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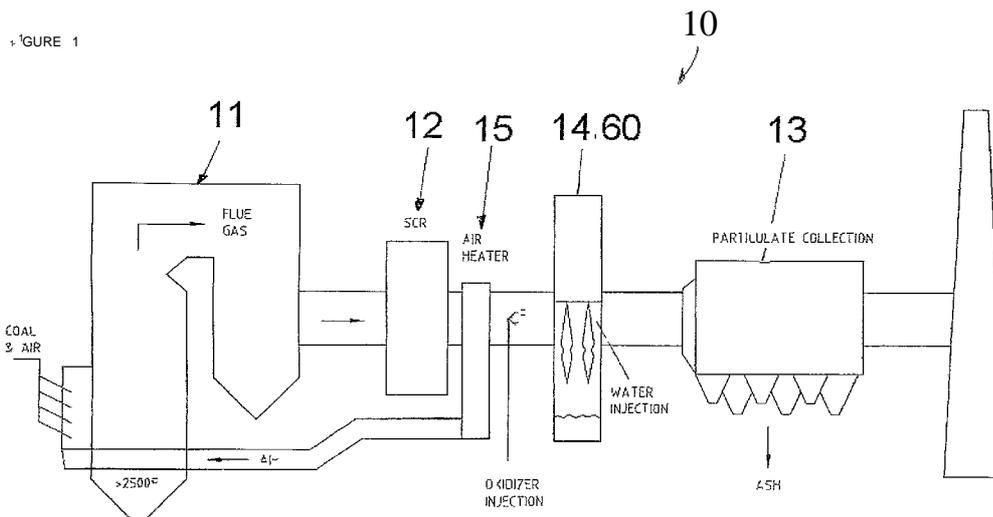
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(54) Title: REMOVAL OF POLLUTANTS FROM A GAS FLOW



(57) Abstract: A method of removing pollutants from a gas flow includes the step of introducing an oxidising agent into the gas flow such that higher level oxides of NO<sub>x</sub> and SO<sub>x</sub> are produced from reactions in the gas flow. A coolant is introduced into the gas flow to hydrate the higher level oxides to form acid gases and to reduce the temperature and thereby condense the acid gases into acid mists and maximise the efficiency of reactions in the gas flow. An alkaline sorbent is introduced to remove excess acidic components. The invention extends to an apparatus for removing pollutants from a gas flow.

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## "REMOVAL OF POLLUTANTS FROM GAS FLOWS"

### FIELD OF THE INVENTION

This invention relates generally to air pollution control.

5 In particular, but not exclusively, the invention is directed to apparatus and methods for removing pollutants from exhaust gases of industrial processes.

### BACKGROUND ART

10 Mere reference to background art herein should not be construed as an admission that such art constitutes common general knowledge in relation to the invention.

An undesired consequence of burning fossil fuels (e.g. coal, oil, and natural gas) in industrial processes, such as coal-fired electricity generators and cement kilns, is the generation of large quantities of air pollutants such as nitrogen oxide ("NO"), and  
15 nitrogen dioxide ("NO<sub>2</sub>") and mercury (Hg). These pollutants are known to have negative health effects on living things, but it is generally difficult to remove them in conventional exhaust gas treatment systems.

It is believed that mercury exists in exhaust gas chiefly as metallic or elemental mercury (Hg) or as oxidized or ionic mercury normally occurring in the form of  
20 mercury chloride (HgCl<sub>2</sub>). Since HgCl<sub>2</sub> is easily absorbed into water, it can be removed in a desulfurizing absorption tower or the like. However, elemental mercury (Hg) has a very low solubility in water and cannot be absorbed in a desulfurizing absorption tower. Consequently, elemental mercury vapor may be discharged from the exhaust stack.

25 In exhaust gases from cement kilns, nearly all mercury is in the elemental mercury form. In this situation, the concentration of chlorine is low, usually less than 50ppm, and concentrations of metal oxides (mainly CaO) are high, usually greater than 40%. Nearly all ionic mercury is removed on the way from the kiln to an electrostatic precipitator.

30 Absorption methods such as activated carbon absorption, sodium hypochlorite absorption and the like have conventionally been employed as mercury removal techniques. These techniques are commonly used in waste incinerators and have been adapted and tested for use on utility boilers. In particular, the activated carbon absorption method, in which activated carbon powder is blown into exhaust gas and

recovered with a bag filter or electrostatic precipitator, has already been put to practical use by US utilities.

In one known sodium hypochlorite absorption method, an additive such as sodium hypochlorite is directly added, for example, to the cooling water of the cooling tower, the absorbing fluid of a desulfurizing absorption tower, or the feed water or circulating water of a wet dust collector. However, in all cases, an additive is added to a main unit in an exhaust gas treatment plant, and some additives involve the risk of interfering with its intrinsic function. For example, the cooling water may have a low pH and hence require a large amount of an oxidizing agent, forming peroxides in the cooling tower, and oxidizing sulfurous acid in the wet dust collector to cause an increase in acidity. Moreover, this method has been adapted chiefly to the treatment of exhaust gas from refuse incineration, and is not suitable for the treatment of a large-volume of gas such as exhaust gas from an electric power plant.

Since elemental mercury is hardly soluble in water, it passes through the desulfurizer, as described above. If elemental mercury can be made soluble in water, it may be removed in a desulfurizer. Accordingly, it is conceivable that, if elemental mercury can be converted into a water-soluble form of oxidized mercury, such as mercury chloride or mercury bromide, with the addition of a halogen compound, such as calcium bromide, in the combustion process, the mercury may be removed in a desulfurizer or SO<sub>2</sub> scrubber installed downstream thereof. However, the addition of a large amount of the halogen agent is problematic as it can cause corrosion of the flue and downstream units of the system and shorten the life of the plant equipment. Moreover, the halogen agent can cause a significant increase in utility costs and may increase particulate emissions.

Nitrogen oxide is removed using a selective catalytic reactor (SCR) to reduce the nitrogen oxide to nitrogen and oxygen. After the SCR, an air heater, a dust collector, a gas-gas heater (heat exchanger) and a SO<sub>2</sub> Scrubber absorption tower are usually installed in that order. Yet amongst those, the halogen agent may have a marked corrosive or damaging effect on the heat exchanger used for cooling purposes. Another problem is that since a halogen agent is introduced in the desulfurizing absorption tower, the increased halogen concentration in the absorbing fluid affects the pH level and causes corrosion or damage of the metallic parts of the tower. Moreover, an increase in halogen concentration within the desulfurizing absorption tower may cause a reduction in oxidation capability during desulfurization or a reduction in desulfurization

capability itself, leading to a reduction in the overall performance of the system. Furthermore, an increase in halogen concentration may cause an increase in the foamability of the absorbing fluid, possibly raising the pressure loss within the absorption tower and causing an increase in operating power.

5 Various methods have been proposed to remove air pollutants such as nitrogen oxides or mercury from the output or exhaust gas flows in an effective and economic manner. Examples of processes for removing such pollutants can be found in US patents 4619608, 6162409, 6284208, 6447740, 6534024, 7048899 and US patent application 2005147549, the disclosures of which are incorporated herein by reference.

10 Carbon dioxide is a major product of most fossil fuel burning processes. The adverse effects of carbon dioxide on global warming and the environment are well documented. Although various methods of removing or absorbing carbon dioxide are known, the cost of stand-alone plants for removing or absorbing carbon dioxide is prohibitively expensive.

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### SUMMARY OF THE INVENTION

According to a first aspect of the invention, there is provided a method of removing pollutants from a gas flow comprising the steps of:

20 introducing an oxidising agent into the gas flow such that higher level oxides of NO<sub>x</sub> and SO<sub>x</sub> are produced from reactions in the gas flow,

introducing coolant into the gas flow to hydrate the higher level oxides to form acid gases and to reduce the temperature and thereby condense the acid gases into acid mists and maximise the efficiency of reactions in the gas flow; and

introducing an alkaline sorbent to remove excess acidic components.

25 The oxidising agent may be introduced in the form of an agent that oxidises nitrogen oxide (NO) to form higher level oxides and introducing the coolant in the form of water.

The steps of introducing the oxidising agent and the coolant into the gas flow may be carried out by injection.

30 The method may include the step of removing particulate material from the gas flow.

The method may include the steps of:

directing the gas flow containing nitrogen oxides and mercury from an inlet to an outlet of a reactor;

injecting an oxidising agent into the gas flow to form higher level nitrogen oxides; and

injecting water into the gas flow such that the higher level nitrogen oxides hydrate and condense into an acid mist that combines with mercury to form mercury nitrate ( $\text{Hg}(\text{NO}_3)_2$ ) for removal from the reactor.

The step of injecting the oxidising agent may be carried out upstream or downstream of the step of injecting the water. Instead, the steps of injecting the oxidising agent and the water may be carried out with an oxidising agent in solution with the water.

The water may be injected into the gas flow in successive stages from respective spaced injectors.

Incoming gas may be passed through a gas-gas heat exchanger to cool the incoming gas and outgoing gas may be passed through the gas-gas heat exchanger to heat the outgoing gas to above a dew point to minimize corrosion.

The sorbent material may be injected into the gas flow to facilitate removal of oxidised nitrogen oxides and sulphur oxides as well as the excess acidic components.

The method may include the step of passing the gas through at least one of a flue gas desulfurization stage and a spray dryer absorber upstream of the reactor.

The method may include the steps of facilitating reactions of acids and anhydrides with calcium acetates or calcium salts of organic acids in the reactor to produce solutions of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CH}_3\text{COOH}$  and solid  $\text{CaSO}_3$  in suspension and collecting the solutions and suspended material as a slurry.

The method may include the steps of feeding compressed air into the slurry to oxidize the  $\text{CaSO}_3$  to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and removing  $\text{CaSO}_4$  to a separation device, such as a centrifuge.

The method may include the steps of directing filtrate from the separation device into storage and removing heavy metals from said filtrate.

The step of receiving the gas in a reactor may include the step of receiving the gas in a two-stage reactor such that said higher level nitrogen oxides and mercury nitrate are formed in a first stage of the reactor and  $\text{CO}_2$  removal is carried out in a second stage of the reactor.

The method may include the step of collecting sorbent material from the first stage reactor and re-circulating the sorbent material back to the first stage.

The method may include the step of spraying a slurry of lime into a second stage of the reactor to react with the  $\text{CO}_2$  to produce  $\text{CaCO}_3 + \text{H}_2\text{O}$ , and with  $\text{CH}_3\text{COOH}$  to produce  $\text{Ca}(\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O}$ . The  $\text{CH}_3\text{COOH}$  may be directed from the second stage back to the first stage as the sorbent material.

5 According to a second aspect of the invention, there is provided an apparatus for removing pollutants from a gas flow, the apparatus comprising

a chamber having an inlet for receiving the gas flow and an outlet for discharging the gas flow;

10 an oxidising agent injecting arrangement positioned in the chamber for injecting an oxidising agent into the gas flow such that higher oxides of  $\text{NO}_x$  and  $\text{SO}_x$  are produced from reactions in the gas flow;

15 a coolant injecting arrangement for injecting a coolant into the gas flow to hydrate the higher level oxides to form acid gases and to reduce the temperature thereof and thereby condense the acid gases into acid mists and maximise the efficiency of reactions in the gas flow; and

a sorbent injection arrangement positioned in the chamber for injecting an alkaline sorbent into the gas flow to remove excess acidic components.

The oxidising agent injecting arrangement may be positioned upstream or downstream of the coolant arrangement.

20 The sorbent injecting arrangement may be positioned downstream of the coolant injecting arrangement for injecting the sorbent into the gas flow.

An agglomerator may be positioned downstream of the chamber for receiving discharged gas from the outlet of the chamber.

25 At least one of a flue gas desulfurization stage and a spray dryer absorber may be positioned upstream of the inlet of the chamber.

The apparatus may include a gas-gas heat exchanger. The chamber and the heat exchanger may be configured so that incoming gas flow passes through the heat exchanger to be cooled and outgoing gas flow passes through the heat exchanger to be heated to above a dew point to minimize corrosion.

30 The chamber may be defined by a reactor. The reactor may be one of an upward and a downward flow reactor. A hopper may be positioned below the reactor to collect reaction products formed in the reactor.

The chamber may be defined by one stage of a multiple reactor installation. In particular, the chamber may be defined by a first stage of a two-stage reactor

installation, a second stage of the reactor installation being configured for carbon dioxide removal.

In one embodiment, the reactor installation may be inclined. In another embodiment, the reactor installation may comprise a pair of sequential vertical reactors.

5 The first and second stages are defined by sequential first and second vertical reactors, respectively. A first cyclone may be interposed between the first and second vertical reactors to assist in the removal of reaction products from the first reactor and a second cyclone may be positioned downstream of the second vertical reactor to assist in the removal of reaction products from the second vertical reactor.

10 One of a flue gas desulfurization stage and a spray dryer absorber may be positioned upstream of the reactor installation.

A first hopper may be operatively arranged with respect to the first stage to receive particulate material from the first stage and the apparatus may include a first tank positioned to receive the particulate material from the first hopper. The first tank  
15 may be in fluid communication with the first stage and the apparatus may include a pump and conduit arrangement for pumping material from the first tank back into the first stage downstream of the cooling injection arrangement.

