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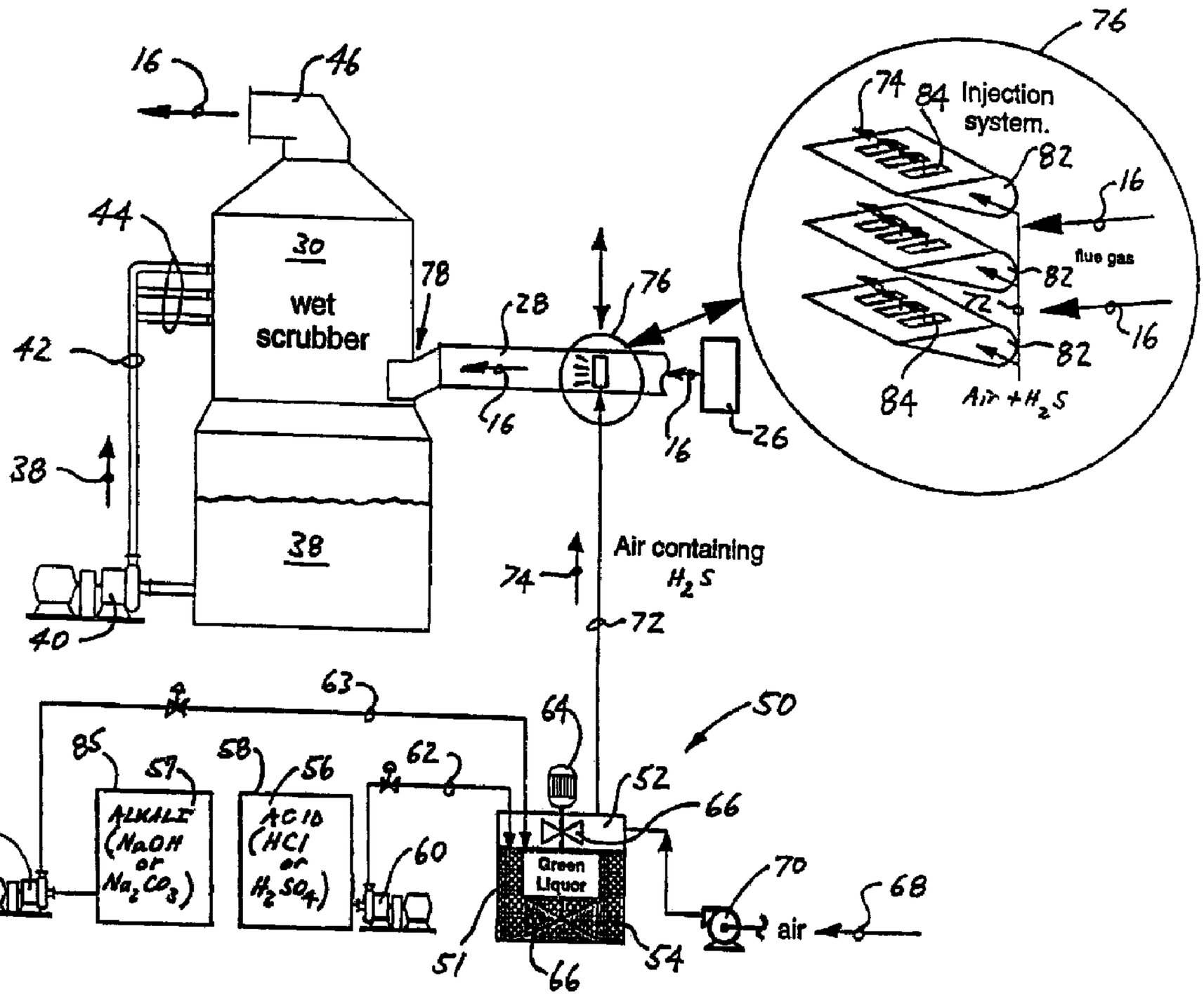
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(54) Title: USE OF SULFIDE-CONTAINING GASES AND LIQUORS FOR REMOVING MERCURY FROM FLUE GASES



(57) Abrégé/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 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.

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 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.

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

This application is a division of co-pending Patent Application No. 2,302,655 filed on March 28, 2000, also entitled USE OF SULFIDE-CONTAINING GASES AND LIQUORS FOR REMOVING MERCURY FROM FLUE GASES.

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, ($HgCl_2$), or in its elemental (Hg^0) 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. 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:

$$M_e^{x} + Hg^{+2} \rightarrow M_e^{x+2} + Hg^{0}$$

$$2M_e^{x} + Hg^{+2} \rightarrow 2M_e^{x+1} + Hg^{0}$$

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

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 hyrdrogen sulfide and/or aqueous sulfide ions. 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 ions, or some other sulfide ion source):

$$S^{-2}(aq) + HgCl_2(g) \rightarrow HgS(s) + 2\,Cl^{-}(aq)$$

and/or

$$H_2S(g) + HgCl_2(g) \rightarrow HgS(s) + 2\,HCl(aq)$$

HgS has a solubility product of $3x10^{-52}$ 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

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, one aspect is drawn to an improvement in a method using a wet scrubber for receiving and scrubbing an industrial gas containing mercury with a wet scrubber slurry, the improvement comprising: adding hydrogen sulfide to the industrial gas; and scrubbing the industrial gas in the wet 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 before it enters the wet scrubber, or within the wet scrubber.

