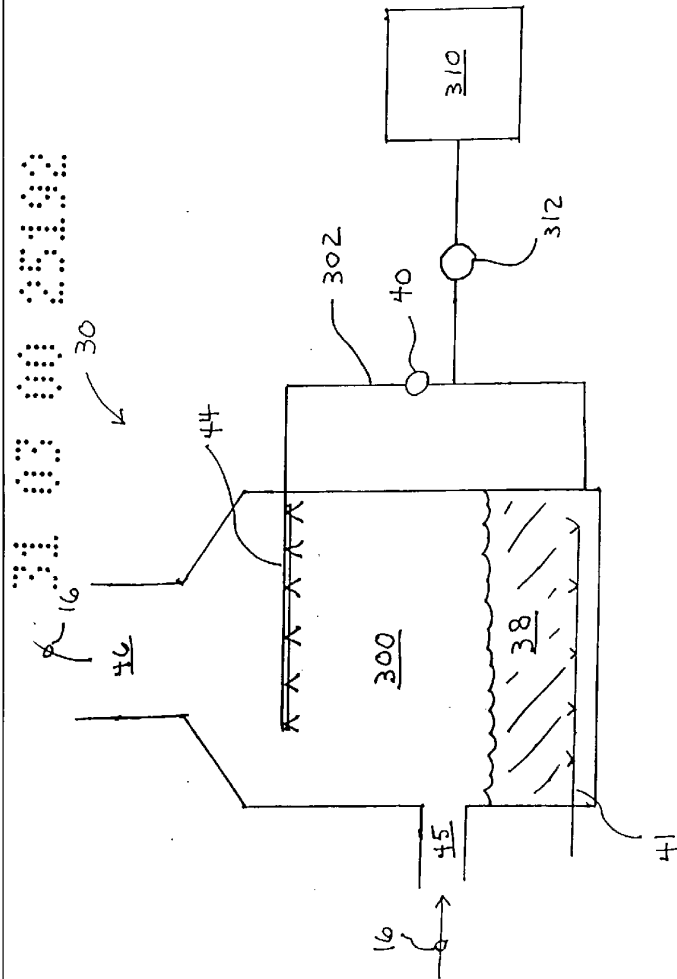


FIG 7