A compressed air supply may be connected to the first tank to facilitate oxidation of material in the first tank.

20 A first separating device may be operatively connected to the first tank for performing a separating operation on the material in the first tank.

A second hopper may be operatively arranged with respect to the second chamber to receive particulate material from the second stage and the apparatus may include a second tank positioned to receive the particulate material from the second  
25 hopper.

The second tank may be in fluid communication with the second stage and the apparatus may include a further pump and conduit arrangement for pumping material from the second tank back into the second stage.

A second separating device may be operatively connected to the second tank to  
30 perform a separating operation on the material in the second tank and the second separating device may be connected to the first tank to direct product from the separating operation to the first tank.

Thus, the invention is directed to apparatus and methods for removing pollutants, such as NO<sub>x</sub>, SO<sub>x</sub> and mercury, from exhaust gases of industrial processes, particularly fossil fuel burning furnaces, by oxidation at relatively low temperatures.

5

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram illustrating a method, in accordance with an embodiment of the invention, and the location of an apparatus, in accordance with one embodiment of the invention, both for removing pollutants from a gas flow, in this example, of an industrial process.

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Figure 2 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow.

Figure 2A is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow.

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Figure 3 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow and having a heat exchanger.

Figure 4 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow having an absorbent injecting arrangement and an agglomerator.

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Figure 5 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, indicating an orientation and position of a coolant injection arrangement.

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Figure 6 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, indicating the orientation and position of an oxidising agent injection arrangement.

Figure 7 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, indicating an orientation and position of a sorbent injection arrangement.

30

Figure 8 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, having an agglomerator.

Figure 9 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, indicating a configuration of an oxidising agent spray arrangement.

Figure 10 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, indicating a configuration of a coolant injection arrangement.

5 Figure 11 is a schematic diagram of an apparatus, in accordance with another embodiment of the invention, for removing pollutants from a gas flow, having sonic horns for removal of build-up.

Figure 12 is a schematic diagram of a multiple reactor process with an inclined two-stage reactor indicating a method, in accordance with an embodiment of the invention, for removing pollutants from a gas flow.

10 Figure 13 is a schematic diagram of a multiple reactor process with a pair of sequential vertical reactors indicating a method, in accordance with an embodiment of the invention, for removing pollutants from a gas flow.

Figure 14 is a schematic diagram of a multiple reactor process incorporating a pair of cyclones indicating a method, in accordance with an embodiment of the invention, for removing pollutants from a gas flow.

### DESCRIPTION OF EMBODIMENTS OF THE INVENTION

In Figure 1 reference numeral 10 generally indicates an apparatus, in accordance with the invention, for removing pollutants from a gas flow. Figure 1 also illustrates an apparatus and industrial process or method, in accordance with an embodiment of the invention, in which flue or exhaust gas from a coal fired utility boiler 11 is passed through a selective catalytic reducer (SCR) 12 before entering a particulate collection stage 13, such as an electrostatic precipitator or fabric filter. The SCR 12 uses selective catalytic reduction to remove some of the nitrogen oxides through a chemical reaction between the exhaust gas, a reducing additive (most commonly ammonia), and a catalyst. The reducing additive reacts with NO<sub>x</sub> in the exhaust gas to form harmless water vapour and nitrogen gas.

The coal fired utility boiler 11 is typically part of a coal fired power station. Although a coal fired utility boiler 11 is illustrated, it is to be understood that the invention may be used with other fuel burning or combustion processes, such as those used in waste incinerators, cement kilns, smelters and tyre burners, which generate mercury and/or oxides of either nitrogen or sulphur in their exhaust gases.

The present invention is concerned with the further removal of pollutants, such as nitric oxides NO<sub>x</sub>, SO<sub>x</sub> and mercury, from the exhaust gas flow, and is embodied in

the form of a reactor 14 located between the SCR 12 or air heater and the particulate collection stage 13. The reactor is shown in more detail in Figures 2 and 2A.

Figure 2 illustrates a 'downward flow' reactor 14 in the form of an upright duct 20 which forms a reaction vessel. The reactor 14 has an inlet 21 at an upper end thereof adapted to receive exhaust gas from the boiler 11 or other industrial combustion process, and an outlet 22 at a lower end. A chamber 17 is interposed between the inlet 21 and the outlet 22.

The gas flow within the reactor 14 is generally from top to bottom. The reactor inlet gas velocity is typically 10-25m/s, and the outlet gas velocity is typically 3-8 m/s, with a contact time of between 5 and 15 seconds in the chamber 17.

One or more injectors 23 are provided near the inlet 21 for injecting an oxidizing agent into the gas flow. Thereafter, one or more injectors 24 are provided in the duct 20 for injecting liquid coolant, typically water, into the gas flow. Preferably, the water is sprayed into the gas stream in successive stages from respective spaced injectors. There should be three levels of nozzles or injectors able to inject the various solutions.

The heavier solid waste and dust particles are collected in a hopper 25 at the bottom of the reaction vessel 20, from which they can be removed for disposal.

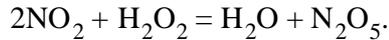
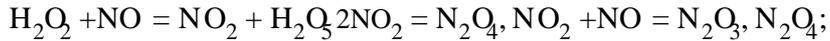
The oxidizing agent may be liquid, gaseous or solid. Normally, a solid oxidizing agent, such as calcium hypochlorite ( $\text{Ca}(\text{ClO})_2$ ), is injected into the gas stream as a fine particulate. Suitable liquid oxidizing agents include hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and sodium hypochlorite ( $\text{NaClO}$ ), while a suitable gaseous oxidizing agent is ozone ( $\text{O}_3$ ).

In a modified form of the invention, the liquid oxidizing agent may be injected into the gas stream in solution with the water through the water injectors 24. The injectors 24 are selected from the spray/cooling tower industry on the basis of their mixing capabilities. It will be appreciated that the efficiency of the process is enhanced as mixing is improved. However, applicant submits that this embodiment of the invention can be put into effect even with poor mixing.

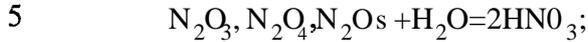
In use, the oxidizing agent and then the water are sprayed into the gas stream in fine sprays using the injectors 23, 24 respectively. As the sprayed water evaporates, the gas is cooled and the insoluble nitrogen oxide (NO) is oxidized to form  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$  and other oxides of nitrogen. The higher level nitrogen oxides ( $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ ) hydrate to form nitric acid  $\text{HNO}_3$  which then reacts with mercury in the gas stream to form mercury nitrate ( $\text{Hg}(\text{NO}_3)_2$ ).

Typical chemical reactions can be represented as follows:

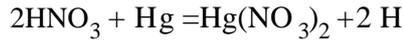
1. Injection Of  $H_2O_2$  as oxidizer:



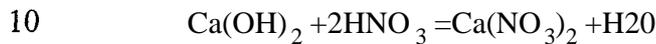
2. Hydration of  $NO_x$  to acidic compounds:



3. Acid-metal reaction between Hg and  $HNO_3$ :



Any excess acidic compounds can be removed with CaO (lime). The lime is hydrated [ $CaO + H_2O = Ca(OH)_2$ ] and then used to react with acidic compounds:



In a cement kiln and some coal fired power stations, CaO is already present in the ash, thereby reducing the amount of sorbent which needs to be injected into the flue gas.

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Figure 2A illustrates an 'upward flow' reactor 14A similar to the reactor 14 of Figure 2, but in which the gas flow within the reactor is generally from bottom to top, i.e. upward. The reactor 14A is also in the form of an upright duct 20A which forms a reaction vessel having an inlet 21A at a lower end thereof adapted to receive exhaust gas from the boiler 11 or other industrial combustion process, and an outlet 22A at an upper end. One or more injectors 23A are provided near the inlet 21A for injecting an oxidizing agent into the gas flow. Thereafter, one or more injectors 24A are provided in the duct 20A for injecting water into the gas flow, preferably in successive stages. The process in the reactor 14A is similar to that in the reactor 14 of Figure 2, and hereinafter the reference numeral 14 is used to refer to both forms of the reactor 14, 14A.

20

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The temperature of the gas entering the reactor 14 is normally between  $120^\circ C$  and  $150^\circ C$ . For improved efficiency, the temperature should be cooled to between  $50^\circ C$  and  $90^\circ C$ , depending on the particular reaction process being used. This cooling is achieved by the water injection stage(s) as part of the process in the reactor.

30 As shown in Figure 3, a heat exchanger 15 can be used in conjunction with the reactor 14 to achieve increased thermal efficiency. The inlet exhaust gas to be treated is passed through a gas-gas heat exchanger 15 before entering the reaction vessel of the reactor 14 where water is injected to cool the gas. (As mentioned above, although an

upward flow reactor is illustrated in Figure 3, it will be understood that the heat exchanger can be used with any type of reactor).

The cooler output gas of the reactor 14 is then passed through the gas-gas heat exchanger 15 to cool the incoming gas, and is itself re-heated by the incoming gas in the heat exchanger. Typically, the incoming exhaust gas has a temperature of about 140°C and is cooled to around 90-100°C in the gas-gas heat exchanger 15. The gas is further cooled to around 60°C by the water sprayed into the reactor 14. This gas is then reheated to around 90-100°C in the gas-gas heat exchanger 15 before exiting the heat exchanger. The temperature of the gas exiting the heat exchanger should be above the dew point before entering the collection stage to minimize corrosion.

When the system is operating under less than full load, the inlet gas temperature may be lower (e.g. 120°C) and the gas-gas heat exchanger may not be as efficient. In such cases, a hot gas (such as heated air or flue gas) with a temperature of around 300 to 400°C may be introduced downstream of the reactor.

Preferably, as illustrated in Figure 4, an additional injector 26 is provided upstream of the outlet of the reactor 14 for injecting a sorbent, such as hydrated lime ( $\text{Ca}(\text{OH})_2$ ), to assist in removing remaining oxidized nitrogen oxides and sulphur oxides, and excess acidic components. (Again, although an upward flow reactor is illustrated in Figure 4, it will be understood that the sorbent injector 26 can be used with any type of reactor).

Advantageously, an agglomerator 27, such as the agglomerator of the type described in our international patent application nos. PCT/NZOO/00223, PCT/AU2005/000160 and PCT/AU2004/000546 is provided downstream of the sorbent injector 26 to enhance sorbent utilization and removal efficiency. The disclosures of those international patent applications are incorporated herein by reference.

For a cement plant, which typically produces a larger amount of fine particulate, the reactor 14 is preferably followed by an agglomerator and then a fabric filter as the collection device.

The reactor used in this invention can be of a type described in our co-pending international patent application no. PCT/AU2008/001023, the disclosure of which is incorporated herein by reference and the relevant part of which is set out below.

As shown in Fig. 5, a reverse flow reactor 60 comprises a generally upright duct 62 which defines a reaction chamber 64 of rectangular cross-section. However, the chamber cross-section may be round or square, or any other suitable shape. The cross-

sectional area of the reaction chamber 64 increases from the bottom to the top, preferably by a factor of between 2 and 10. The increase in cross-sectional area need not be linear or uniform.

5 Gas from the industrial process is fed to a gas inlet 66 of the duct 62, and flows upwardly in the reaction chamber 64 with reducing velocity as the chamber cross-sectional area increases, to an outlet 68. The gas velocity at the bottom of the chamber 64 is typically in the range of 8m/s to 32m/s, while the velocity at the top of the chamber 64 is typically in the range of 2m/s to 8m/s, for a increase in chamber cross-sectional area of a factor of 4.

10 Spray devices 70 are located adjacent the top of the reaction chamber 64 to spray cooling water in a downward direction. The spray devices 70 can be nozzles having multiple apertures, and are preferably mounted on the roof of the reactor 60, as shown in Figure 5, or on a spray lance (not shown) in the top or upper region of the reactor. When mounted in that way, the spray devices 70 can be directed downwardly to  
15 enhance mixing.

In use, water droplets from the spray devices 70 flow in a downward direction, due to gravity or initial velocity, until the viscous force due to the upwardly flowing gas is sufficient to reverse their flow and carry them in an upward direction.

20 More specifically, as the water droplets flow downwards, they evaporate and their mass reduces, thereby reducing the gravitational force acting on them. As the droplet size reduces, the downward gravitational force reduces in proportion to the volume (which is proportional to the cube of the diameter), while the upward viscous force reduces in proportion to the surface area (which is proportional to the square of the diameter). Hence, the ratio of the downward gravitational force to the upward  
25 viscous force will reduce in proportion to the reducing droplet diameter.

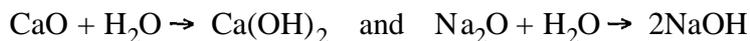
The gas temperature is higher at the bottom of the chamber 64 (generally about 140<sup>0</sup>C), compared to the gas temperature at the top of the chamber 64 (generally about 70<sup>0</sup>C). Moreover, the water droplets encounter a counter gas flow of increasingly higher velocity as they fall. Thus, as the water droplets descend through the chamber 64, the  
30 evaporation rate increases due to increasing gas temperature and gas velocity. Once the droplet flow reverses, they continue to evaporate while moving in an upward direction until complete evaporation occurs at the top of the chamber 64 where their velocity is lowest.