Another aspect of the present invention is drawn to an apparatus using a wet scrubber for receiving and scrubbing an industrial gas containing mercury with a wet scrubber slurry, and particularly the improvement comprising: means for generating hydrogen sulfide; and means for supplying the hydrogen sulfide to 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 aqueous sodium and/or potassium sulfide to generate the hydrogen sulfide. Advantageously, the hydrogen sulfide generating system may use equipment and methods

wherein the acid is added to 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.

Nevertheless, another aspect of the present invention is drawn to an improvement in a method using a scrubber for receiving and scrubbing an industrial gas containing mercury, the improvement comprising: adding an aqueous sulfide salt 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.

Another aspect of the present invention is drawn to an apparatus using a scrubber for receiving and scrubbing an industrial gas containing mercury with an aqueous alkali reagent, and particularly the improvement comprising: means for providing sulfide ions and means for controlling the sulfide ions provided to the industrial gas in the scrubber. The present invention is again particularly suited to utility 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.

Another aspect of the present invention is drawn to an apparatus for receiving and scrubbing an industrial gas containing mercury with an aqueous alkali reagent, comprising a scrubber, having a scrubber 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. The present invention is again particularly suited to utility installations which burn fossil fuels, such as coal, and may be incorporated into a wet or dry scrubber.

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:

$$S^{-2}\,(aq) + H_20 \overset{\leftarrow}{\rightarrow} HS^-\,(aq) + OH^-\,(aq)$$

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, sodium sulfide, and/or thioacetamide, 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.

The various features of novelty which characterize 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 ions. 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

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 aqueous sulfide ions 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. While the 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 manufacturers.

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 recalculate 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 flue gas 16 where it absorbs SO_2. 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.

Referring now to Fig. 2 in particular, there is shown an embodiment of a system for accomplishing the method of injecting small amounts of H_2S into flue gas for mercury removal according to the present invention. An H_2S 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 H_2S are mixed and the mixture 74 of air and H_2S is transferred to an injection apparatus 76, described *infra*. The H_2S vapor pressure in the tank 51 is controlled by pH. The pH in the tank 51 liquid solution 54 is controlled by the addition of a strong mineral acid 56, or by the addition of an alkali solution 57 such as sodium carbonate or sodium hydroxide (NaOH or Na_2CO_3) from a tank or container 85. The acid is added to lower the pH and increase the H_2S vapor pressure in tank 51. The alkali is added to raise the pH and lower the H_2S vapor pressure in tank 51. The H_2S 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.

Air 68 is provided by fan (blower or compressor) means 70 into the upper section 52 of tank 51 where it mixes with the H_2S. Line 72 from the upper section of the tank 51 conveys the mixture 74 of air and H_2S to an injection system 76 in flue 28 for injecting the H_2S-air mixture 74 into the flue gas 16.

The rate of hydrogen sulfide generation is controlled by the rate of acid addition. The rate of air 68 provided into the tank 52 is controlled by the fan means 70 that supplies the air 68 in the quantity and at the pressure necessary for rapid mixing of the H_2S mixture 74 with the flue gas 16 at an inlet 78 to the wet scrubber 30.

The H_2S-air injection system 76 can comprise one or more pipes 77 arranged in a simple grid, each of the pipes 77 being provided with a plurality of apertures 80, the pipes 77 arranged across a width W and height H of flue 28, as shown in Fig. 3. Alternatively, the H_2S-air injection system 76 could utilize a more sophisticated structure incorporating air foil mixing technology such as that illustrated in Fig. 4. In the system of Fig. 4, one or more air foils 82 would be provided, each having a plurality of slots or apertures 84 for introducing the H_2S-air mixture 74 into the flue gas 16 as the flue gas 16 flows across the air foils 82. In either case, the flue gas 16 flowing past the pipes 77 or air foils 82 picks up the H_2S-air mixture 74 and conveys it to the wet scrubber 30 to increase the H_2S content in the flue gas 16 to a desired level, preferably between about 0.05 and 10 ppm, or more preferably 2 ppm or below.

Fig. 5 depicts test results obtained when a pilot scale wet scrubber was used to capture mercury. In Fig. 5, the legends "WS Inlet" and "WS Outlet" refer to conditions at the wet scrubber 30inlet and outlet, respectively. The left two bars represent baseline.....

conditions of the elemental mercury content of the flue gas 16 at the wet scrubber inlet and outlet, without H_2S 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 H_2S 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 SO_2 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 ion 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. Most preferably, sulfide ions can be provided by means of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, or an aqueous solution containing potassium sulfide, sodium sulfide, and/or thioacetamide.

Alternatively, sulfide ion solution 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 ions 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 ion 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 8×10^3 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 ions added to recirculation line 302 allow spray header 44 to mix the sulfide ions 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 H_2S 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 H_2S 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. Most preferably, sulfide ions can be provided by means of sulfidic waste water, kraft caustic liquor, kraft carbonate liquor, or an aqueous solution containing potassium sulfide, sodium sulfide, and/or thioacetamide.

Alternatively, sulfide ion solution 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 ions 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 ion 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 ions provided to the gas may also be achieved by periodic and/or manual addition of the aqueous sulfide ions 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 ions added to feed line 402a and/or bulk storage vessel 401 allow spray header 44 to mix the sulfide ions 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 ions can be incorporated with minimal modifications or additions to current emissions control systems. Most significantly, use of aqueous sulfide ions 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 ions 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 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 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 roasters.