In this manner, the gas temperature is reduced from about 140°C at the bottom of the chamber 64 to about 65 degrees *Celsius* at the top of the chamber 64. The moisture content of the gas flow increases from about 7% at the bottom of the chamber 64 to about 15% at the top of the chamber 64. These conditions enable alkaline hydroxides and other material, contained in the dust suspended in the gas, to sorb gaseous pollutants such as SO<sub>x</sub>, NO<sub>x</sub>, Hg and VOCs.

The arrangement of the inlet ducts, and the shape and size of the reactor, can change from site to site. The size of the reactor depends on the volume of gas being treated and the temperature drop required. The spray flow is controlled to maintain the outlet temperature at the desired value, and feed forward from gas flow is used to adjust spray flow as gas flow changes. The large droplet sprays are reduced first when staged sprays are used to allow increased gas flow variation.

By reducing the gas temperature and increasing the moisture content (humidity) of the gas, the reverse flow reactor enables two processes to occur efficiently, namely:-

a) The hydration of the alkaline oxides to hydrates is increased, for example



Hydrates are far more reactive absorbents than oxides, so this process increases the efficiency of pollutant removal by the absorption process.

b) The sorption process efficiency also increases at low temperatures, which increases the removal of gaseous pollutants such as SO<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub> and other nitrogen oxides other than NO plus oxidized mercury.

Other advantages of the reverse flow reactor 60 include:

- Increased evaporation.

Due to the initial downward flow of the water droplets from the top to the bottom of the chamber 64, followed by an upward flow from the bottom to the top of the chamber 64, a duration and hence evaporation of the droplets in the chamber 64 is maximised, compared to normal upward flow reactors in which the water sprays are at the bottom and droplet flow is only in an upward direction.

- Less maintenance.

Placing the water sprays at the top of the chamber 64 where the gas velocity is lower, reduces both erosion and dust build-up on the sprays.

- Lower droplet carry out.

Relatively low gas velocity at the top of the chamber 64 reduces the potential for droplet carry out from the chamber 64 compared to normal upward flow reactors that operate at higher exit velocities.

- Fewer obstructions

5 As the water sprays are located at the top of the chamber 64, compared to the bottom on normal upward flow reactors, there is no obstruction above the ash hoppers that can cause problems when large lumps of agglomerated ash fall from the walls of the reactor.

- Larger droplets / fewer nozzles

10 The size of the droplets is determined by the gas carrying capacity, dependent on the velocity and density, at the bottom of the reactor. Since the droplets evaporate on the way down in the chamber 64, the initial droplet size can be much larger than that in normal upward flow reactors which have the sprays at the bottom. The droplet size increases with nozzle capacity, so fewer nozzles each with a larger capacity can  
15 be used in the reverse flow reactor, thereby reducing cost.

As shown in Fig. 1, the reverse flow reactor 60 would normally be installed at the gas outlet of an industrial installation such as a coal fired power station, and before a particulate collection device 13, such as an electrostatic precipitator or fabric filter, so that any particulates generated in the reactor can be collected in the existing particulate  
20 collection device. As the reactor 60 reduces the gas temperature and increases the gas moisture content (humidity), it enhances the dust collection efficiency of an electrostatic precipitator following the reactor, which also results in a significant reduction in the particulate emission to the atmosphere. Most power stations use electrostatic precipitators to remove dust from the gas flow, and the reverse flow reactor 60 can be  
25 installed between an air-heater 15 and the electrostatic precipitator 13 as shown in Figure 1.

An agglomerator can optionally be installed at the outlet of the reactor 60 to provide micro-mixing and thereby improve or enhance the sorption process.

In an alternative arrangement, the reactor 60 can be installed after the particulate  
30 collection device 13 to treat the gas prior to emission to the atmosphere.

Additional processes that can be used to enhance the operation of the reverse flow reactor 60 to improve the pollutant removal include:

1. Injection of additional sorbent at the top or outlet of the reverse flow reactor to increase the sorption of pollutants.

2. Injection of an organic acid at the bottom or at the inlet to the reverse flow reactor, or at a point in the reactor where the temperature of the flue gas is most conducive for oxidation reactions, to increase the efficiency by which alkaline oxides are activated in the reverse flow reactor, thereby improving the sorption process.
3. Injection of an oxidizing reagent at the bottom or at the inlet to the reverse flow reactor, or at a point in the reactor where the temperature of the flue gas is most conducive for oxidation reactions, to oxidize NO, Hg and VOCs so as to allow removal by a sorbent material.
4. Installation of sonic horns in the reverse flow reactor to improve cleaning of the internal walls.
5. Installation of staged sprays to reduce droplet size when gas flow reduces.

These will be described in more detail with reference to Figs 6 to 11.

The addition of organic acids such as acetic or formic acid enhances the activation of alkaline oxides to alkaline hydrates by increasing the hydration rate or creating water soluble organic salts which react with stronger acids in the reactor. The organic acids can be added at the chamber inlet 66 in solid or liquid form, but can also be added in solution with the spray water from the spray devices or nozzles 70.

As shown in Figure 6, additional spray devices 74 can be installed before the chamber inlet in the inlet duct leading to the reactor chamber 64, or in the reactor chamber 64 to allow the injection of the organic acids in liquid or solution form. To inject the organic acid salts in solid form they are first ground into a fine powder, generally less than 50 micrometres in diameter, and air conveyed to a multi-port distribution lance in the inlet duct or in the chamber 64. The activator flow is controlled to maintain the outlet pollutant ( $\text{SO}_2$ ) level at the desired value, and feed forward from gas flow is used to adjust activator flow as gas flow changes.

If there is insufficient sorbent suspended in the gas flow to achieve the required pollutant removal, additional spray devices 76 can be installed in the outlet duct or in the upper part of the reactor 60 to allow the injection of the sorbents in liquid or solution form, as shown in Figure 7. The spray devices 76 inject additional sorbent in the chamber 64 in solution with the spray water, or in the outlet duct 68 where the gas temperature is lowest and the moisture content (humidity) of the gas is highest and hence the pollutant sorption rate will be highest.

Alkaline hydrates such as calcium hydrate ( $\text{Ca}(\text{OH})_2$ ) or sodium hydrate ( $\text{NaOH}$ ) are normally injected in solid or liquid form to increase the gaseous pollutant removal. Again, to inject the sorbents in solid form, they are first ground into a fine powder, generally less than 50 micrometres in diameter, and air conveyed to a multi-  
5 port distribution lance in the outlet duct or in the top of the reactor 60. The sorbent material is controlled to maintain the outlet pollutant ( $\text{SO}_2$ ) level at the desired value, and feed forward from gas flow is used to adjust sorbent flow as gas flow changes.

An agglomerator generates micro-mixing using small vortices, as described in international patent applications nos. PCT/NZOO/00223, PCT/AU2005/000160 and  
10 PCT/AU2004/000546. This micro-mixing increases the interaction between the sorbent and the pollutant gases being removed, thereby increasing the removal efficiency and increasing the sorbent utilization. As shown in Figure 8, an agglomerator 78 can be located in the reactor outlet 68 where the removal process is most effective due to the reduced gas temperature and increased moisture content.

15 Some pollutants, such as NO and elemental Hg, are not removed effectively by sorbents and must be oxidized, for example NO to  $\text{NO}_2$  and elemental Hg to oxidized Hg, to allow efficient removal in the reactor. This can be achieved by adding an oxidizing agent, such as  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaClO}$ ,  $\text{Ca}(\text{ClO})_2$ , or  $\text{ClO}_2$  at the inlet 66 of the reactor 60.

20 As shown in Figure 9, additional spray devices 80 can be installed in the inlet duct leading to the reactor, in the bottom of the reactor or in the low temperature region of the reactor, to allow the injection of the oxidizing agents in gaseous form ( $\text{O}_3$ ), solid form ( $\text{Ca}(\text{ClO})_2$ ) or liquid form ( $\text{H}_2\text{O}_2$ ). However, the oxidising agent can also be added in solution with the spray water.

25 To inject the oxidizing agents in solid form, they are first ground into a fine powder, generally less than 50 micrometres in diameter, and air conveyed to one of the additional spray devices 80 in the form of a multi-port distribution lance in the inlet duct or in the bottom of the reactor. The oxidizer flow is controlled to maintain the outlet pollutant (NO) level at the desired value, and feed forward from gas flow is used to  
30 control oxidizer flow as gas flow changes.

In many applications, such as power station boilers, the gas flow varies greatly, by up to 60%. As the flow is reduced, the spray droplet size also needs to be reduced to prevent the droplets from falling into the hopper, due to reduced evaporation and reduced upward force resulting from the reduced gas velocity. As shown in Figure 10,

this can be accommodated by using multiple sprays 70A, 70B with different droplet sizes. The larger the spray droplet size, the larger the nozzle capacity, so fewer nozzles are required.

5 If large changes in gas flow are expected, then two or three different nozzles producing different droplet sizes can be used. As the gas flow reduces, the spray flow in the largest droplet nozzles is reduced first. For example 50% of the spray flow can be delivered by the large droplet nozzles (located in the centre of the reactor), 30% by medium size droplet nozzles (located at the sides of the reactor) and the final 20% by small droplet nozzles (located at the bottom of the reactor to allow the addition of an oxidizer or an activator). As the gas volume is reduced, the large droplet nozzle flow is reduced until at 50% gas flow only the medium and the small droplet nozzles are operating, and at 20% gas flow only the small droplet nozzles are operating.

10 If large changes in gas flow are expected, then two or three different nozzles producing different droplet sizes can be used. Alternatively, a nozzle that allows variations in solution and air flow to produce larger or smaller droplet sizes can be used.

15 Build-up can occur on the internal walls of the chamber 64 depending on the nature of the dust suspended in the gas and the spray requirements. In order to minimise this build-up, sonic horns 82 can be installed in the reactor chamber 64 as shown in Figure 11. The horns 82 are operated periodically, say for 10 seconds every 20 minutes, to help remove any build-up before it becomes excessive.

20 The process and apparatus described above have the following novel features and/or advantages:

- both nitrogen oxides and mercury can be removed in a single reactor chamber;
- additional absorbents can be added also to remove SO<sub>2</sub>;
- 25 • as the oxidised and/or hydrated forms HNO<sub>3</sub>, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and Hg (NO<sub>3</sub>)<sub>2</sub> are soluble, they can also be removed from the gas in a wet scrubber, which is installed following the particulate collector to remove SO<sub>2</sub>;
- with the injection of a sorbent such as hydrated lime, the hydrated by-products of NO<sub>x</sub> and SO<sub>x</sub> oxidation as well as mercury can be collected in a standard dust collector such as an electrostatic precipitator or fabric filter;
- 30 • the reduced gas temperature and increased moisture content of the gas exiting the chamber improves the efficiency of particulate collection in an electrostatic precipitator;
- the process does not prevent the sale of dust collected following the process;

- if necessary, the mercury can be removed from the collected dust or liquid;
- the reactor can be implemented at relatively low capital cost;
- the use of a gas-gas heat exchanger reduces water usage, reheats the outgoing gasses and increases system efficiency;
- 5 • the reactor process does not require the addition of a catalyst, ammonia or urea, and does not produce ammoniated by-product; and
- ammonia that may be released from an SCR through slippage is removed by reacting with the nitric acid to produce  $\text{NH}_4\text{NO}_3$ , which can then be collected in a particulate removal device, i.e.  $\text{HNO}_3 + \text{NH}_3 = \text{NH}_4\text{NO}_3$

10 Figure 12 illustrates a multiple reactor installation 30 according to an embodiment of the invention, which, in addition to removing pollutants such as nitrogen oxides  $\text{NO}_x$ , and mercury, also reduces  $\text{CO}_2$  emissions.

Flue gas is passed through a flue gas desulfurization stage (FGD) or spray dryer absorber (SDA) 29, before flowing into a first stage 31 of two-stage reactor installation 15 30. The first stage 31 defines the chamber 17.

The flue gas stream comprises  $\text{CO}_2$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ , Hg,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and particulate material (PM), typically at a temperature of 50 - 90° C and humidity of 10-100% (dependant on the FGD/SDA).

20 In the first stage 31, an oxidizer (such as  $\text{O}_3$  or  $\text{H}_2\text{O}_2$ ) is introduced into the flue gas stream by nozzle(s) 32 with the nozzle(s) directed into the flow. NO in the gas stream is oxidized to  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ . Simultaneously, sorption solutions containing calcium acetate ( $\text{Ca}(\text{CH}_3\text{COO})_2$ ), calcium salt of organic acids ( $\text{Ca}(\text{org. acids})$ ), or a mixture of these solutions, are injected by a pump 84 into the first stage 31 via a pipe 34.

25 In the resulting reactions,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$  &  $\text{N}_2\text{O}_5$  bond with the water component forming  $\text{HNO}_2$  and  $\text{HNO}_3$  acids;  $\text{SO}_2$  bonds with the water component producing sulphuric acid  $\text{H}_2\text{SO}_3$ ; and the nitric acid  $\text{HNO}_3$  dissolves mercury.

30 The acids and anhydrides also react with calcium acetate or calcium salts of organic acids. The products of the reactions are solutions of  $\text{Ca}(\text{NO}_3)_2$ , volatile  $\text{CH}_3\text{COOH}$  and slightly soluble  $\text{CaSO}_3$ , which undergoes oxidation to  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ .

The products fall under gravity through a hopper 35 operatively arranged with respect to the chamber 17 of the first stage 31, and form a slurry which is collected in a tank 36 below the chamber 35 and re-circulated to the first stage 31.

Compressed air is fed continuously into the tank 36 via the pipe 37, and oxidizes the  $\text{CaSO}_3$ , to  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ . The slightly soluble  $\text{CaSO}_4$  that forms in the tank 36 is continuously or periodically removed into a centrifuge 38 and, after rinsing with water introduced by pipe 39, is directed to a storage facility, or is sent to a system of gypsum production in a flue-gas desulfurization stage (FGD).

Filtrate containing dissolved salts  $\text{Ca}(\text{NO}_3)_2$  is directed into a storage tank 40 and, after mercury and other heavy metals are removed (by the addition of  $\text{Na}_2\text{S}$ ), can be used as artificial fertilizer.

The gas emerging from the first stage 31 is wet (~100% humidity) and comprises low concentrations of  $\text{SO}_2$ ,  $\text{NO}_x$ , PM (trace) and 10 - 14 %  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CH}_3\text{COOH}$ . This gas passes to a second stage 41 of the reactor 30 for  $\text{CO}_2$  removal.

A slurry of lime is sprayed by nozzle(s) 42 into the gas in the second stage 41, and reacts with the  $\text{CO}_2$  producing  $\text{CaCO}_3 + \text{H}_2\text{O}$ , while the volatile  $\text{CH}_3\text{COOH}$  becomes  $\text{Ca}(\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O}$ . These products fall under gravity into a tank 44 located under a hopper 43 of the second stage 41, and are re-circulated by a pump 86 into the second stage 41, via the nozzle/s 42.

The slightly soluble  $\text{CaCO}_3$  is continuously or periodically removed from the tank 44 and delivered to a centrifuge 45, rinsed with water from a pipe 46, and then utilized or disposed of in a suitable facility. A solution of  $\text{Ca}(\text{CH}_3\text{COO})_2$  is returned to the first stage reactor 31 via pipe 47.

Cleaned flue gas comprising mainly nitrogen, water vapour, oxygen and some  $\text{CO}_2$  is directed via conduit 48 (assisted by fan 49) into a cooling tower 50 or is utilised in a different manner e.g. in nitrogen production.

In Figure 13, reference numeral 60 generally indicates another embodiment of an apparatus, in accordance with the invention, for the removal of pollutants from a gas flow.

The apparatus 60 includes sequential vertical reactors in the form of a first vertical reactor 52 and a second vertical reactor 54. With reference to the previous Figures, like reference numerals refer to like parts, unless otherwise specified.

The reactions described in the first stage 31 with reference to Figure 12 take place in the first reactor 52. Likewise, the reactions described in the second stage 41 with reference to Figure 12 take place in the second reactor 54. Thus, the first reactor 52 can be similar to either of the reactors shown in Figures 2 to 11.

Also, other embodiments can include particulate collection devices to increase collection of reaction products that would otherwise be collected by gravity settling. Such particulate collection devices can include cyclones.

5 For example, in Figure 14, reference numeral 70 generally indicates another embodiment of an apparatus, in accordance with the invention, for the removal of pollutants from a gas flow.

The apparatus 70 includes a first vertical reactor 74 and a second vertical reactor 76 for housing reactions similar to those that occur in the first and second stages 31, 41 of the inclined reactor of Figure 12.

10 However, in this example, a first cyclone 78 is interposed between the first and second reactors 74, 76 to assist in the removal of reaction products generated in the first vertical reactor 74. Also, a second cyclone 80 is interposed between the conduit 48 and the hopper 43 to assist in the removal of the reaction products from the second vertical reactor 76.

15 It is to be understood that the terminology employed above is for the purpose of description and should not be regarded as limiting. The described embodiments are intended to be illustrative of the invention, without limiting the scope thereof. The invention is capable of being practised with various modifications and additions as will readily occur to those skilled in the art.

20 For example, although the invention has been described with particular reference to the removal of nitric oxides and mercury from gas streams, it may also be used for removing other pollutants such as lead and cadmium.

## CLAIMS

1. A method of removing pollutants from a gas flow comprising the steps of:  
introducing an oxidising agent into the gas flow such that higher level oxides of NO<sub>x</sub> and SO<sub>x</sub> are produced from reactions in the gas flow;  
introducing a coolant into the gas flow to hydrate the higher level oxides to form acid gases and to reduce the temperature and thereby condense the acid gases into acid mists and maximise the efficiency of reactions in the gas flow; and  
introducing an alkaline sorbent to remove excess acidic components.
2. A method as claimed in claim 1, which includes the step of introducing the oxidising agent in the form of an agent that oxidises nitrogen oxide (NO) to form the higher level oxides and introducing the coolant in the form of water that hydrates said higher level oxides to form acidic compounds that react with heavy metals in the gas flow, the water being introduced as the coolant to condense the acid gases and to maximise the efficiency of the acid-metal reaction.
3. A method as claimed in claim 1, in which the steps of introducing the oxidising agent and the coolant into the gas flow are carried out by injection.
4. A method as claimed in claim 1, which includes the step of removing particulate material from the gas flow.
5. A method as claimed in claim 1, including the steps of:  
directing the gas flow containing NO and mercury from an inlet to an outlet of a reactor;  
injecting an oxidising agent into the gas flow to form higher level nitrogen oxides; and  
injecting water into the gas flow, such that the higher level nitrogen oxides hydrate and condense into an acid mist to combine with mercury to form mercury nitrate (Hg(NO<sub>3</sub>)<sub>2</sub>) for removal from the reactor.
6. A method as claimed in claim 5, in which the steps of injecting the oxidising agent and the water are carried out with an oxidising agent in solution with the water.

7. A method as claimed in claim 5, which includes the step of passing incoming gas through a gas-gas heat exchanger to cool the incoming gas and passing outgoing gas through the gas-gas heat exchanger to heat the outgoing gas to above a dew point to minimize corrosion.

8. A method as claimed in claim 5, which includes the steps of facilitating reactions of acids and anhydrides with calcium acetates or calcium salts of organic acids in the reactor to produce solutions of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CH}_3\text{COOH}$  and suspended solid  $\text{CaSO}_3$ , collecting the solutions and suspended material as a slurry and feeding compressed air into the slurry to oxidize the  $\text{CaSO}_3$  to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and removing  $\text{CaSO}_4$  to a separation device, such as a centrifuge.

9. A method as claimed in claim 5, in which the step of receiving the gas in a reactor includes the step of receiving the gas in a two stage reactor such that said higher level nitrogen oxides and mercury nitrate are formed in a first stage of the reactor and  $\text{CO}_2$  removal is carried out in a second stage of the reactor.

10. A method as claimed in claim 9, which includes the step of collecting sorbent material, formed in the first stage of the reactor, from the second stage of the reactor and re-circulating the sorbent material back to the first stage of the reactor.

11. A method as claimed in claim 10, which includes the step of spraying a slurry of lime into a second stage of the reactor to react with the  $\text{CO}_2$  to produce  $\text{CaCO}_3 + \text{H}_2\text{O}$ , and with  $\text{CH}_3\text{COOH}$  to produce  $\text{Ca}(\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O}$ .

12. A method as claimed in claim 11, which includes the step of directing the  $\text{CH}_3\text{COOH}$  from the second stage back to the first stage as a sorbent material.

13. An apparatus for removing pollutants from a gas flow, the apparatus comprising

a chamber having an inlet for receiving the gas flow and an outlet for discharging the gas flow;

an oxidising agent injecting arrangement positioned in the chamber for injecting an oxidising agent into the gas flow such that higher oxides of NO<sub>x</sub> and SO<sub>x</sub> are produced from reactions in the gas flow;

a coolant injecting arrangement for injecting a coolant into the gas flow to hydrate the higher level oxides to form acid gases and to reduce the temperature and thereby condense the acid gases into acid mists and maximise the efficiency of reactions in the gas flow; and

a sorbent injecting arrangement positioned in the chamber for injecting an alkaline sorbent into the gas flow to remove excess acidic components.

14. An apparatus as claimed in claim 13, which includes a gas-gas heat exchanger, the chamber and the heat exchanger being configured so that incoming gas flow passes through the heat exchanger to be cooled and outgoing gas flow passes through the heat exchanger to be heated to above a dew point to minimize corrosion.

15. An apparatus as claimed in claim 13, in which the chamber is defined by a reactor.

16. An apparatus as claimed in claim 15, in which the reactor is one of an upward and a downward flow reactor, a hopper being positioned below the reactor to collect reaction products formed in the reactor.

17. An apparatus as claimed in claim 16, in which the chamber is defined by a first stage of a two-stage reactor installation, a second stage of the reactor installation being configured for carbon dioxide removal.

18. An apparatus as claimed in claim 17, in which a first hopper is operatively arranged with respect to the first stage to receive particulate material from the first stage, the apparatus including a first tank positioned to receive the particulate material from the first hopper, the first tank being in fluid communication with the first stage, the apparatus including a pump and conduit arrangement for pumping material from the first tank back into the first stage downstream of the cooling injection arrangement.

19. An apparatus as claimed in claim 18, in which a second hopper is operatively arranged with respect to the second chamber to receive particulate material from the second stage, the apparatus including a second tank positioned to receive the particulate material from the second hopper, the second tank being in fluid communication with the second stage, the apparatus including a further pump and conduit arrangement for pumping material from the second tank back into the second stage.

20. An apparatus as claimed in claim 17, in which the first and second stages are defined by an inclined reactor.

21. An apparatus as claimed in claim 17, in which the first and second stages are defined by sequential first and second vertical reactors, respectively.

22. An apparatus as claimed in claim 21, in which a first cyclone is interposed between the first and second vertical reactors to assist in the removal of reaction *products from* the first reactor and a second cyclone is positioned downstream of the second vertical reactor to assist in the removal of reaction products from the second vertical reactor.