CLAIMS

1. In a method for receiving and scrubbing an industrial flue gas containing mercury with an aqueous alkali reagent in a scrubber, the improvement comprising:

generating hydrogen sulfide proximate to the scrubber by providing alkali to a solution comprising sodium sulfide or potassium sulfide; and

supplying the hydrogen sulfide to the scrubber to remove mercury from the industrial flue gas.

2. The method according to claim 1, further comprising supplying air to the hydrogen sulfide to produce a mixture of air and hydrogen sulfide and wherein the step of supplying the hydrogen sulfide comprises providing the mixture of air and hydrogen sulfide to the industrial flue gas.

3. The method according to claim 1, further comprising controlling the supplying the hydrogen sulfide step by adjusting at least one of the supply of acid and alkali to said solution to alter the pH of said solution and, correspondingly, a vapor pressure of the generated hydrogen sulfide.

4. The method according to claim 2, wherein the mixture of air and hydrogen sulfide is supplied to the industrial flue gas at multiple locations by way of at least one of a plurality of pipes and a plurality of air foils, each having apertures therein, for discharging the mixture of hydrogen sulfide and air into a flue conveying the industrial flue gas to the scrubber.

5. The method according to claim 1 or claim 3, wherein said solution comprising sodium sulfide or potassium sulfide is kraft green liquor.

6. The method according to claim 5, further comprising controlling the supplying the hydrogen sulfide step by adjusting the pH of the kraft green liquor and, correspondingly, a vapor pressure of the generated hydrogen sulfide.

7. The method according to claim 1, wherein the scrubber is a wet scrubber.

8. The method according to claim 1, wherein the scrubber is a dry scrubber.

9. The method according to claim 1, wherein the step of supplying the hydrogen sulfide to the industrial flue gas occurs at a rate sufficient to produce a concentration of hydrogen sulfide in the industrial flue gas of about 0.05 to 10 ppm.