10

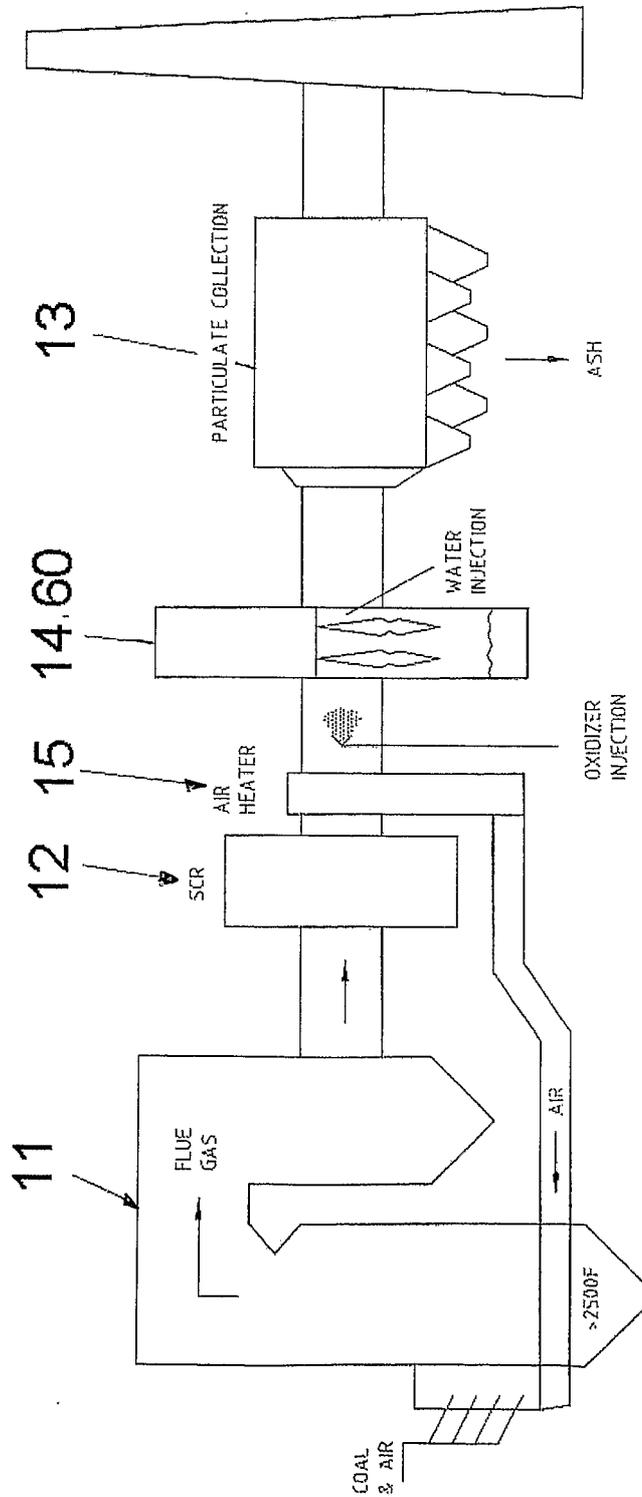


FIGURE 1

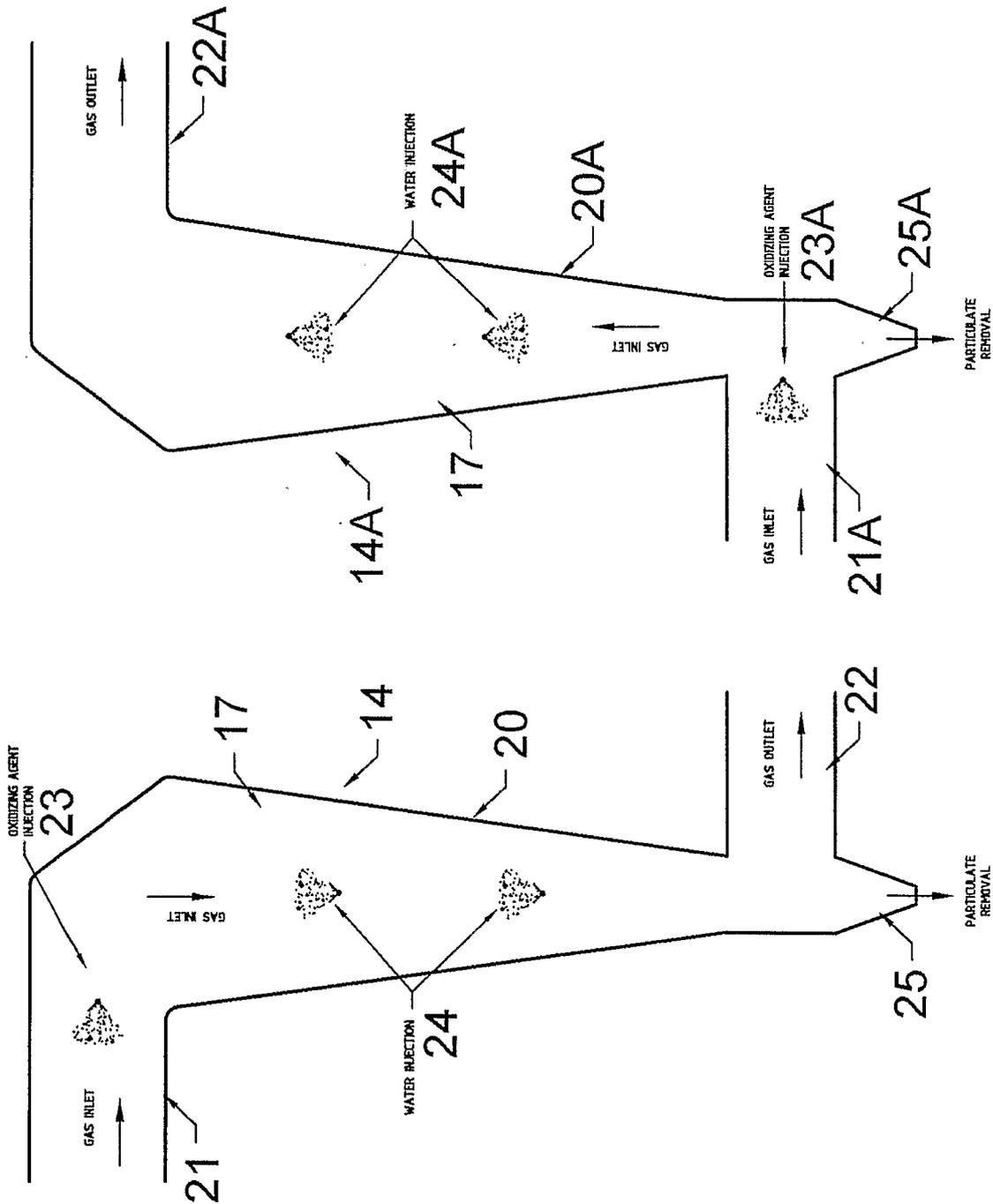


FIGURE 2A

FIGURE 2

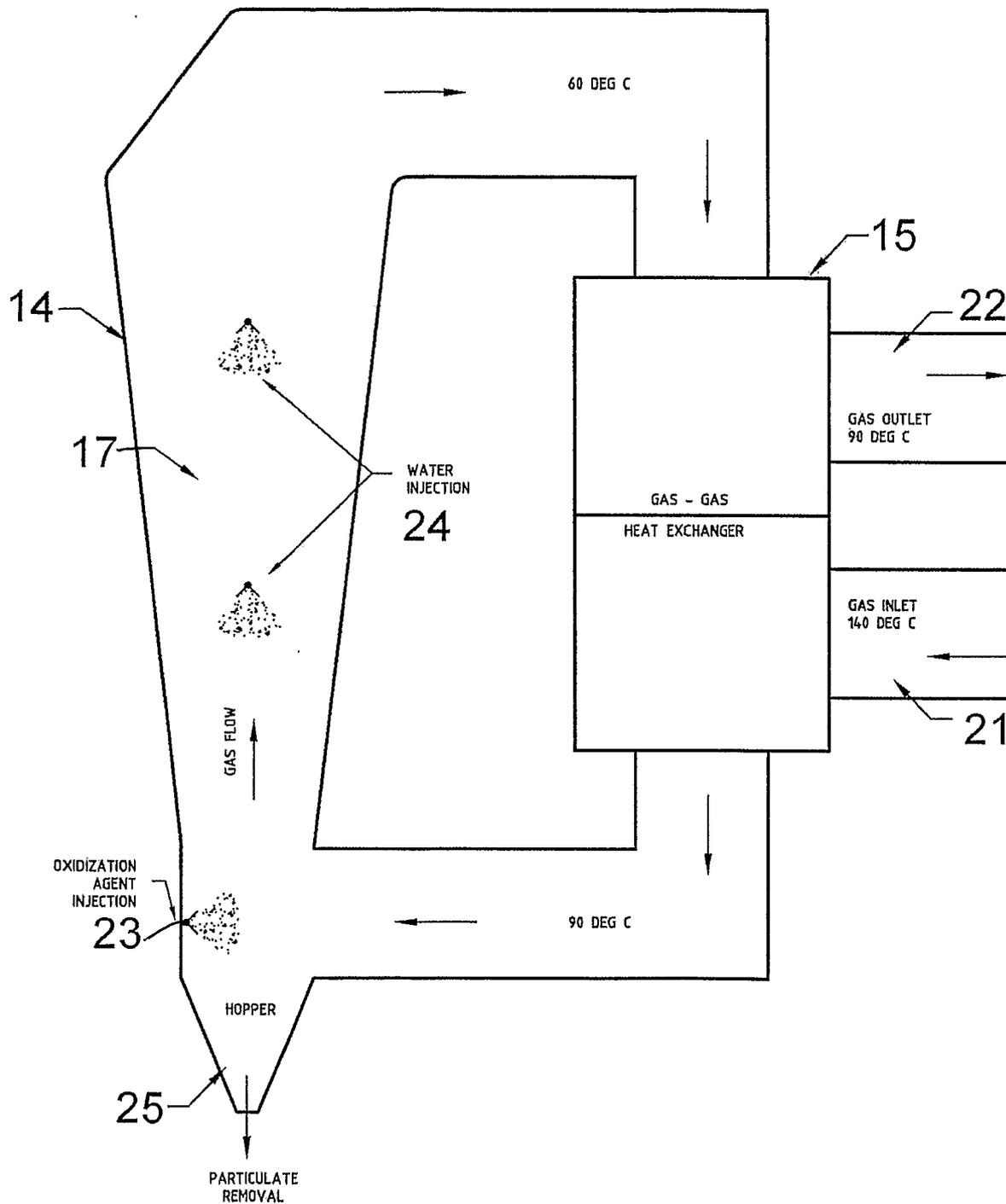


FIGURE 3

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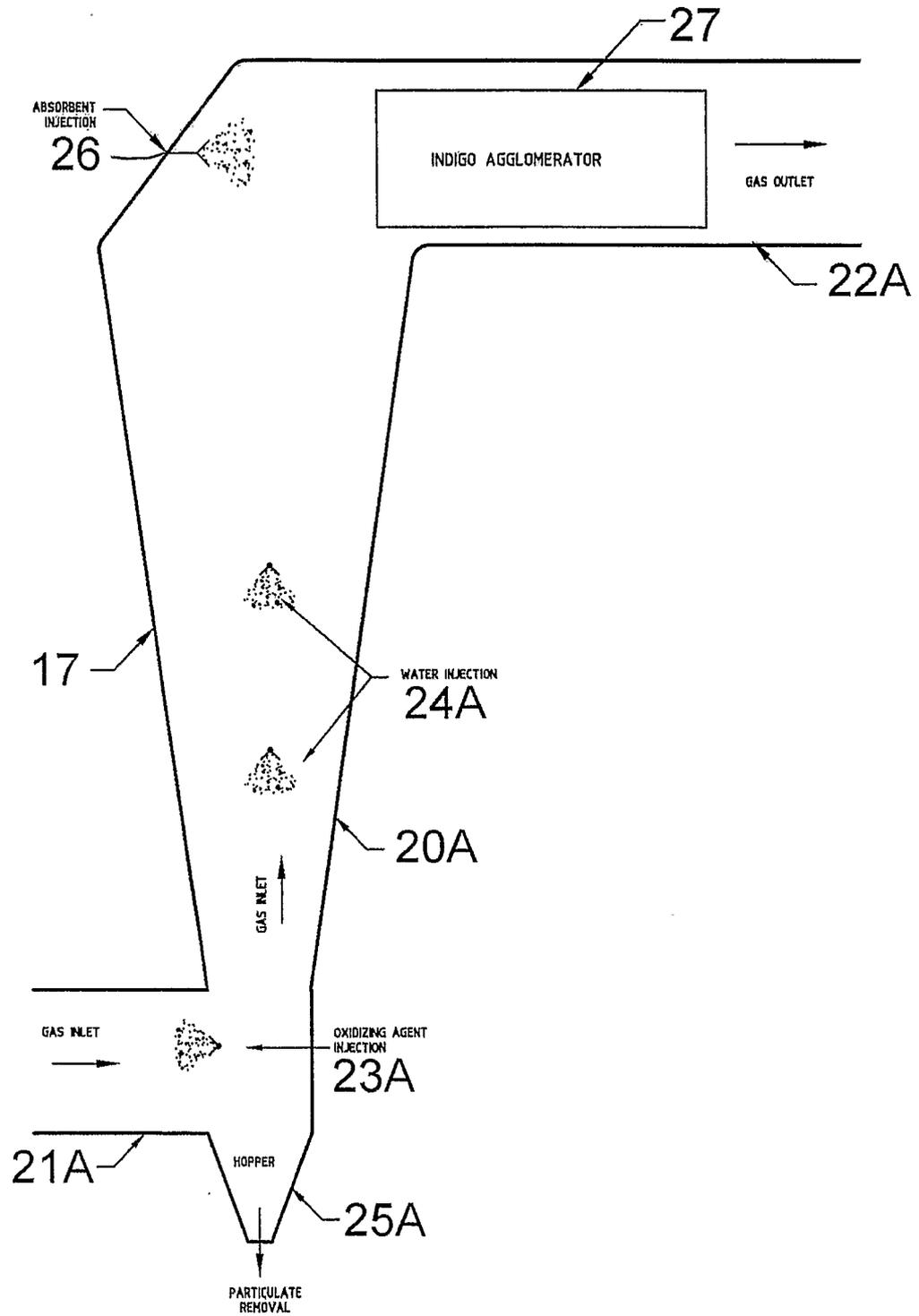


FIGURE 4

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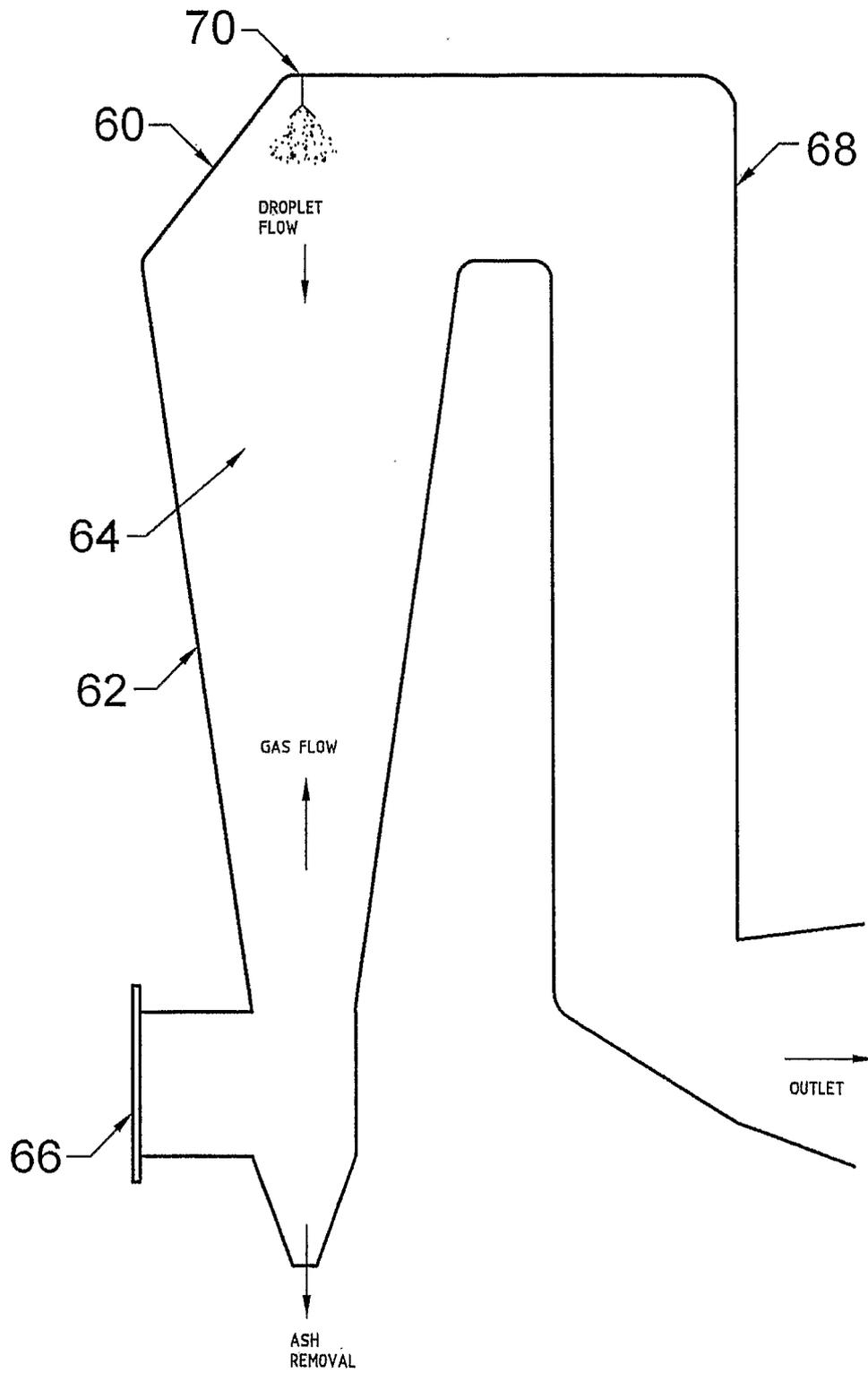


FIGURE 5

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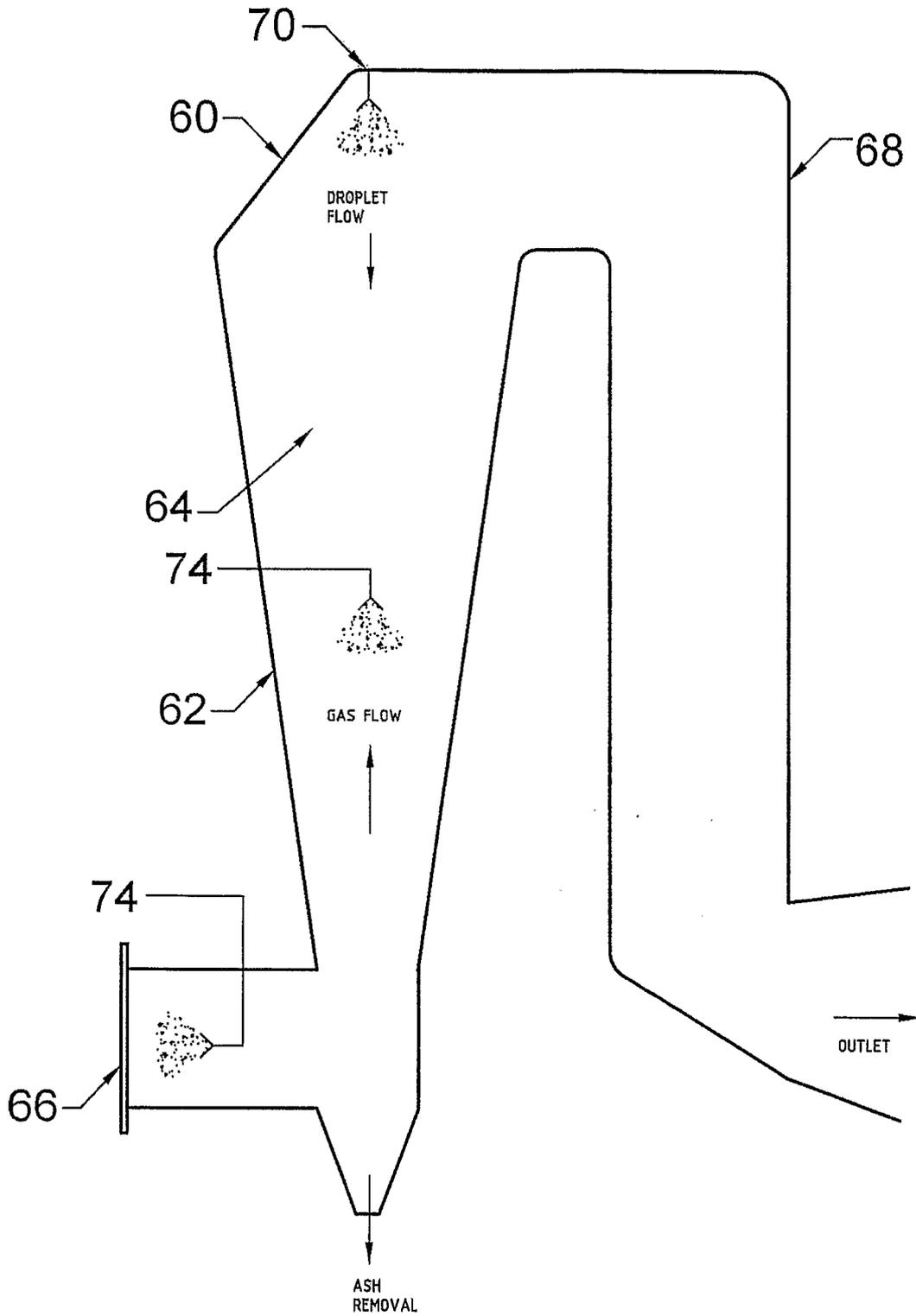


FIGURE 6

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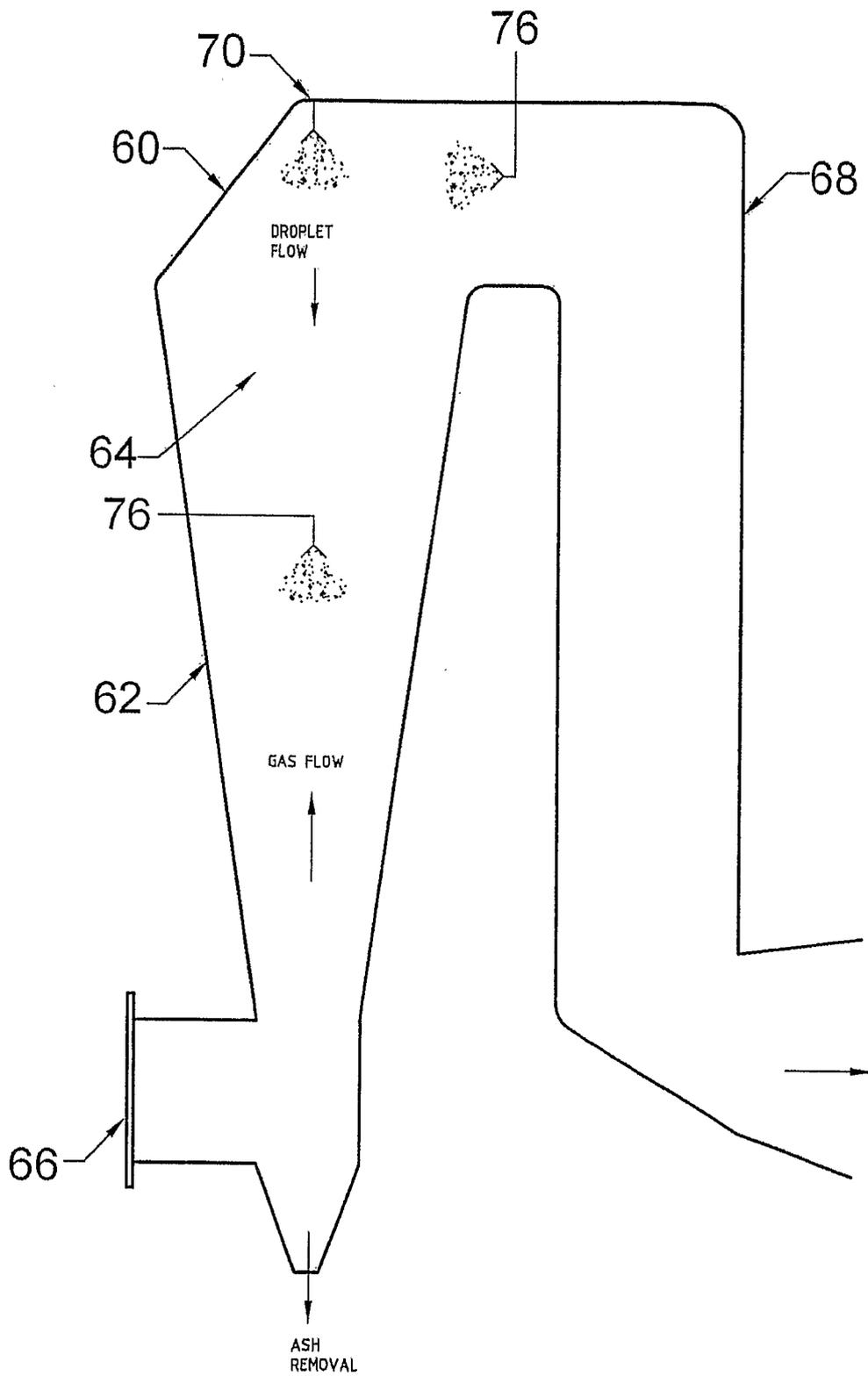


FIGURE 7

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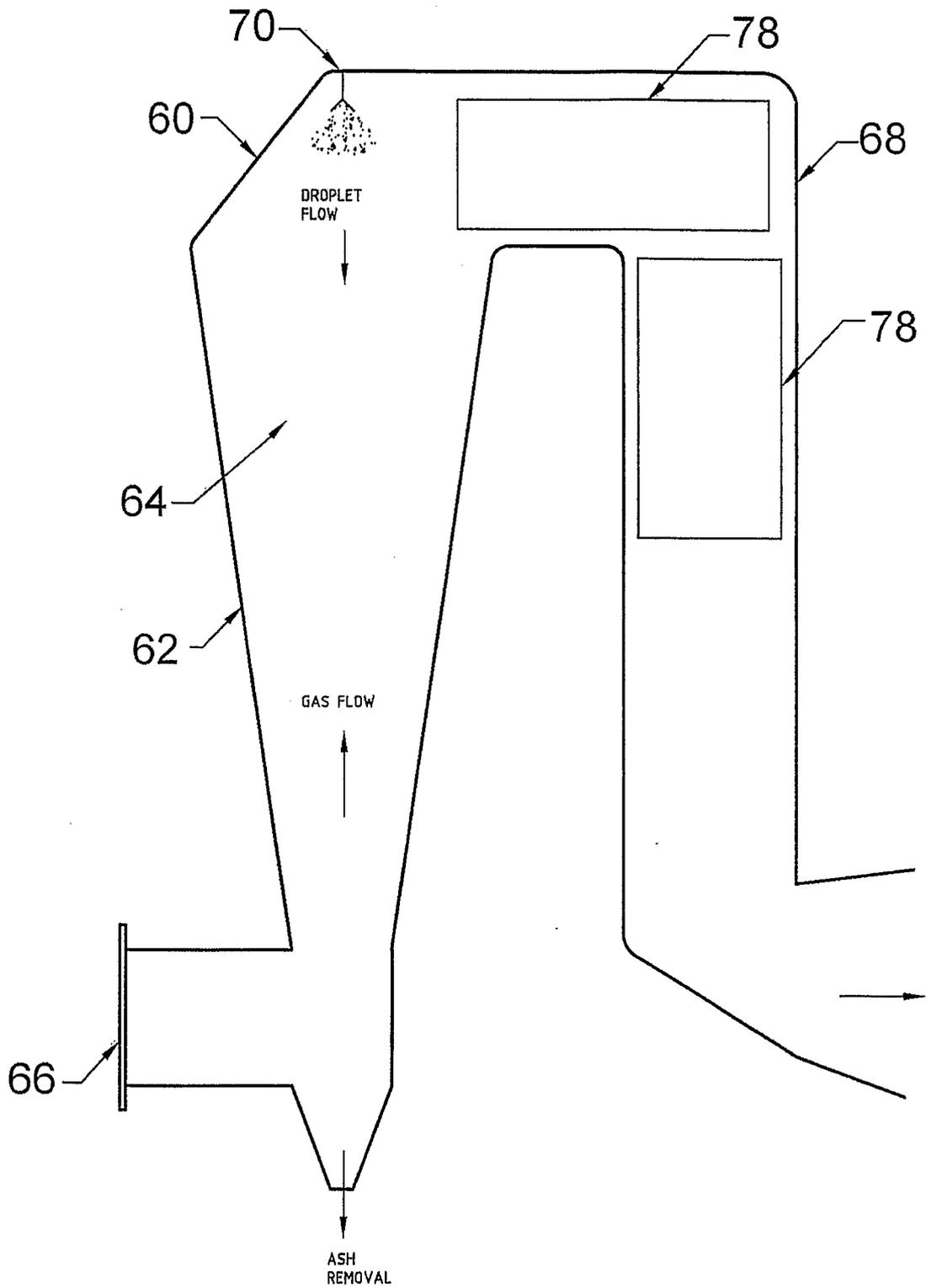