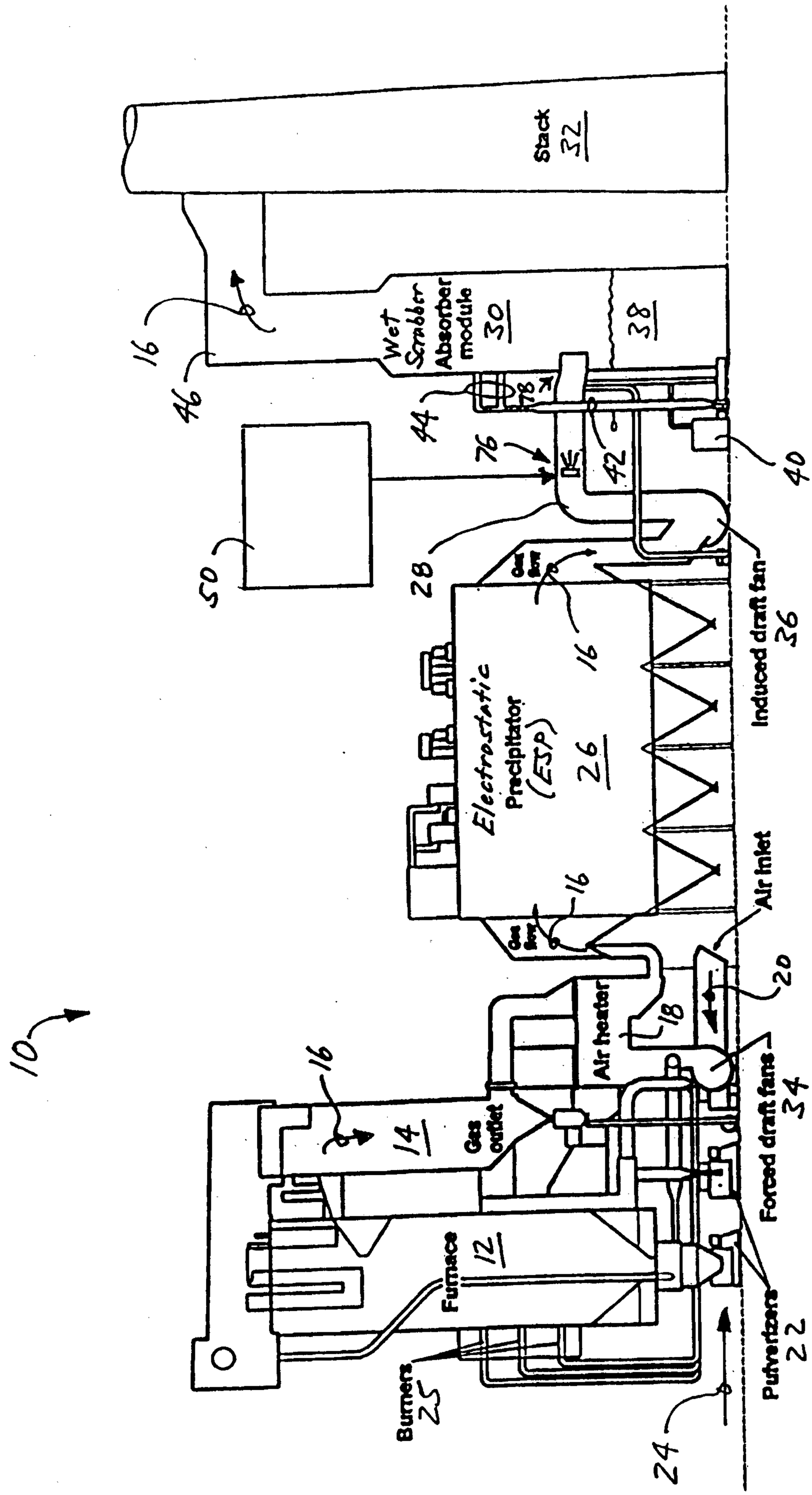

10
Stack 32
16
46
Wet Scrubber Absorber module 30
38
44
48
76
42
40
50
28
Electrostatic Precipitator (ESP) 26
Induced draft fan 36
Air inlet
20
18
Air heater
Forced draft fans 34
14
Gas outlet
Furnace 12
Burners 25
Pulverizers 22
24

FIG. 1

FIG. 2

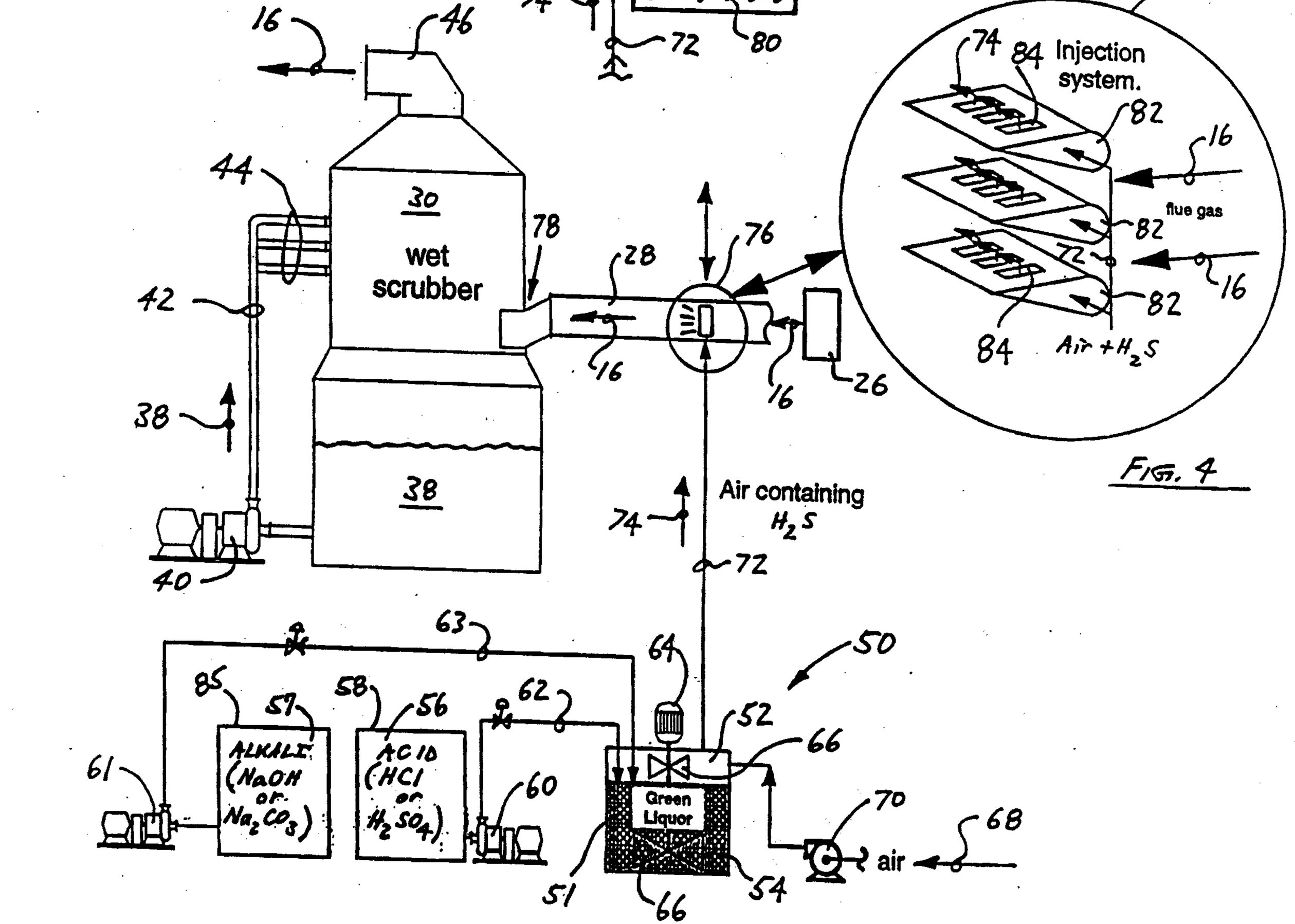


FIG. 3

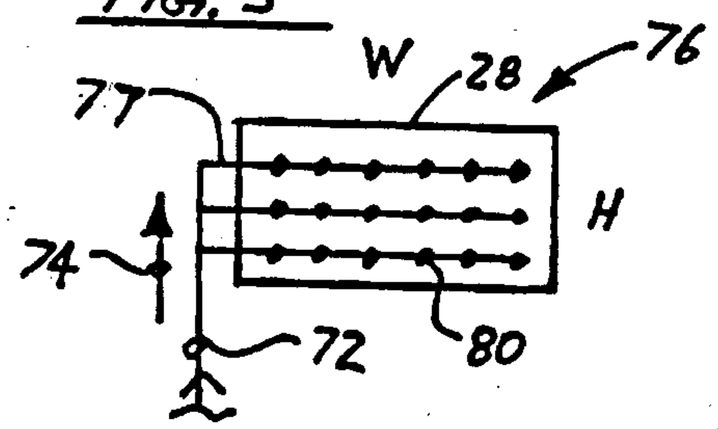


FIG. 4

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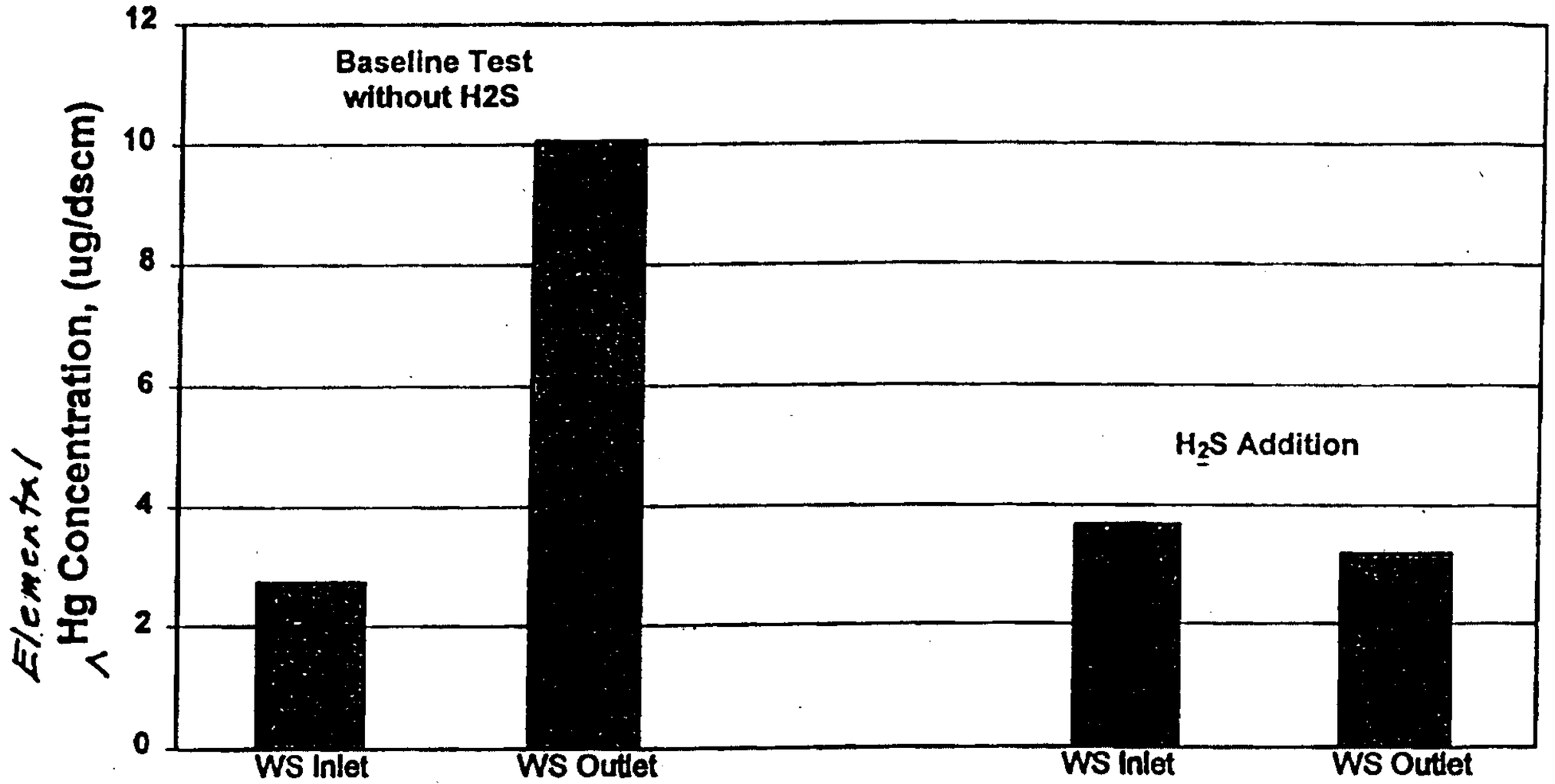

Baseline Test
without H2S
H2S Addition
Elemental Hg Concentration, (ug/dscm)
12
10
8
6
4
2
0
WS Inlet
WS Outlet
WS Inlet
WS Outlet

FIG. 5

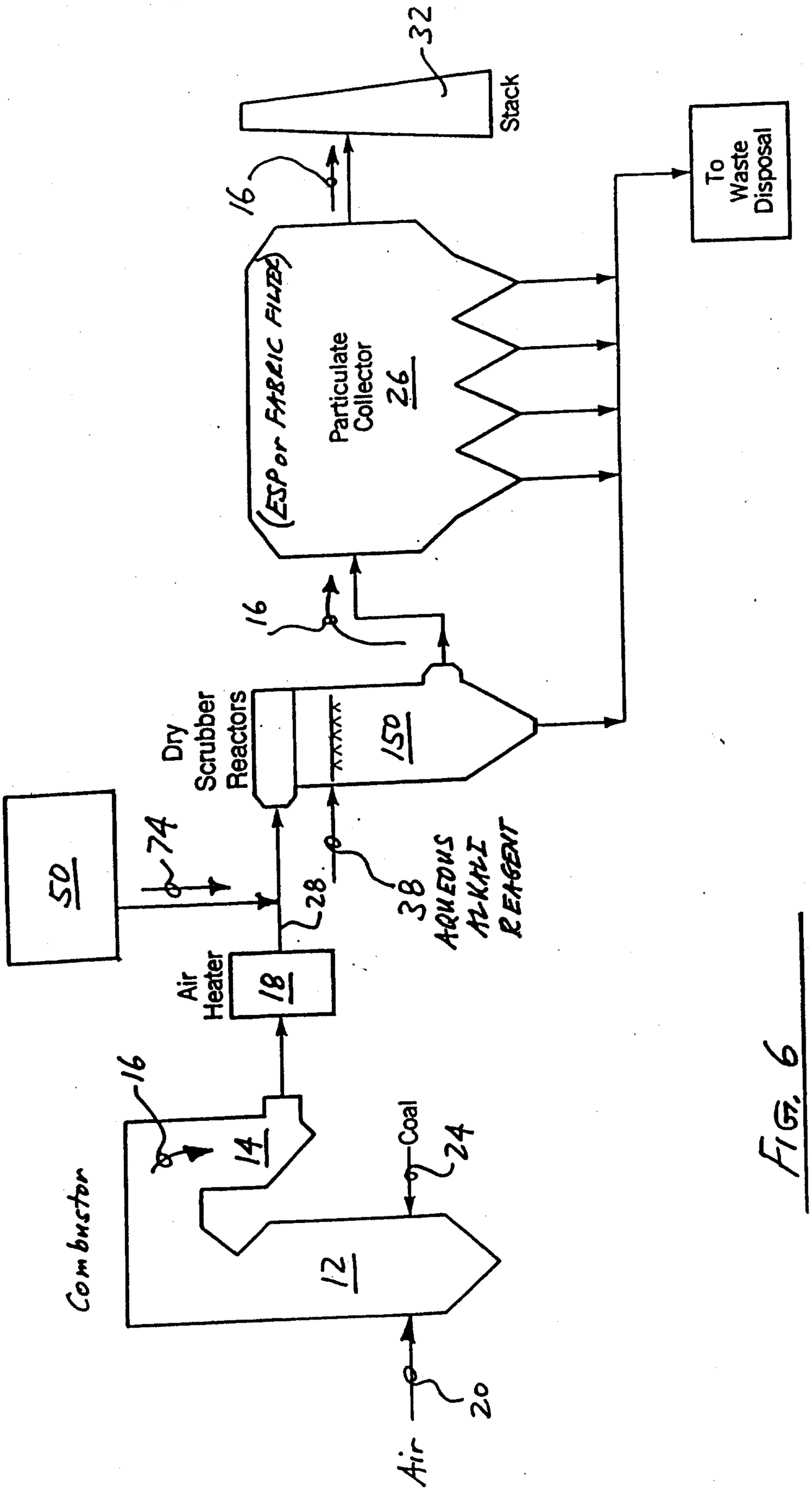

Combustor
14
12
16
Air
20
Coal
24
Air Heater
18
50
74
Dry Scrubber Reactors
150
28
38
AQUEOUS ALKALI REAGENT
Particulate Collector
26
(ESP or FABRIC FILTER)
32
Stack
To Waste Disposal

FIG. 6

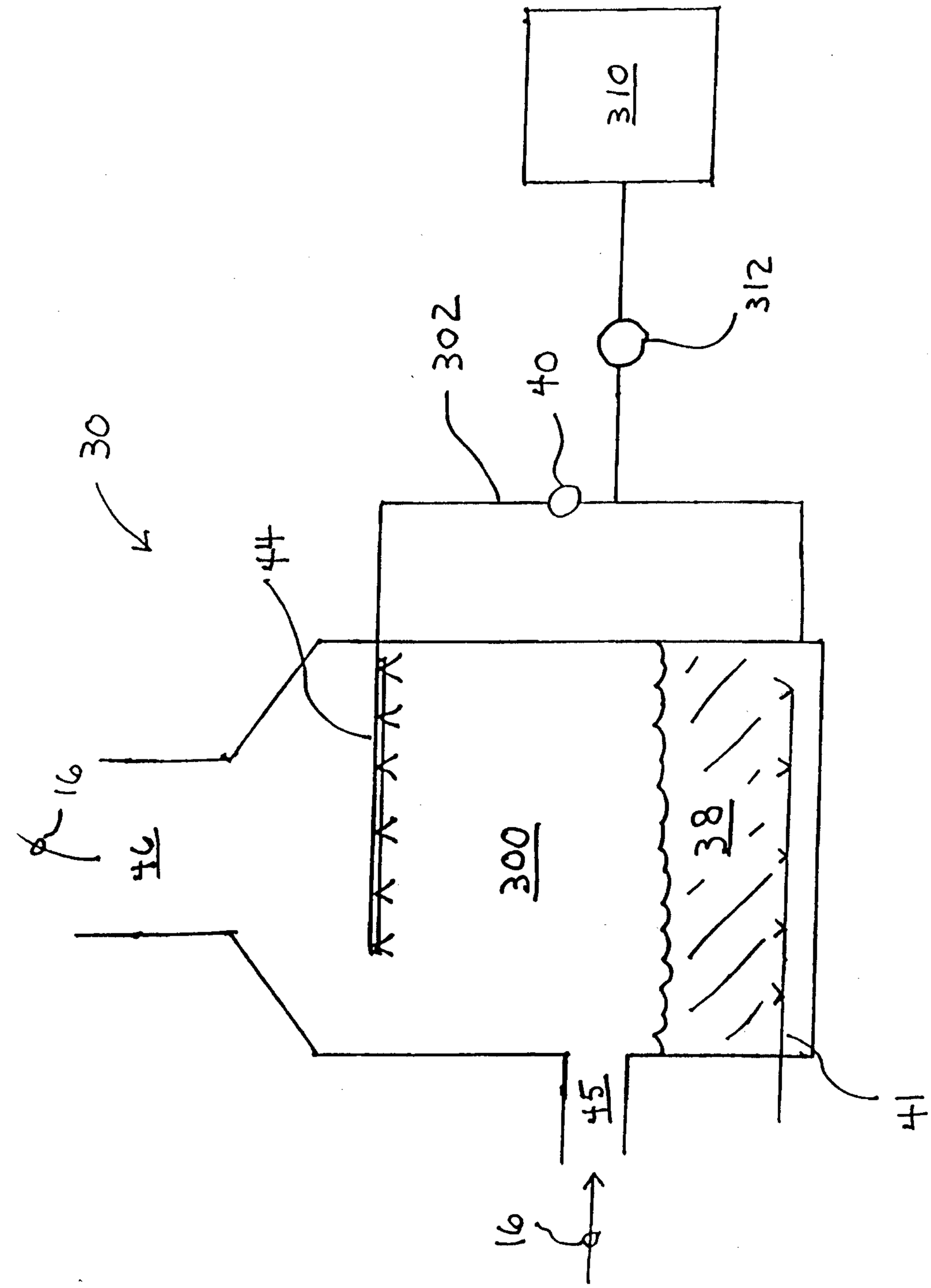


FIG 7

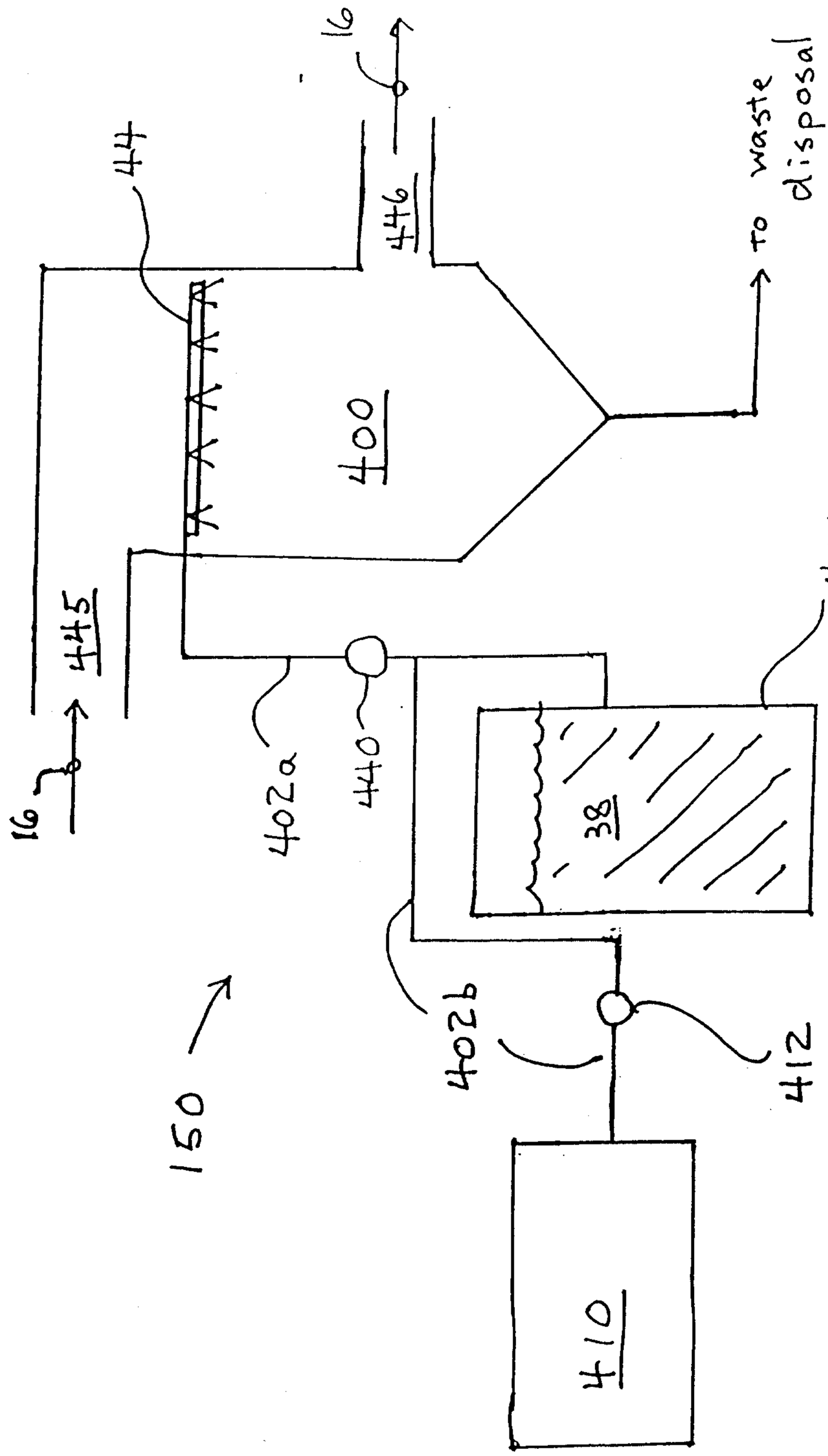
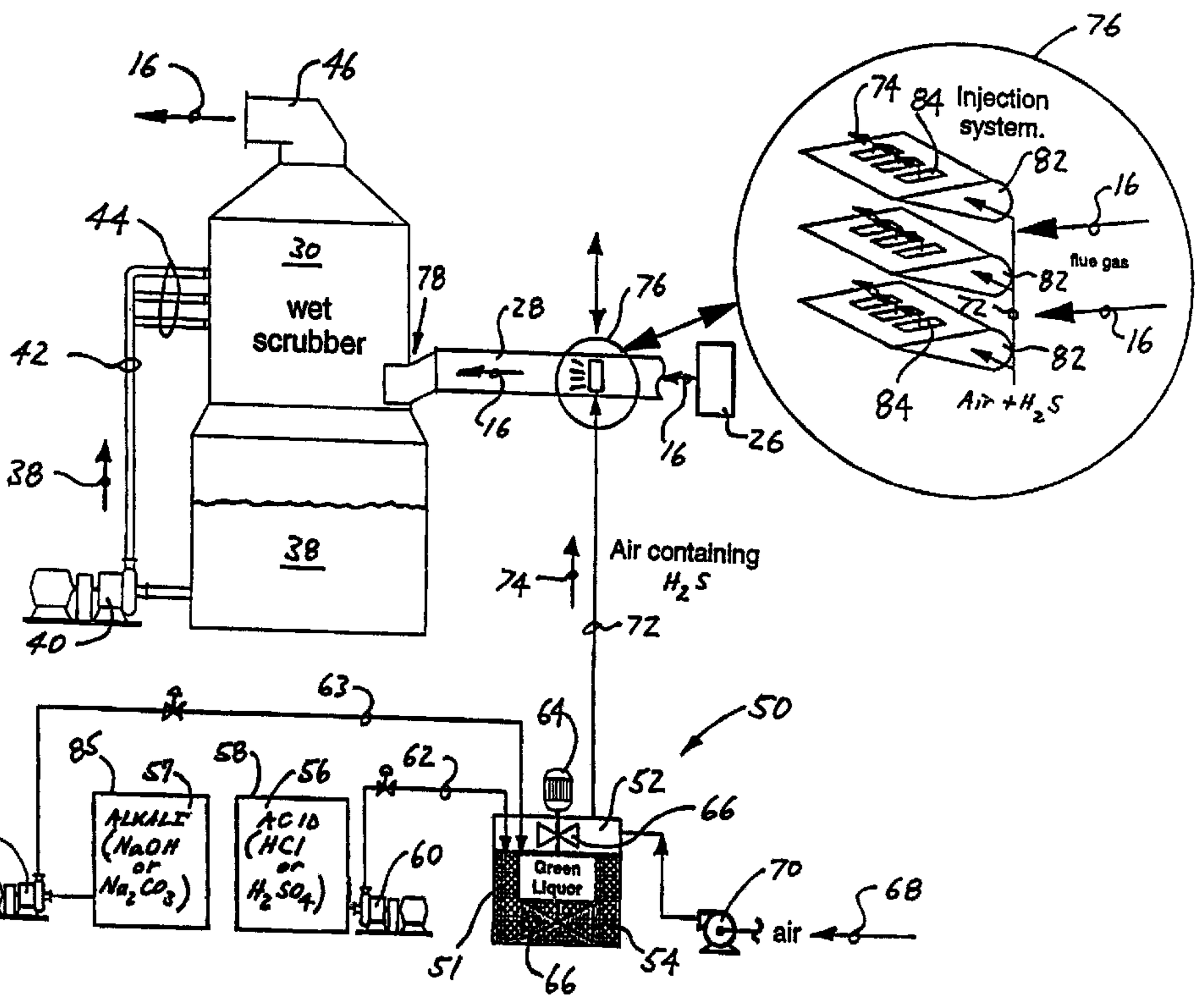

16
44
446
400
445
16
402a
440
38
402b
412
150
401
410
To waste disposal

FIG 8


16
46
44
30
wet scrubber
78
28
76
42
16
16
26
38
38
40
74
Air containing H_2S
72
63
64
50
85
57
58
56
62
52
66
61
ALKALI (NaOH or Na_2CO_3)
ACID (HCl or H_2SO_4)
60
Green Liquor
70
68
air
51
66
54
76
74
84
Injection system.
82
16
flue gas
82
72
16
82
84
Air + H_2S