FIGURE 8

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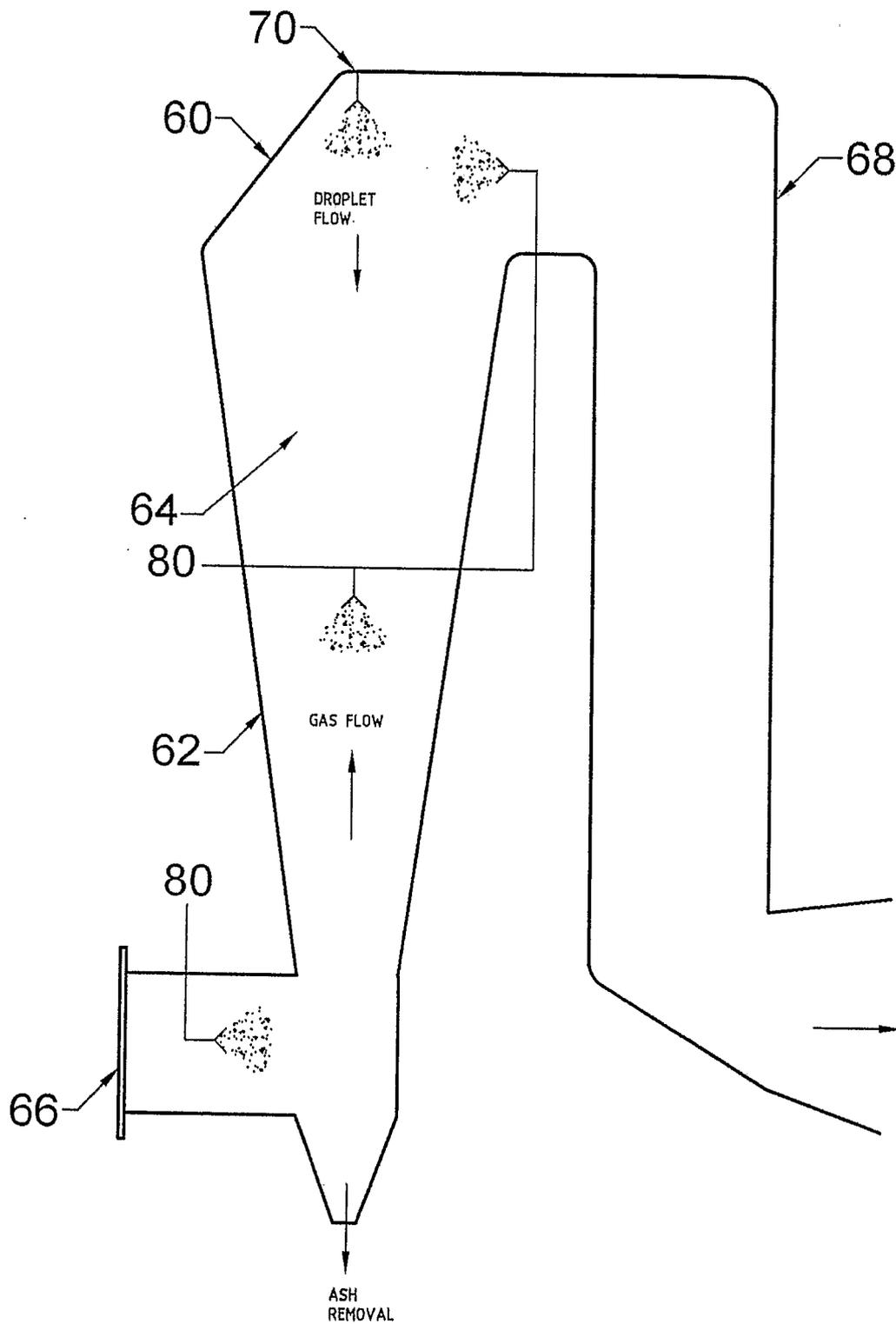


FIGURE 9

10/14

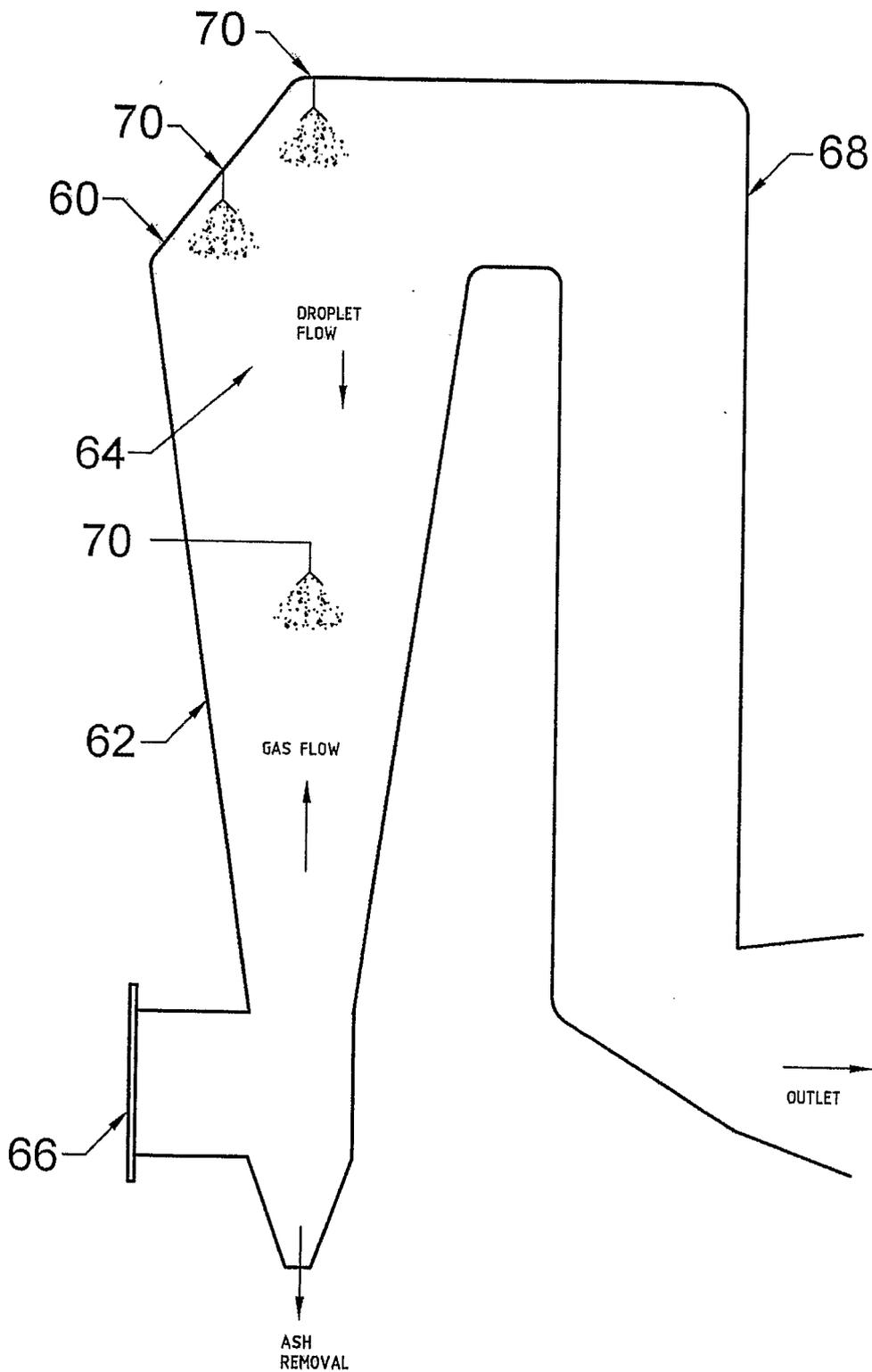


FIGURE 10

11/14

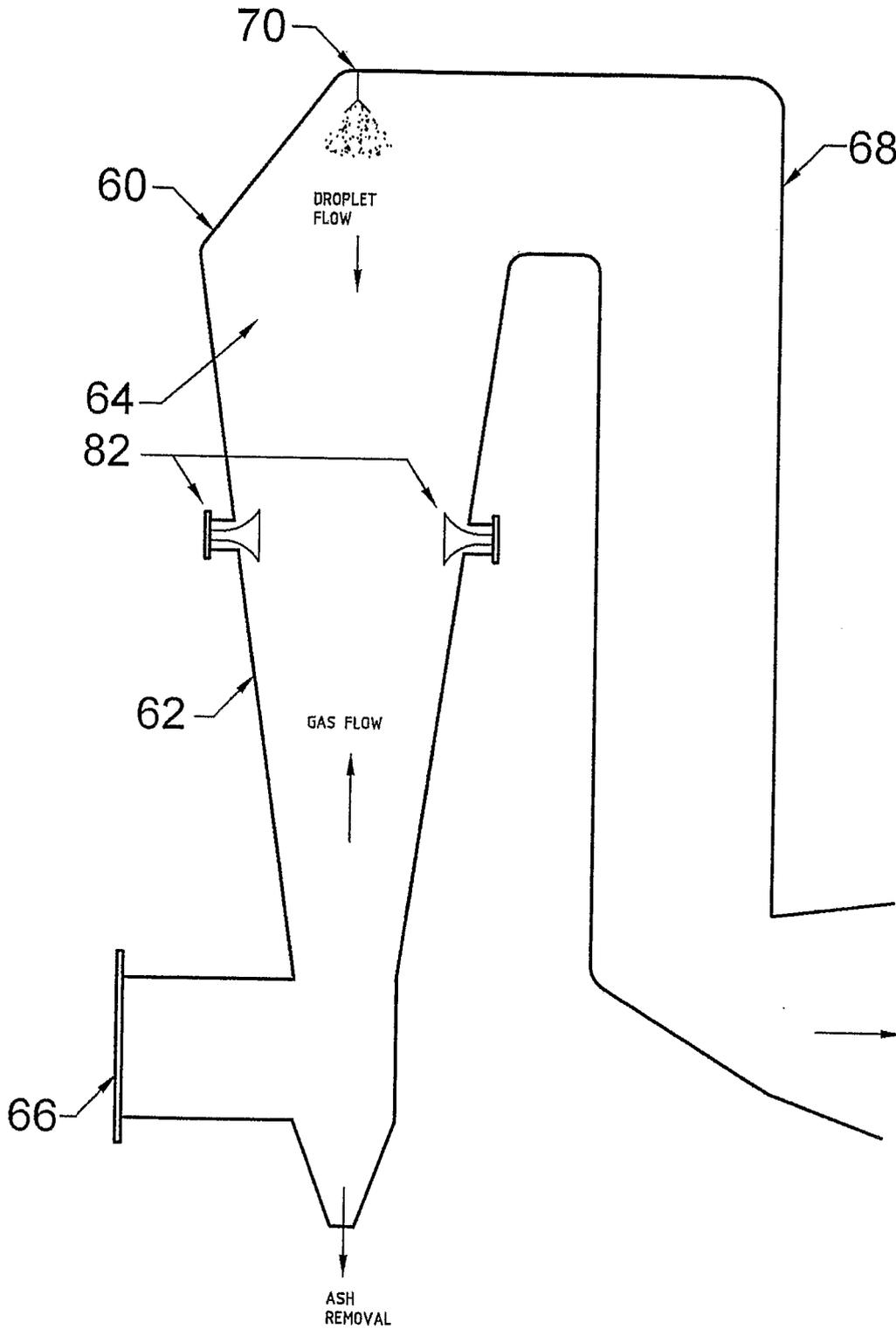


FIGURE 11

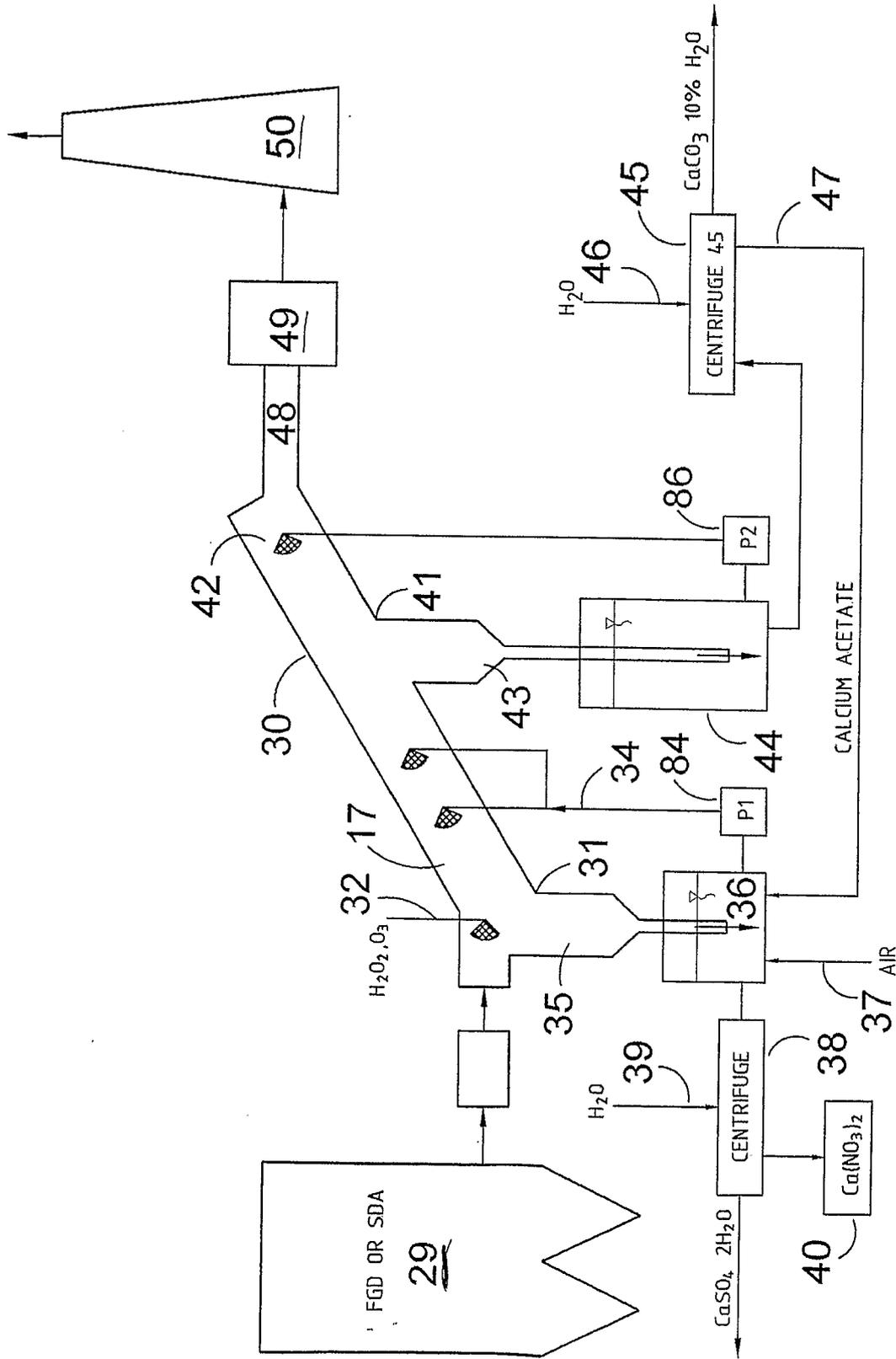


FIGURE 12

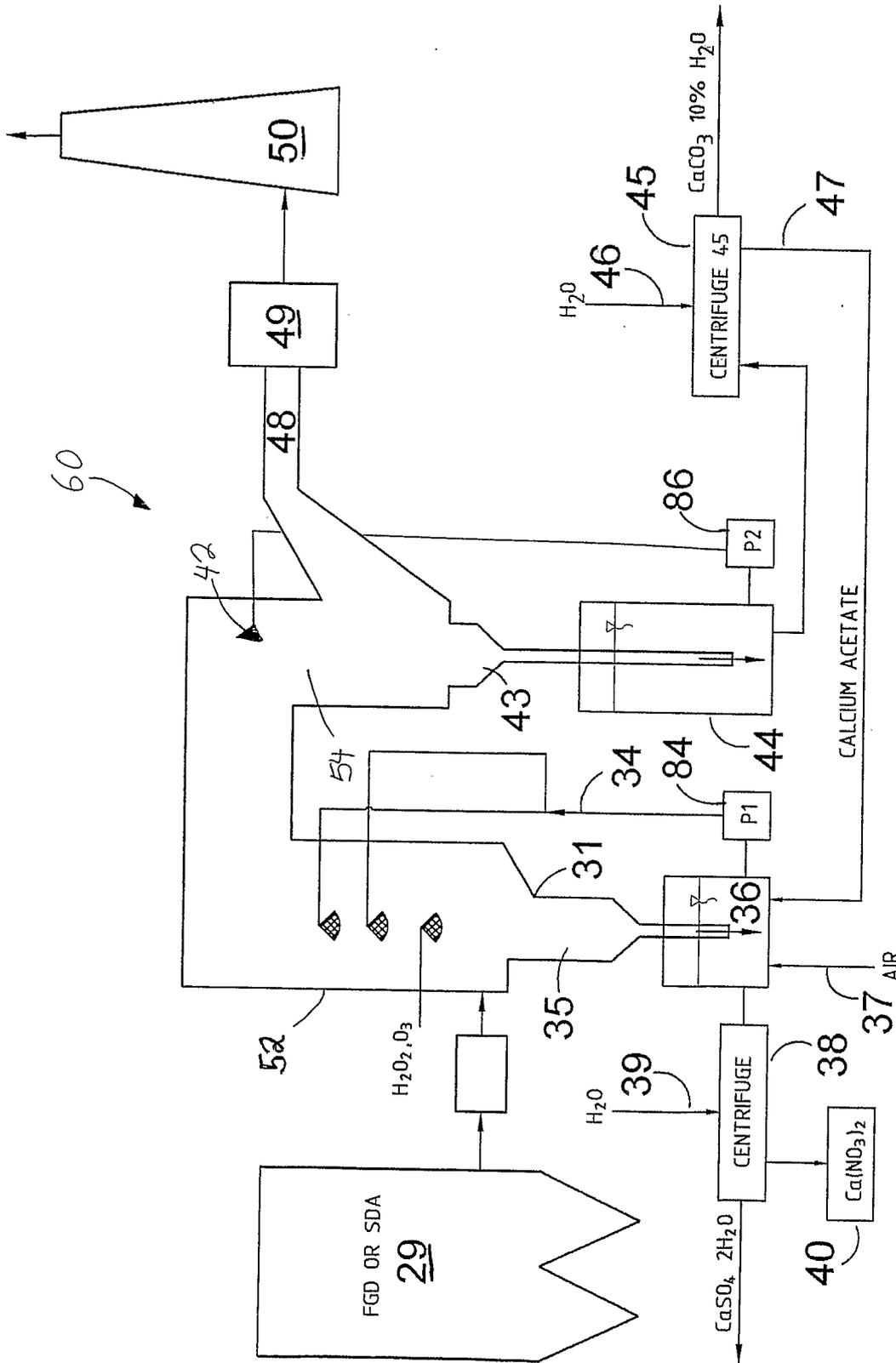


FIGURE 13

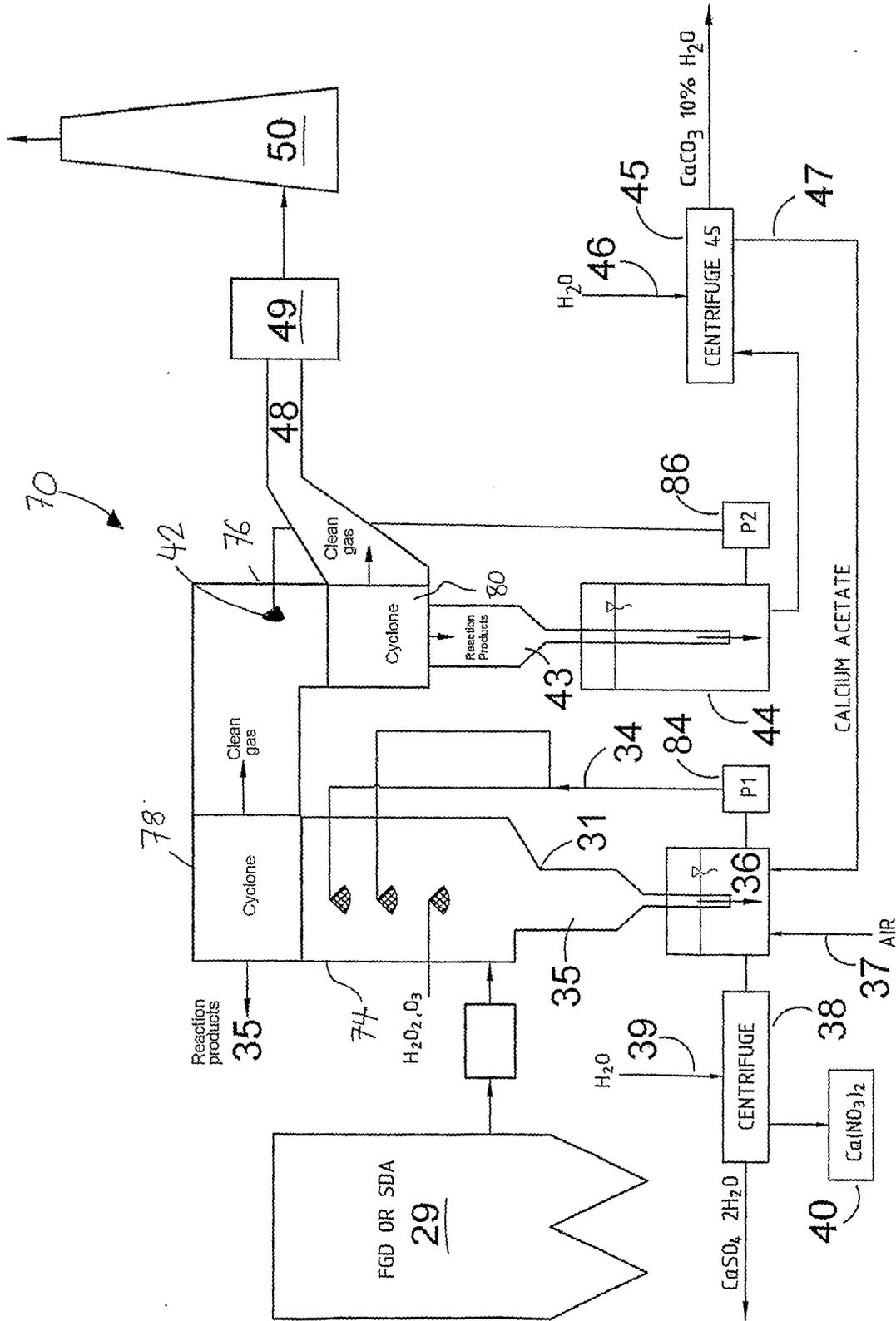


FIGURE 14

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU2008/001471

<p>A. CLASSIFICATION OF SUBJECT MATTER</p> <p>Int. Cl.</p> <p><b>B02L 53/74(2006.01)</b>      <b>BOW 53/14 (2006.01)</b>      <b>BOW 53/60 (2006.01)</b></p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>																	
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols)</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI &amp; EPIDOC: IPC: B02L 53/74, 53/60, 53/14 &amp; keywords (NOx, SOx, Nitrogen oxide, sulphur oxide, metal, cool, condense, water); Google Patents: keywords (metal, mercury, control, flue gas, combustion gas, NOx, SOx, water)</p>																	
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X Y</td> <td>U S 2005/0255019 A 1 (PARRISH) 17 November 2005 Abstract; para 0006; para 0014-0020; para 0036-0038; fig.1</td> <td>1-7, 9-22 8</td> </tr> <tr> <td>X Y</td> <td>U S 5875722 A (GOSSELIN JR. et al.) 2 March 1999 Abstract; col 2, lines 31-54; col 3, line 35 to col 5, line 9; fig.2</td> <td>1, 3-4, 9-12, 13-22 8</td> </tr> <tr> <td>Y</td> <td>GB 1493980 A (MITSUBISHI JUKOGYO KABUSHIKI KAISHA) 7 December 1977 Page 2, lines 22-48</td> <td>8</td> </tr> <tr> <td colspan="3"> <p>Note: For Y indications, GB 1493980 can be combined with any one of U S 2005/0255019 or U S 5875722</p> </td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X Y	U S 2005/0255019 A 1 (PARRISH) 17 November 2005 Abstract; para 0006; para 0014-0020; para 0036-0038; fig.1	1-7, 9-22 8	X Y	U S 5875722 A (GOSSELIN JR. et al.) 2 March 1999 Abstract; col 2, lines 31-54; col 3, line 35 to col 5, line 9; fig.2	1, 3-4, 9-12, 13-22 8	Y	GB 1493980 A (MITSUBISHI JUKOGYO KABUSHIKI KAISHA) 7 December 1977 Page 2, lines 22-48	8	<p>Note: For Y indications, GB 1493980 can be combined with any one of U S 2005/0255019 or U S 5875722</p>		
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<p><input type="checkbox"/> Further documents are listed in the continuation of Box C      <input checked="" type="checkbox"/> See patent family annex</p>																	
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O" document referring to an oral disclosure; use, exhibition or other means</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O" document referring to an oral disclosure; use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed						
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"P" document published prior to the international filing date but later than the priority date claimed																	
<p>Date of the actual completion of the international search</p> <p>18 November 2008</p>		<p>Date of mailing of the international search report</p> <p>03 DEC 2008</p>															
<p>Name and mailing address of the ISA/AU</p> <p>AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. +61 2 6283 7999</p>		<p>Authorized officer</p> <p>HATINDER SHARMA AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6225 6151</p>															

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/AU2008/001471**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2005255019	AU	2005245336	CA	2565750	CN	1950139
		EP	1761325	KR	20070040752	MX	PA06012988
		US	7404938	US	2005255022	WO	2005113115
		WO	2005113116				
US	5875722	EP	0755496	<b>US</b>	5553555	WO	9530113
GB	1493980	DE	2512883	FR	2267822	JP	50136285
		US	4009244				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX