

(12) UK Patent Application (19) GB (11) 2 296 490 (13) A

(43) Date of Printing by UK Office 03.07.1996

(21) Application No 9522404.4

(22) Date of Filing 11.05.1995

(30) Priority Data

(31) 06097425	(32) 11.05.1994	(33) JP
07020625	08.02.1995	
07040315	28.02.1995	
07040316	28.02.1995	
07040318	28.02.1995	

(86) International Application Data
PCT/JP95/00921 En 11.05.1995

(87) International Publication Data
WO95/31272 En 23.11.1995

(51) INT CL⁶
B01D 53/34

(52) UK CL (Edition O)
C1A ASB AS22Y AS221 AS41Y AS412 AS413 AS414
AS475 AS492 AS493 AS641 AS644 AS682 AS711

(56) Documents Cited by ISA
Japanese Utility Model Application No. 93314/1991
7 May 1993 pages 5 and 8

(58) Field of Search by ISA
INT CL⁶ B01D 53/34
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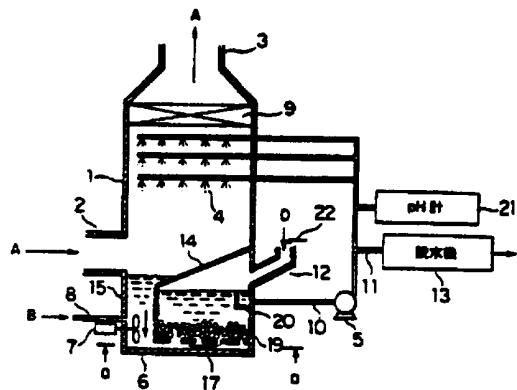
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(54) Wet type exhaust gas desulfurization apparatus and method utilizing solid desulfurizing agent

(57) A wet type exhaust gas desulfurization method wherein an exhaust gas discharged from a combustion apparatus, such as a boiler and an absorption liquid are brought into contact with each other to have sulfur oxide in the exhaust gas absorbed in the absorption liquid and neutralize the sulfur oxide-absorbed absorption liquid, characterized in that lime stones of a large grain size are allowed to stay selectively in a position in which the absorption liquid is neutralized, the absorption liquid which contains as main components gypsum produced from the sulfur oxide and water being discharged selectively from the neutralization position. In the neutralization position, an ascending current of the absorption liquid is formed, or an ascending current of air or water is formed with or separately from the ascending current of the absorption liquid, to produce a fluidized bed of lime stone particles, whereby the reactivity of the lime stone is maintained with the scaling of gypsum particles around the lime stones prevented. Thus, even when aluminum and fluorocomponents coexist in the absorption liquid, the desulfurization performance does not substantially lower. Moreover, the cost of power for pulverizing the lime stones can be reduced, and high desulfurizing performance can be attained.



13 ... dehydrator
21 ... pH meter

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FIG. 1

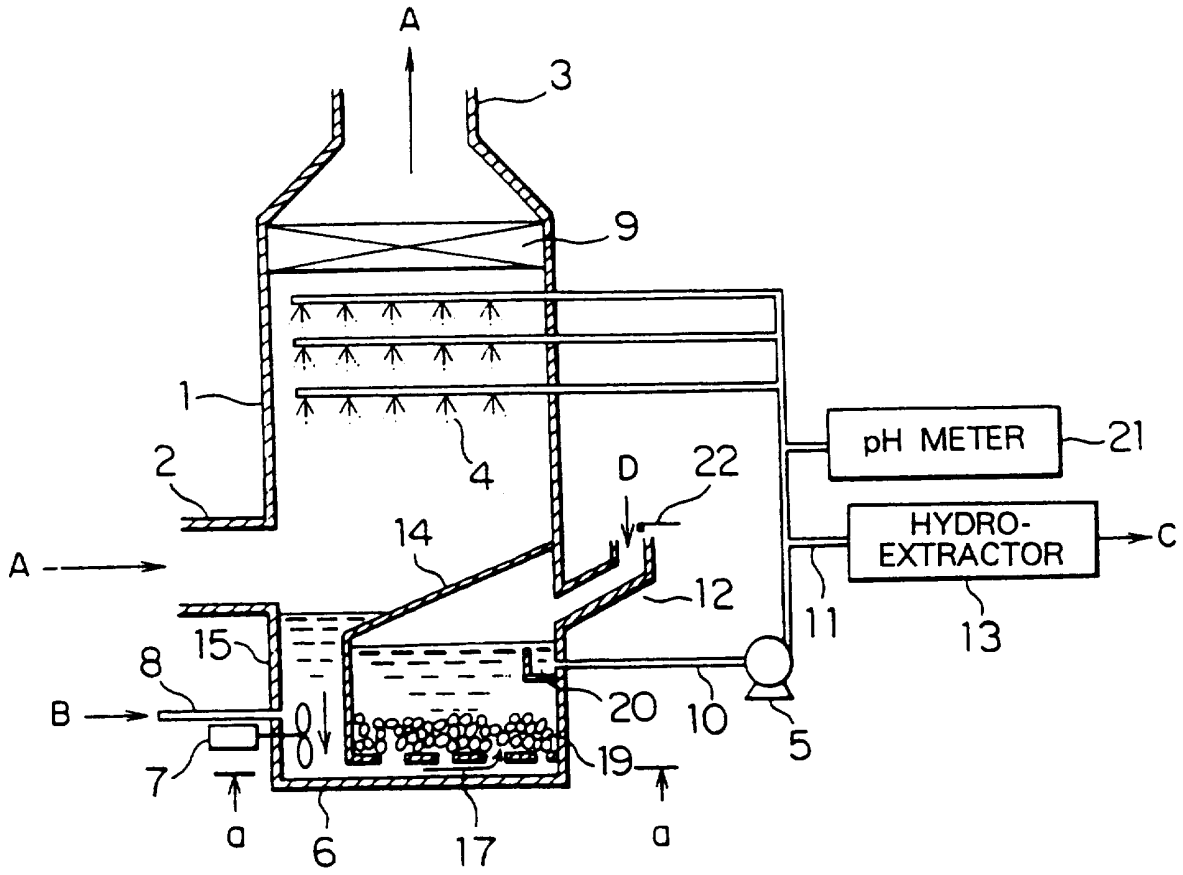


FIG. 2

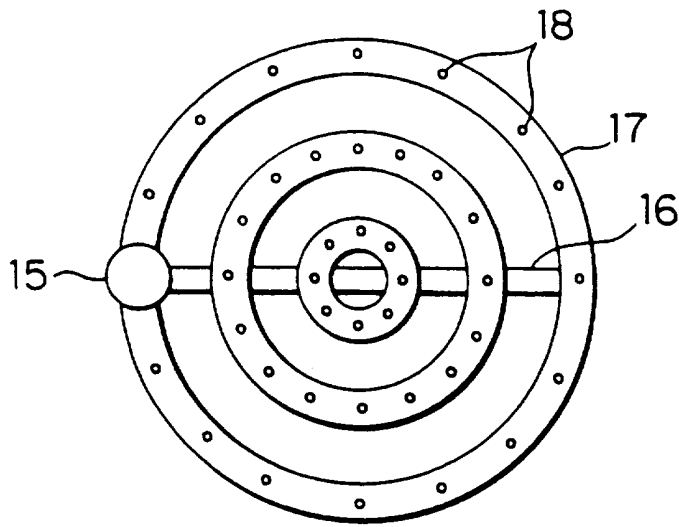


FIG. 3

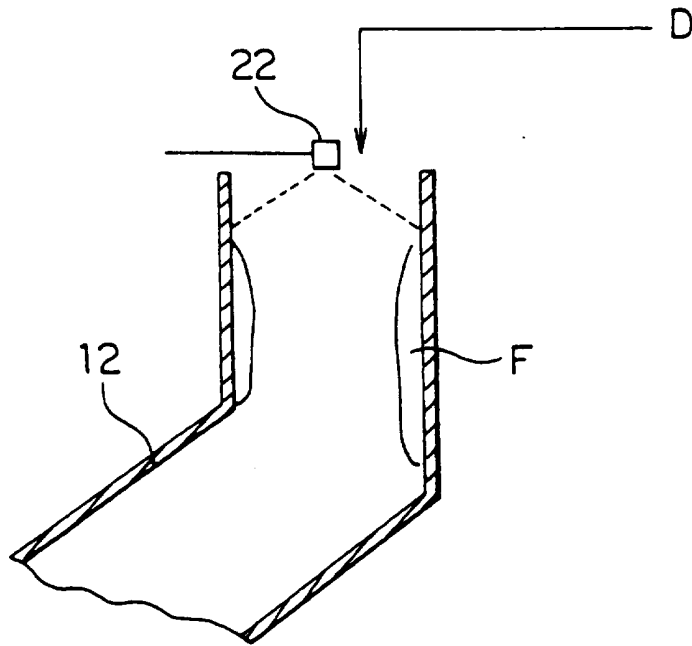


FIG. 4

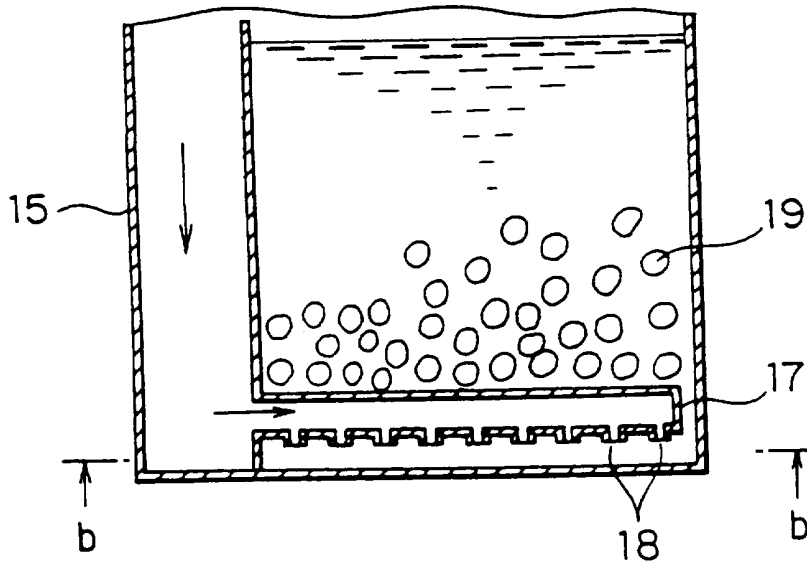


FIG. 5

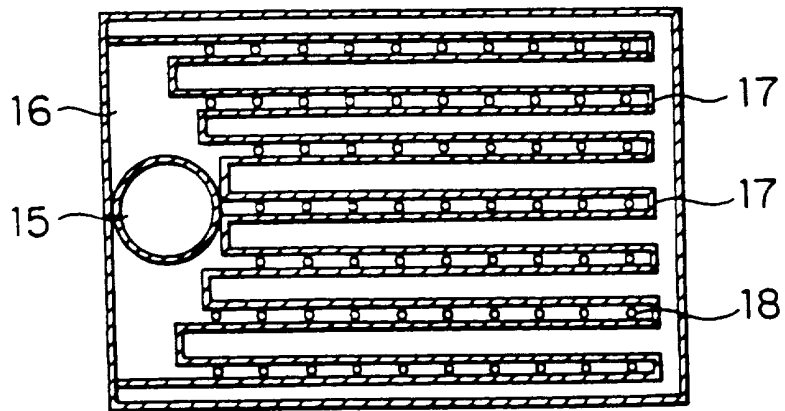


FIG. 6

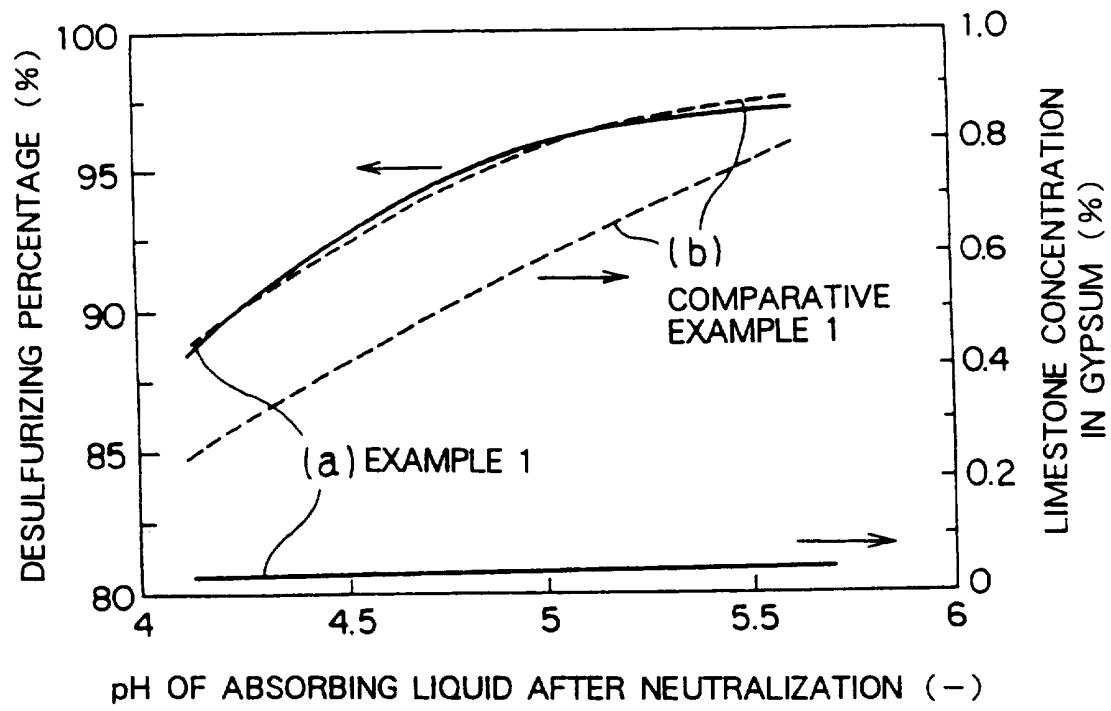


FIG. 7

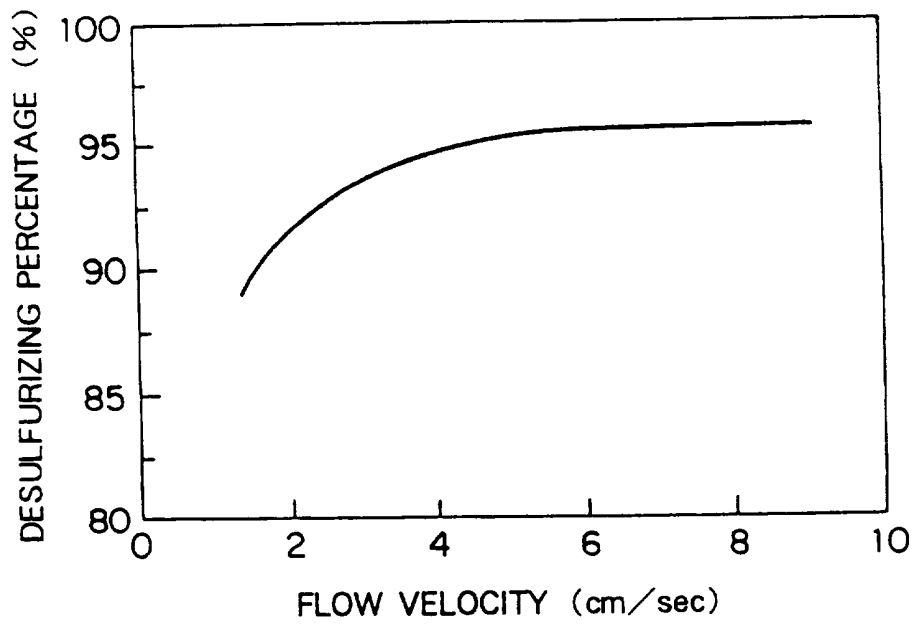


FIG. 8

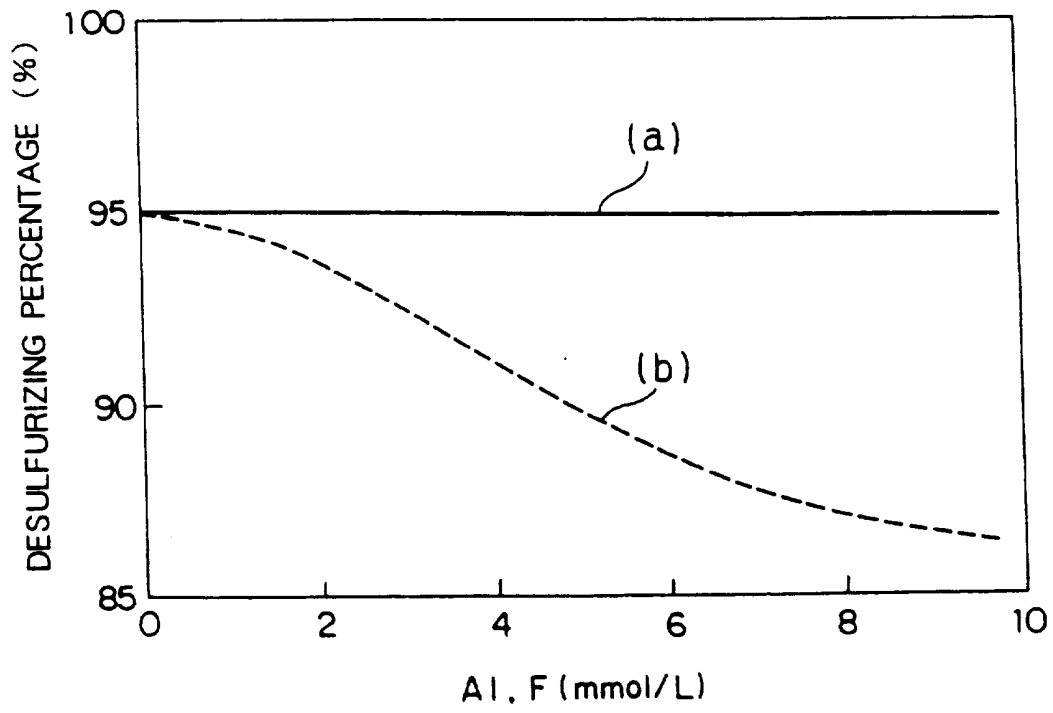


FIG. 9

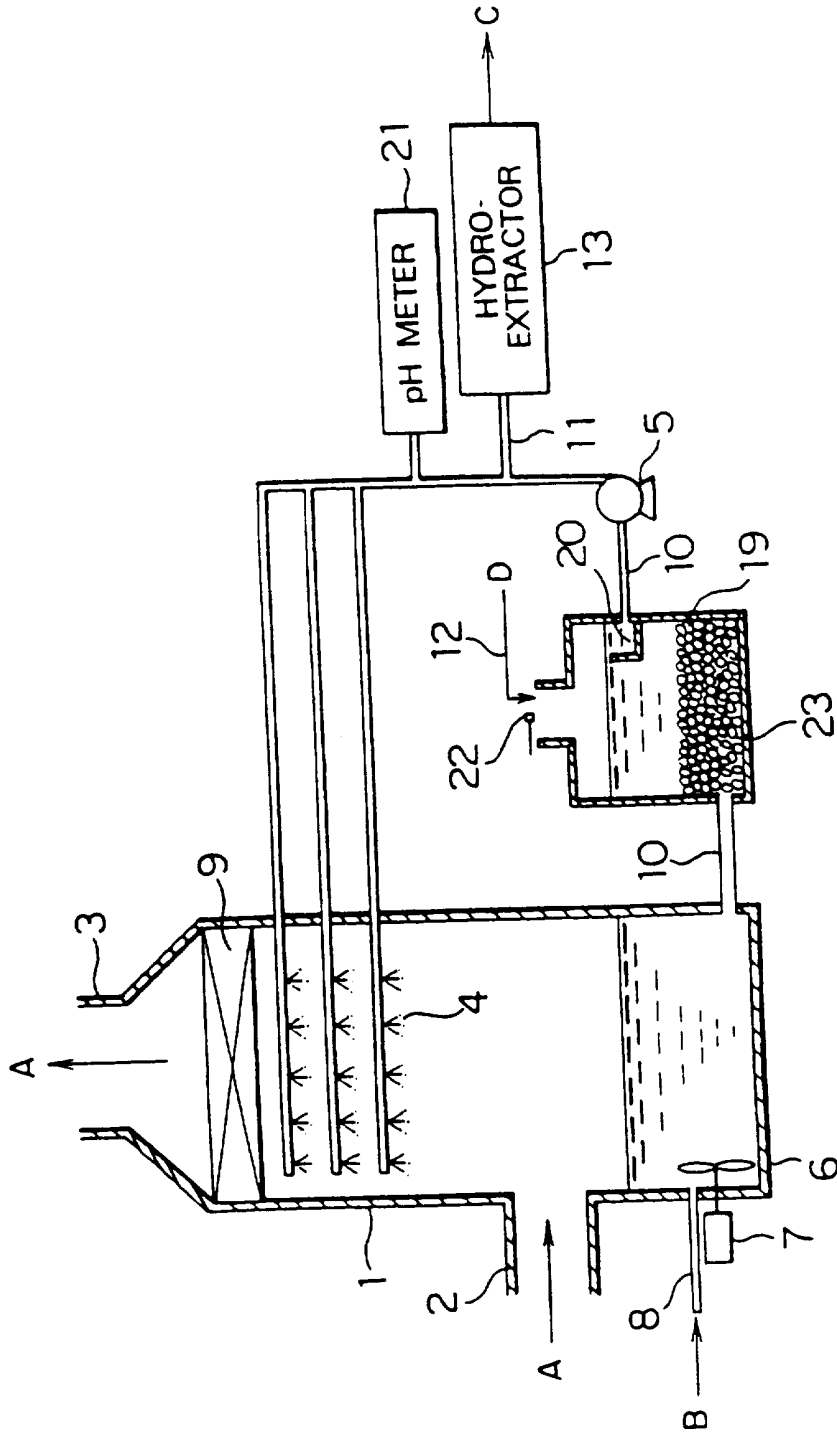


FIG. 10

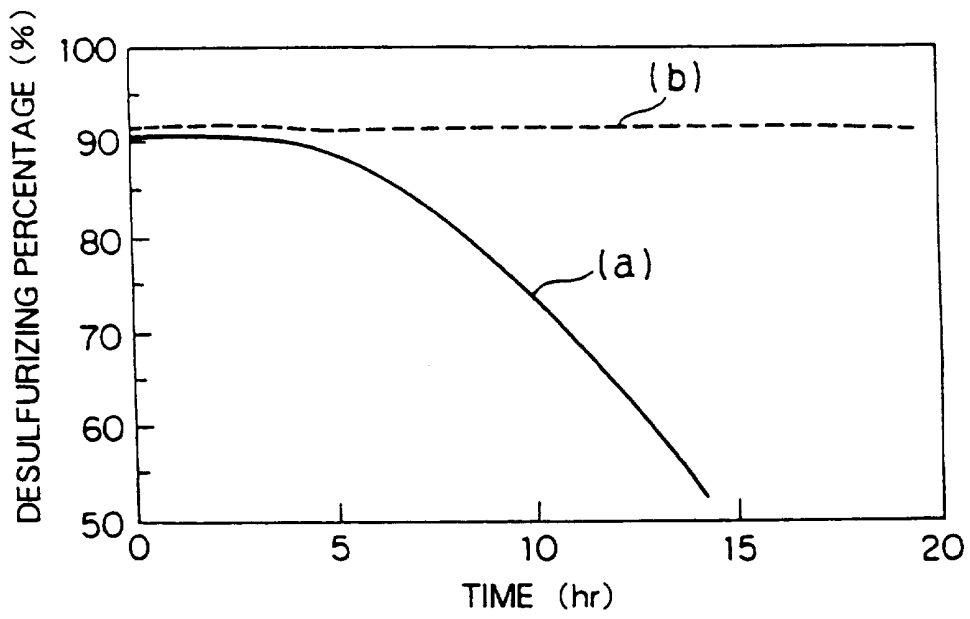


FIG. 11

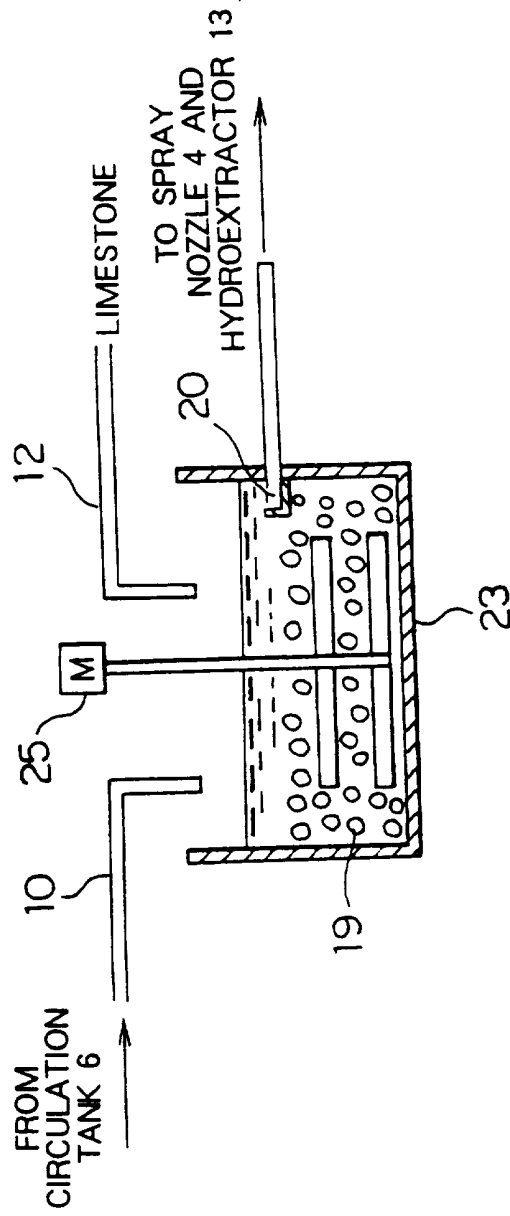


FIG. 12

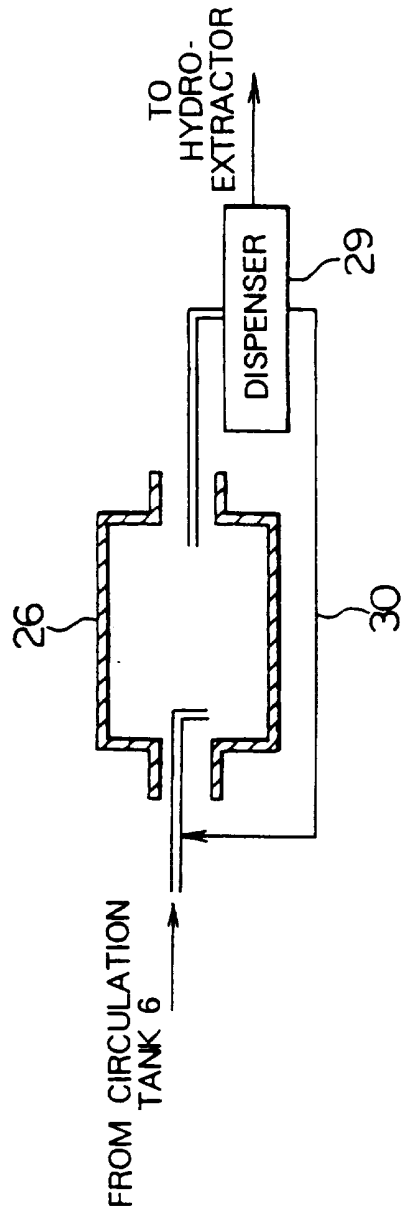


FIG. 13

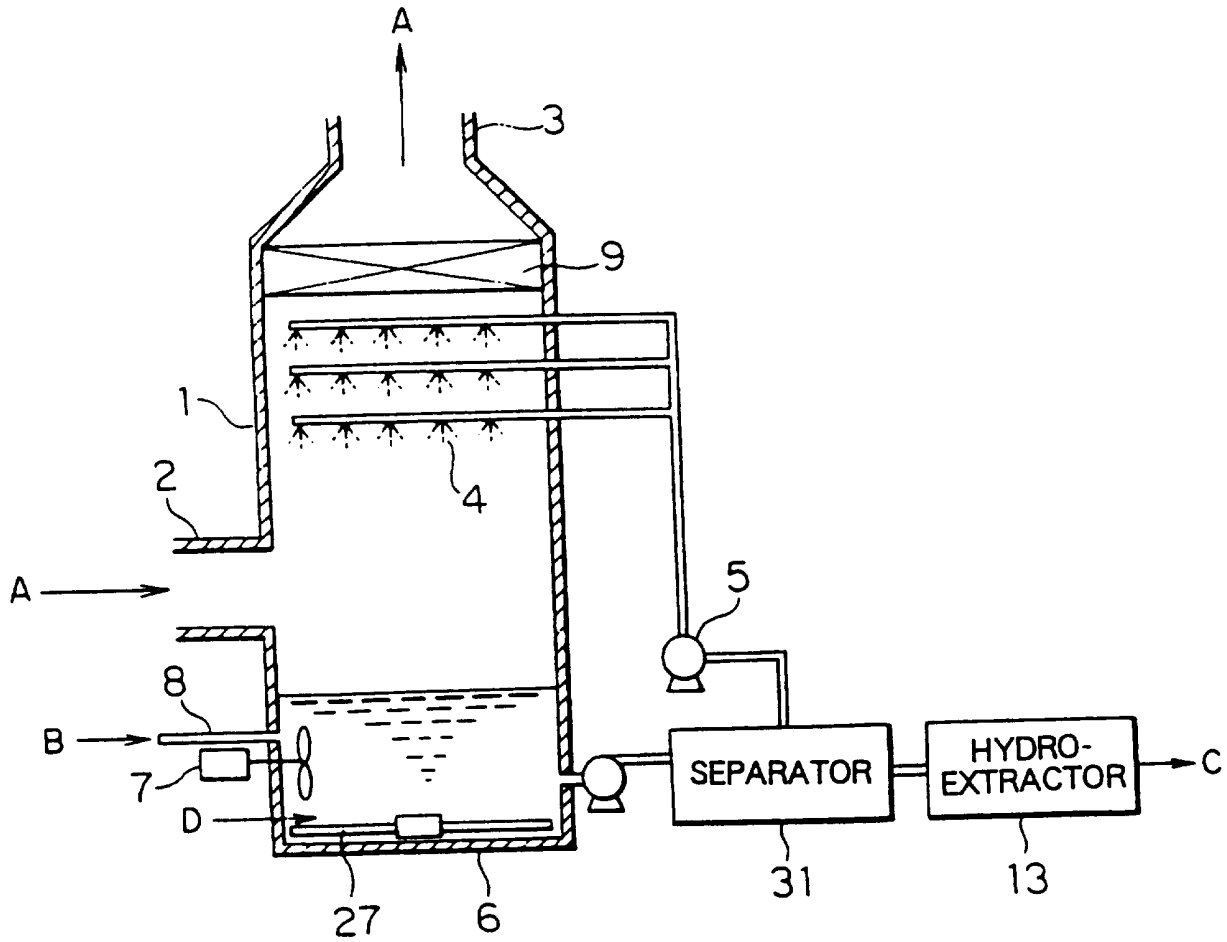


FIG. 14

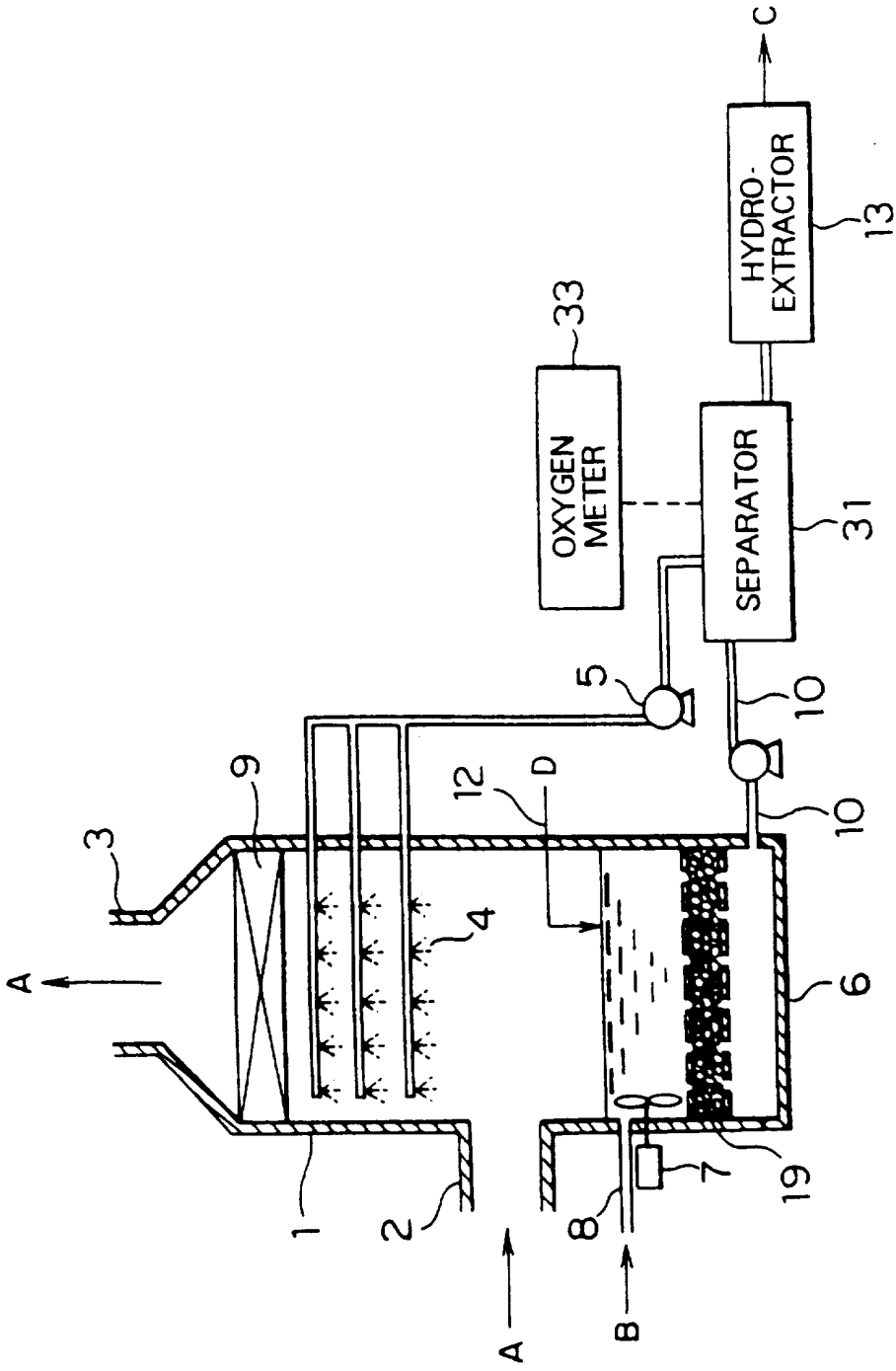


FIG. 15

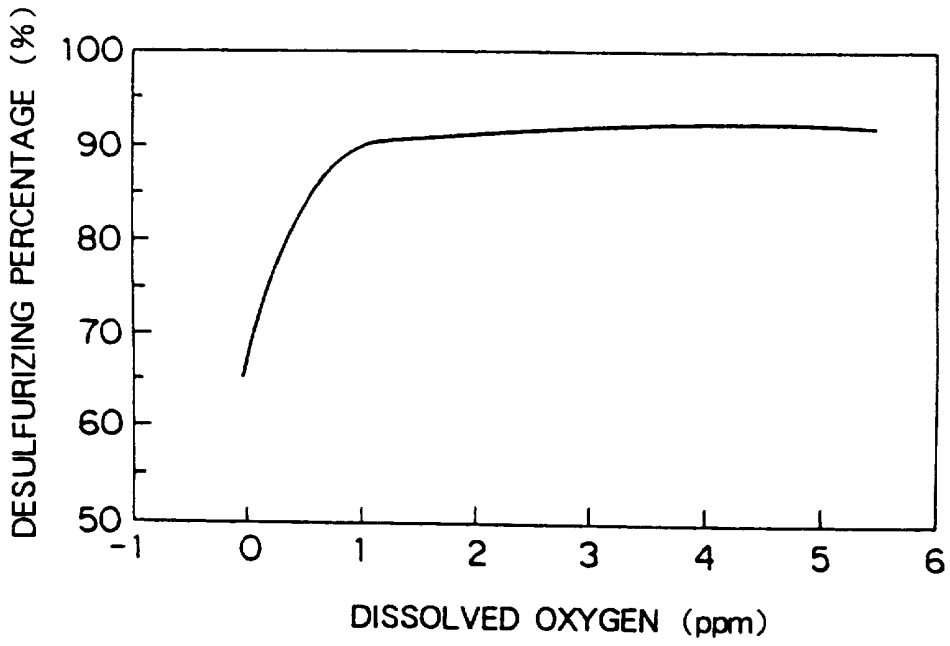


FIG. 16

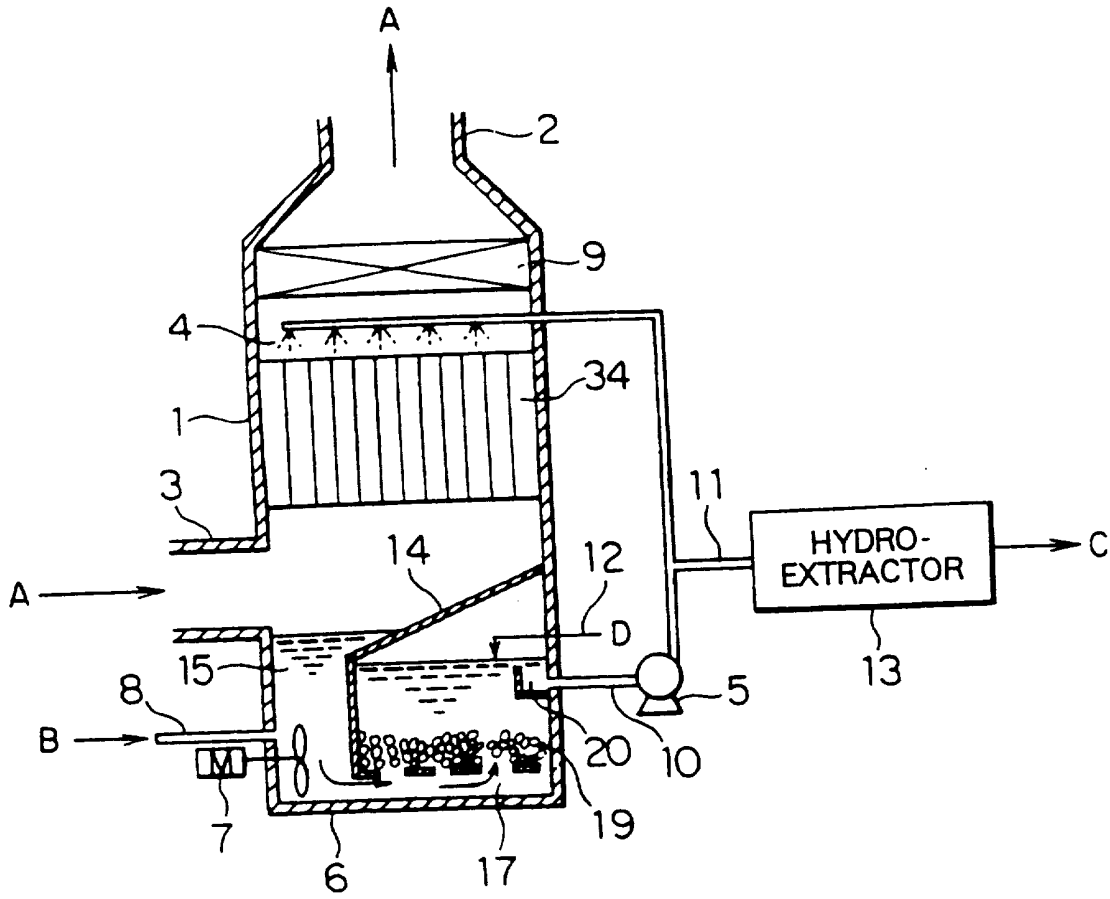


FIG. 17

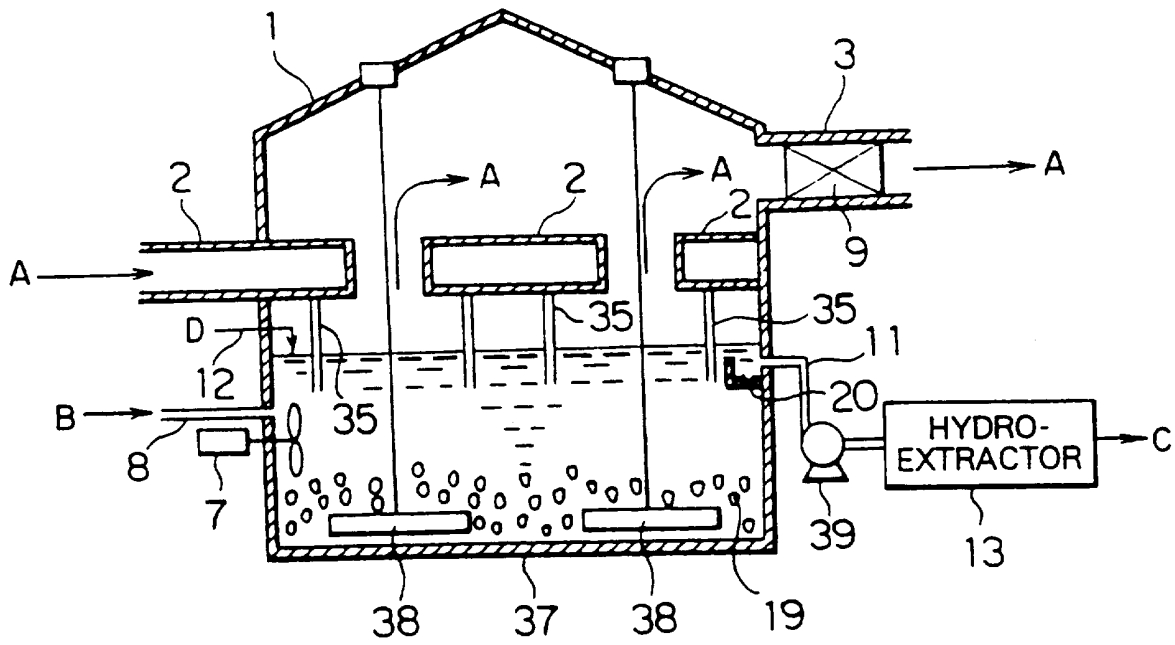


FIG. 18

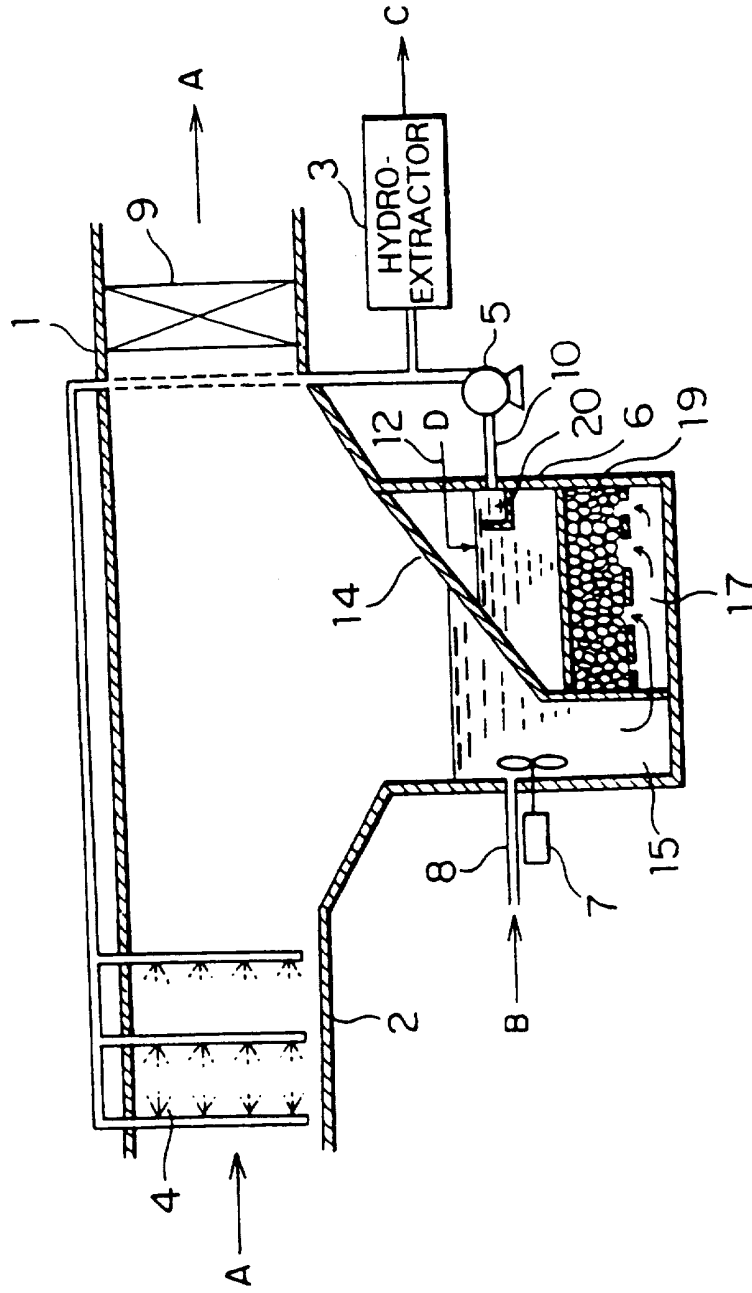


FIG. 19

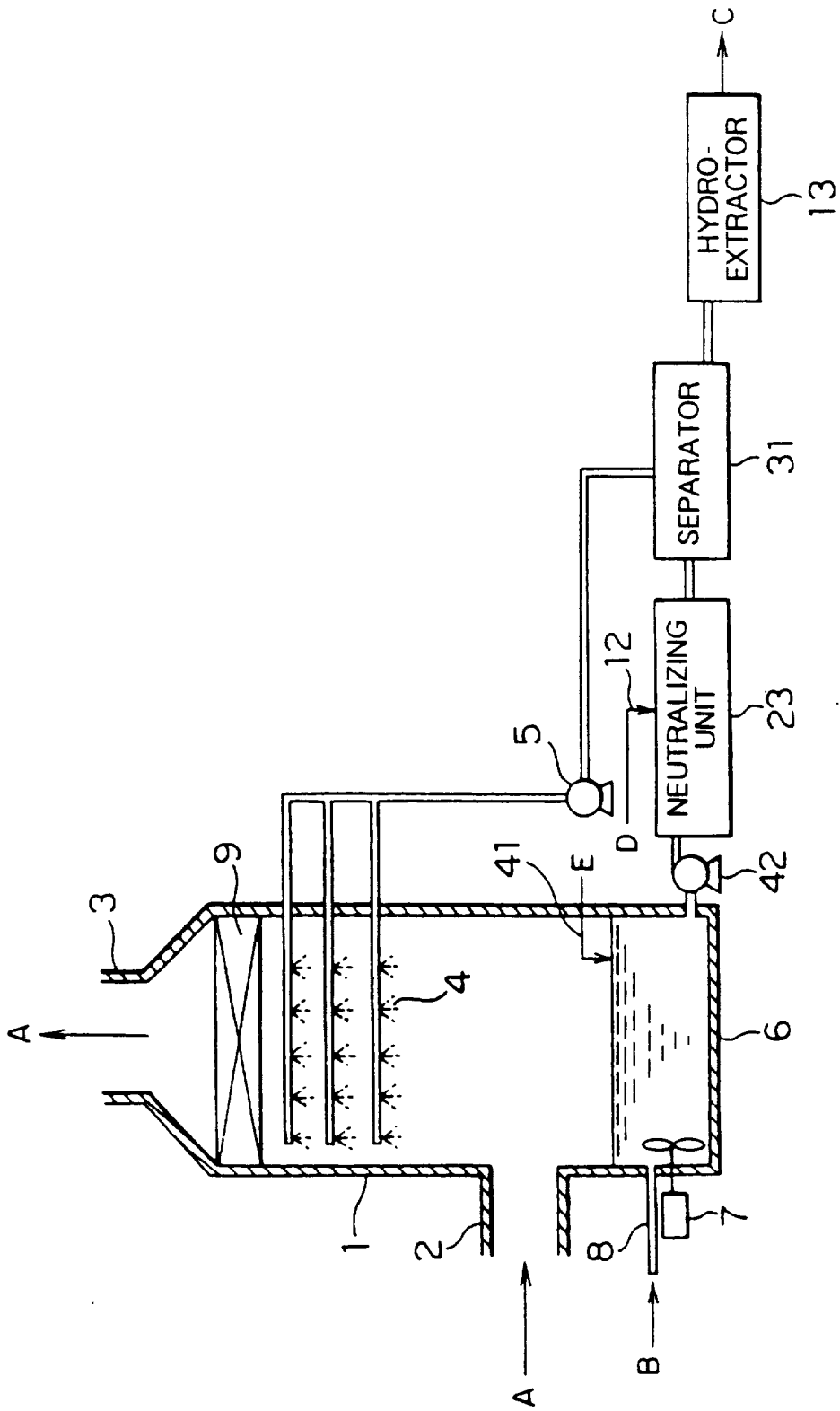


FIG. 20

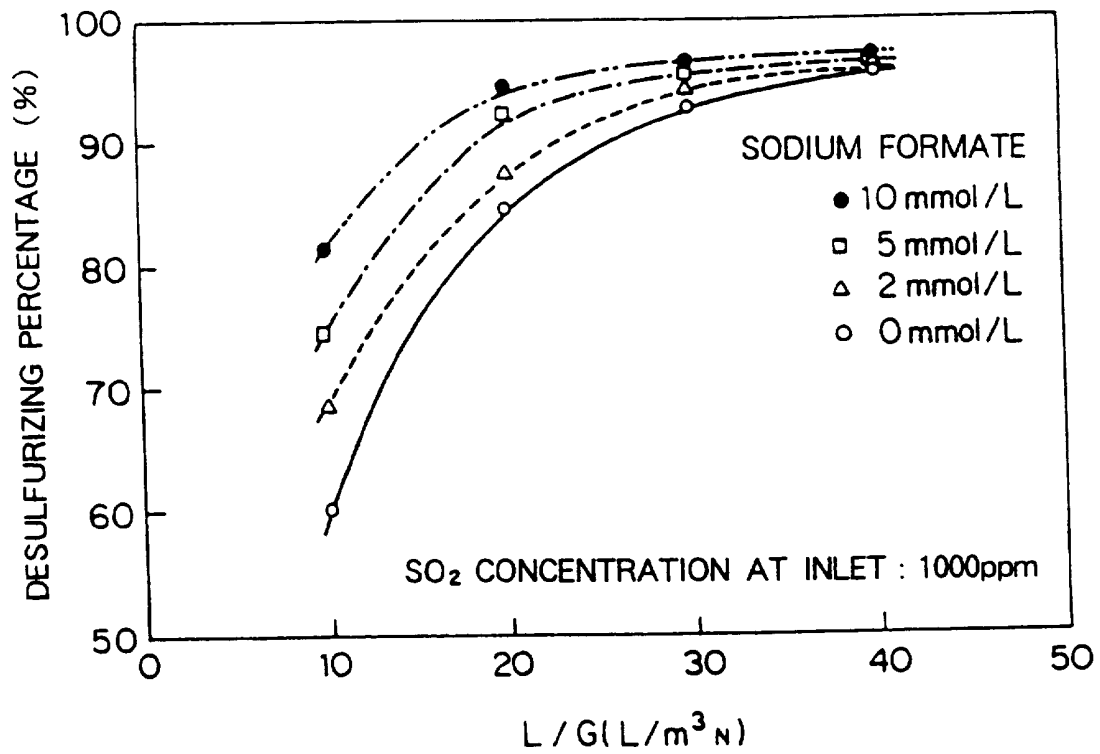


FIG. 21

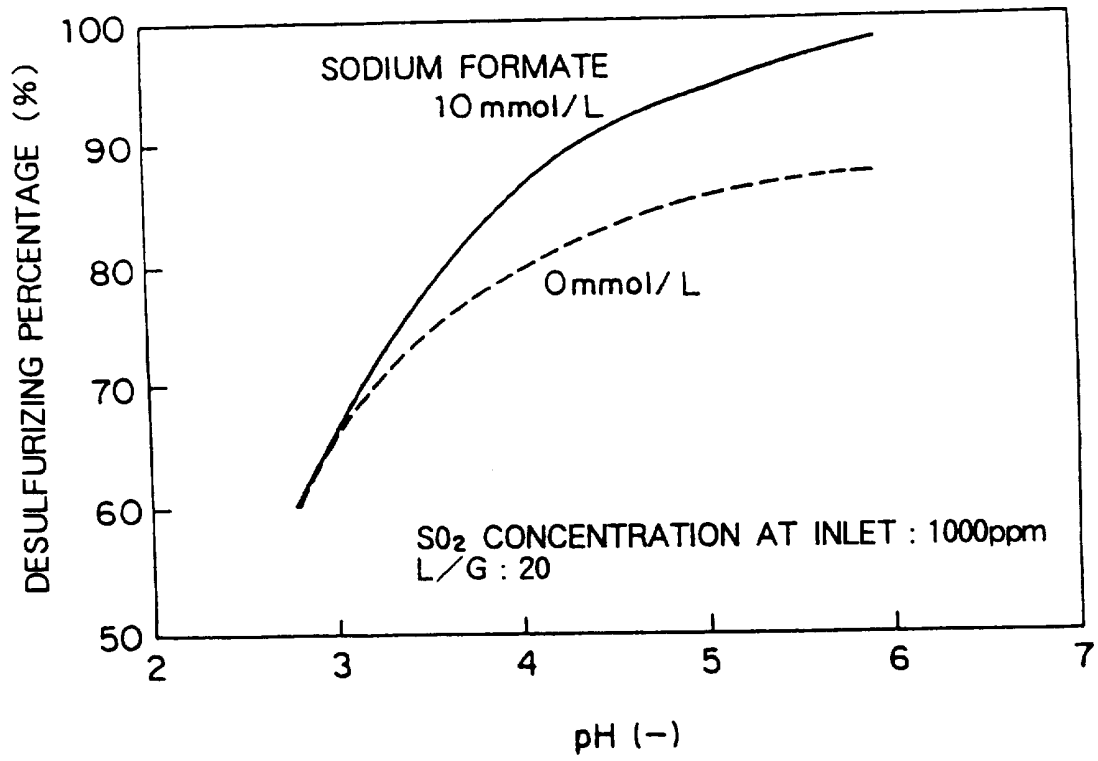


FIG. 22

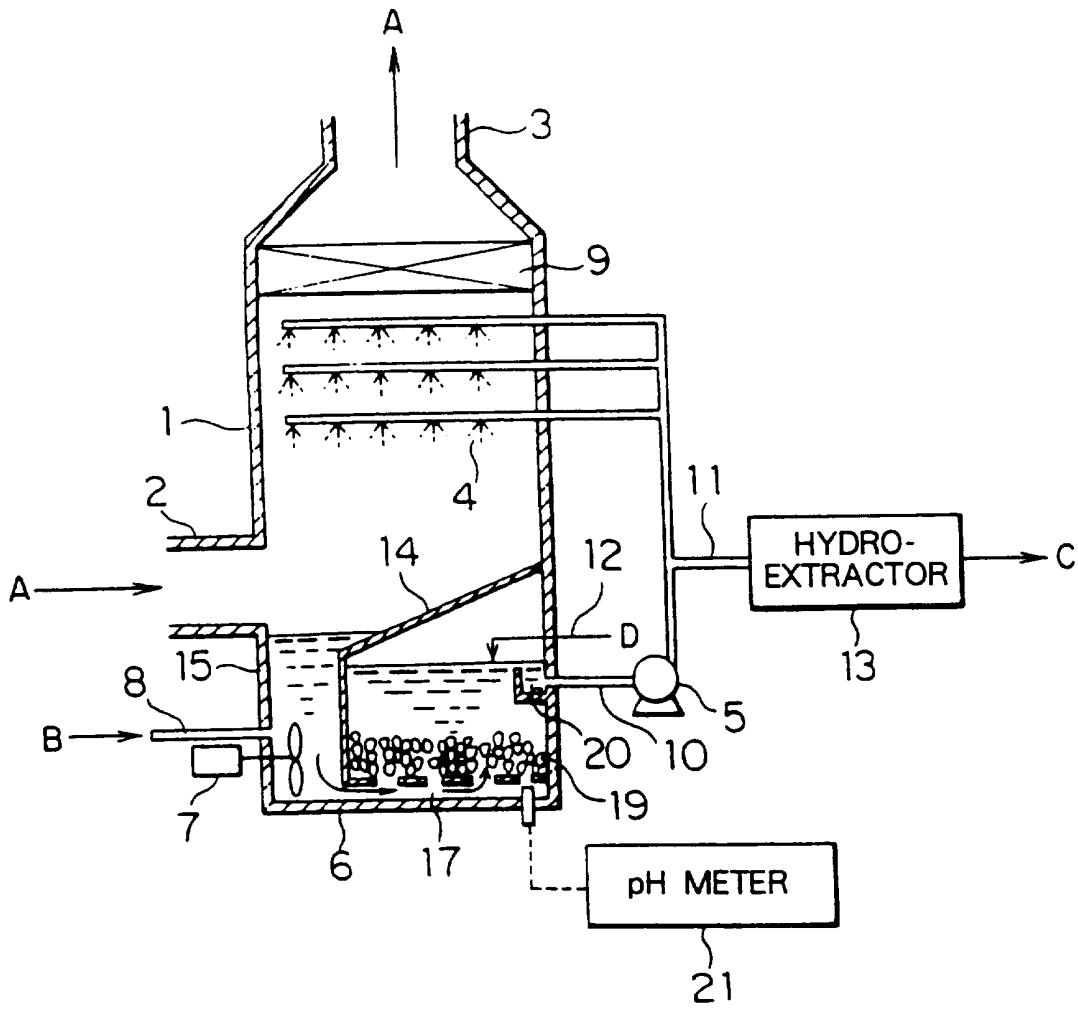


FIG. 23

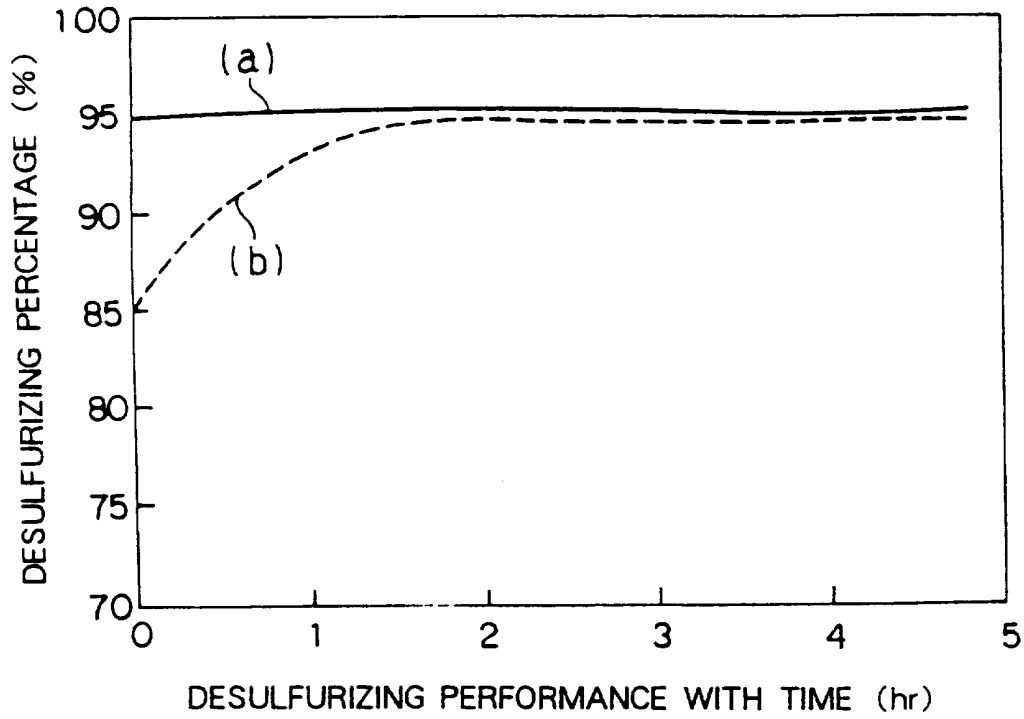


FIG. 24

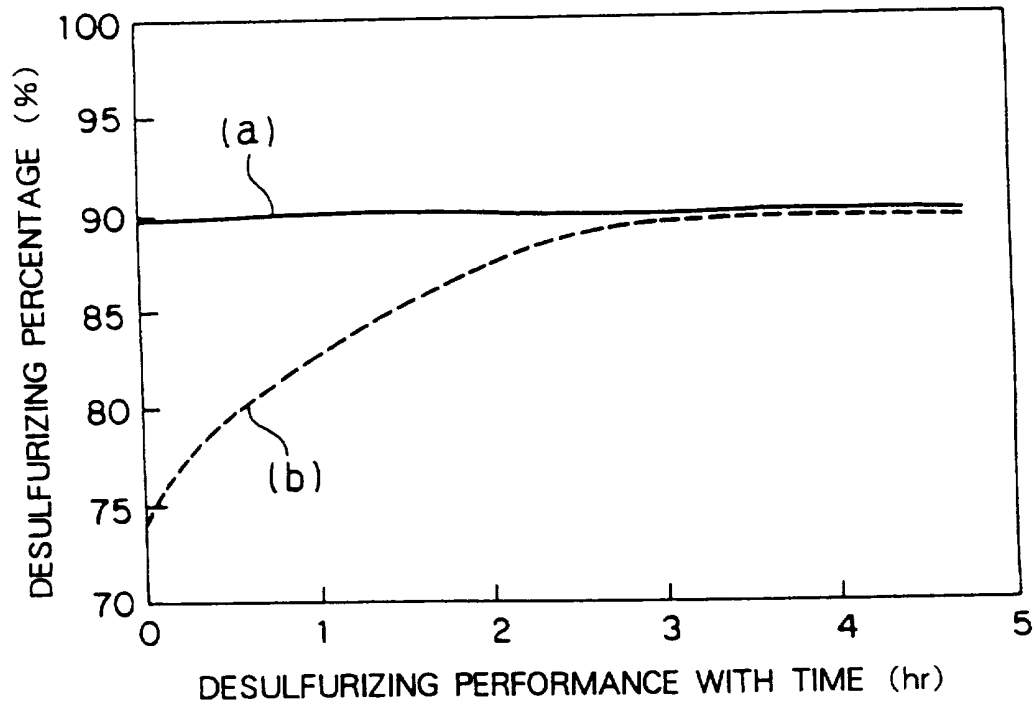


FIG. 25

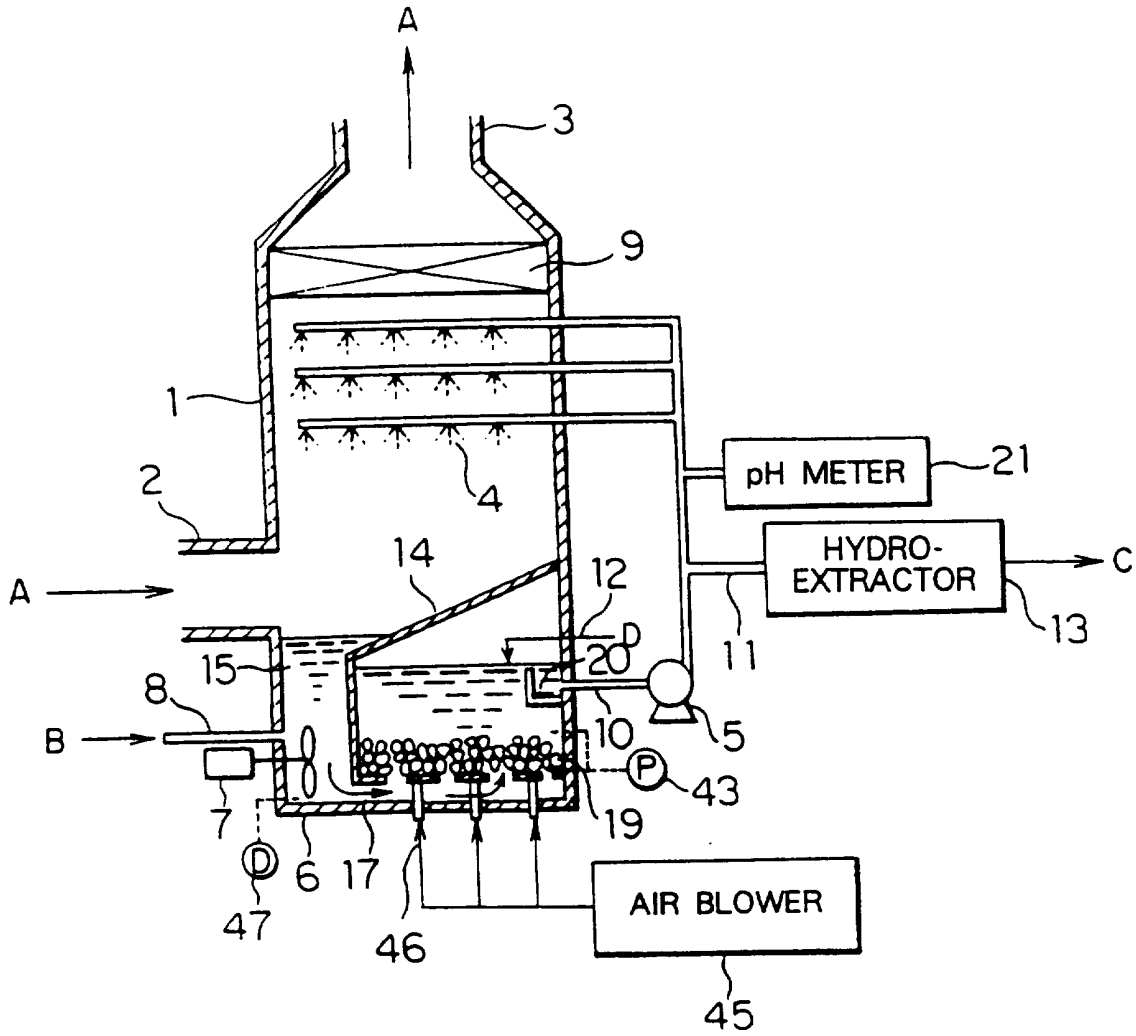


FIG. 26

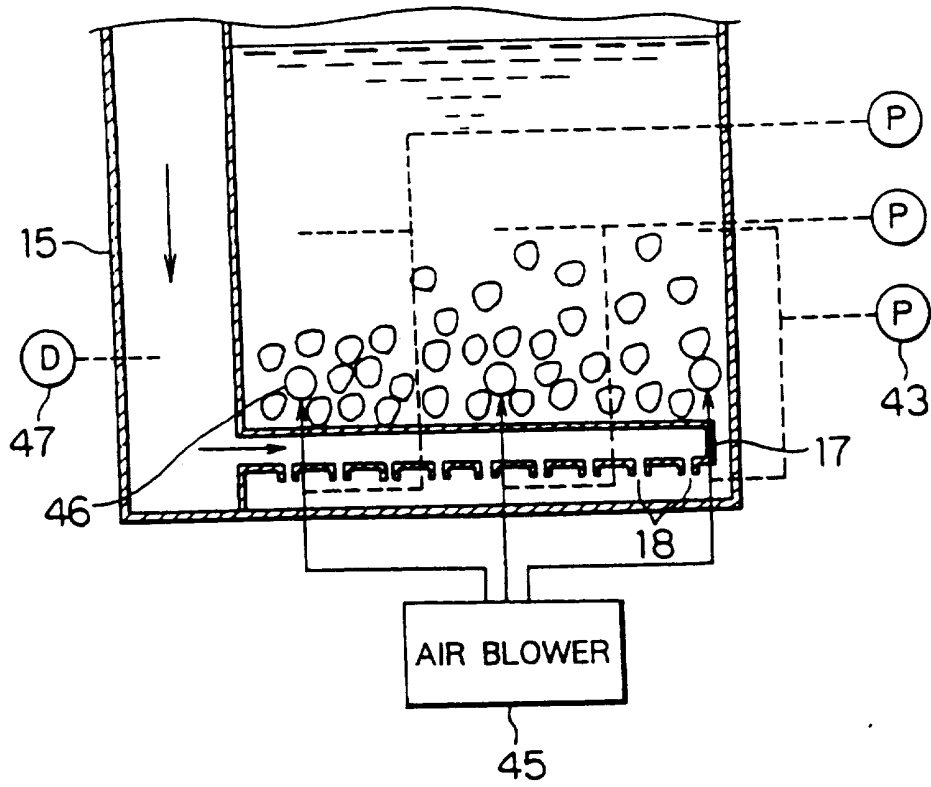


FIG. 27

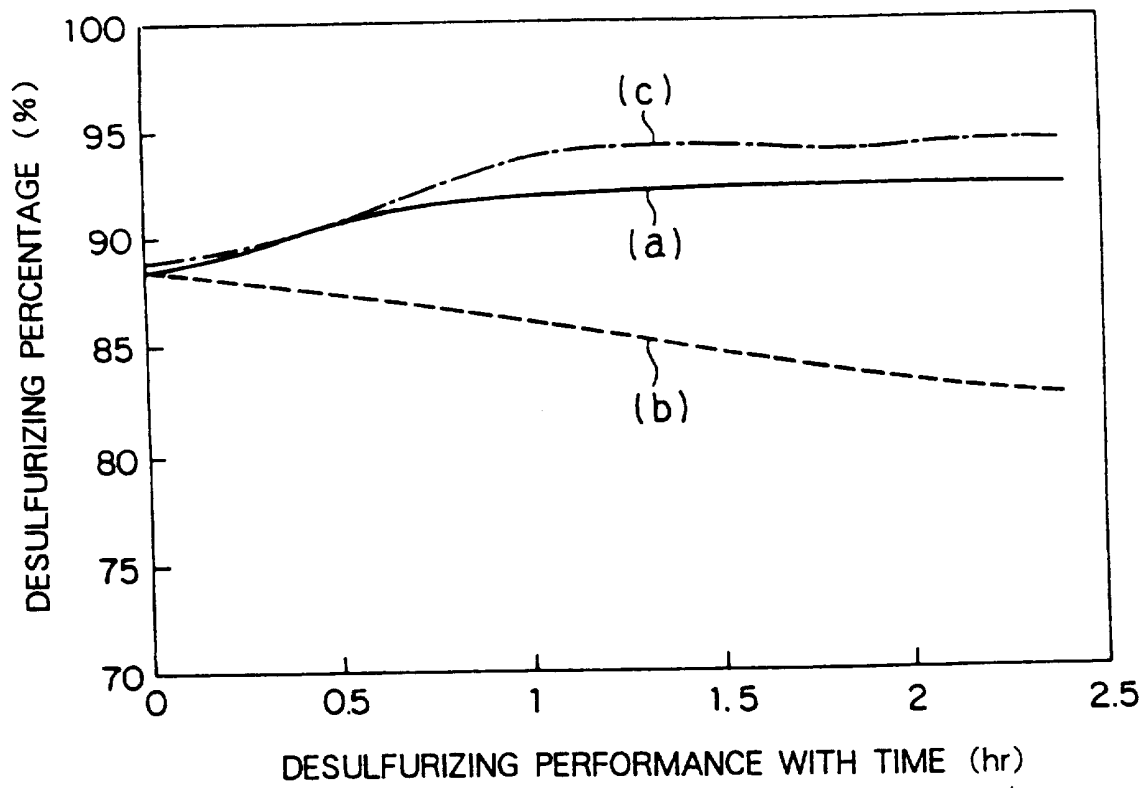


FIG. 28

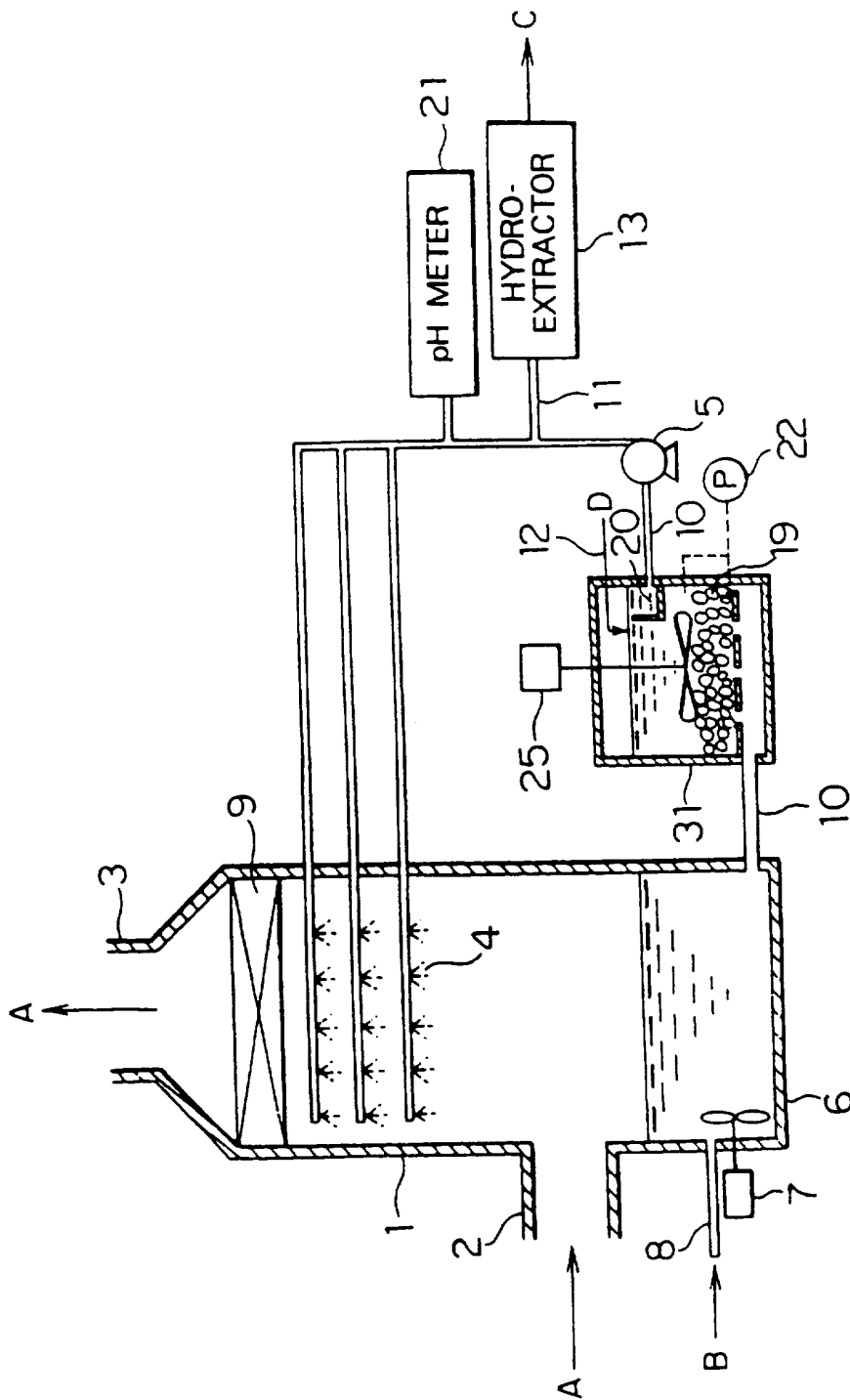


FIG. 29

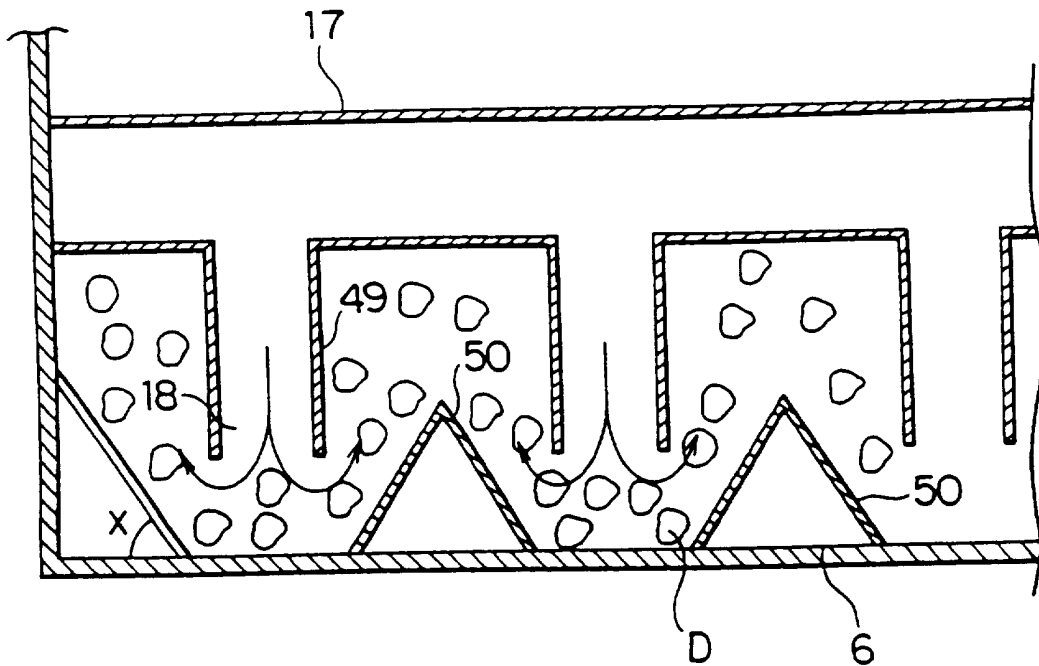


FIG. 30

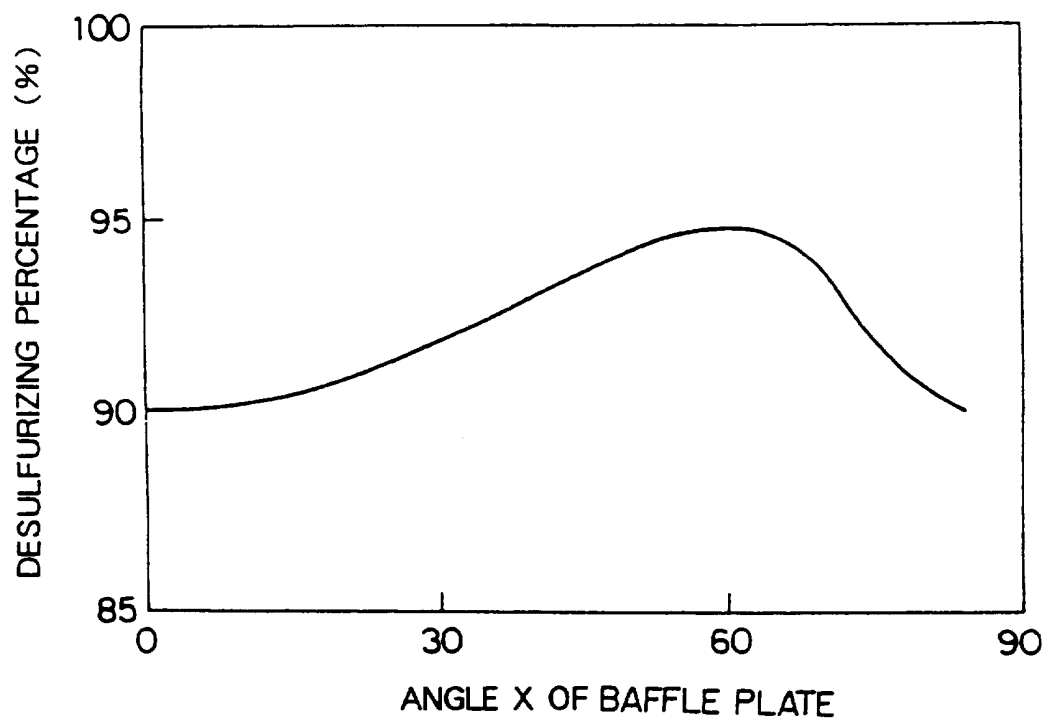


FIG. 31

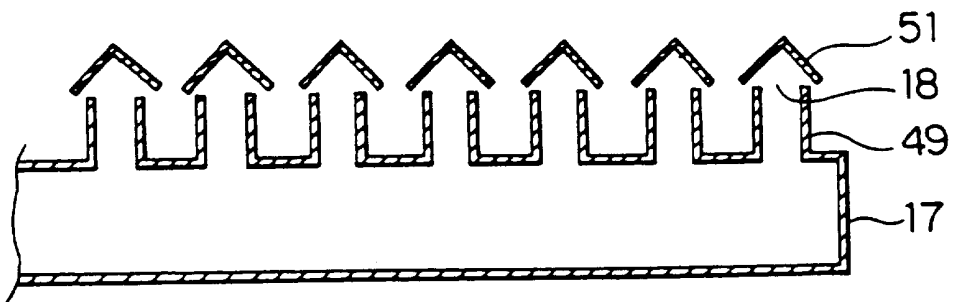


FIG. 32

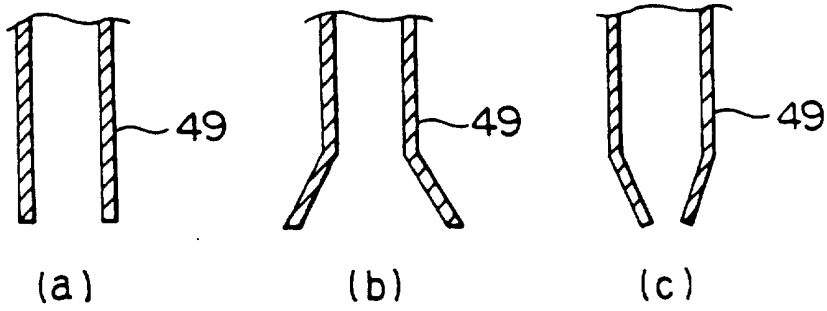


FIG. 33

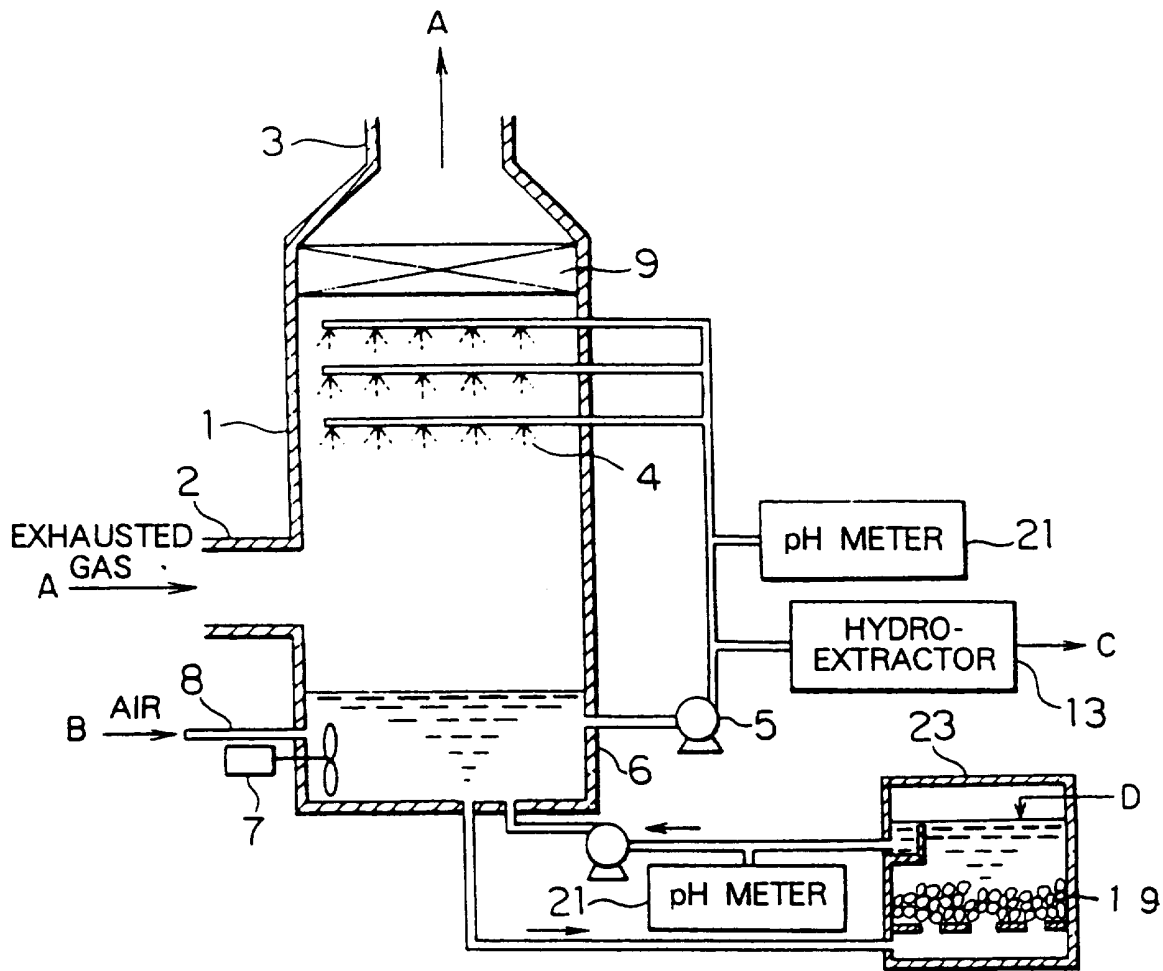


FIG. 34

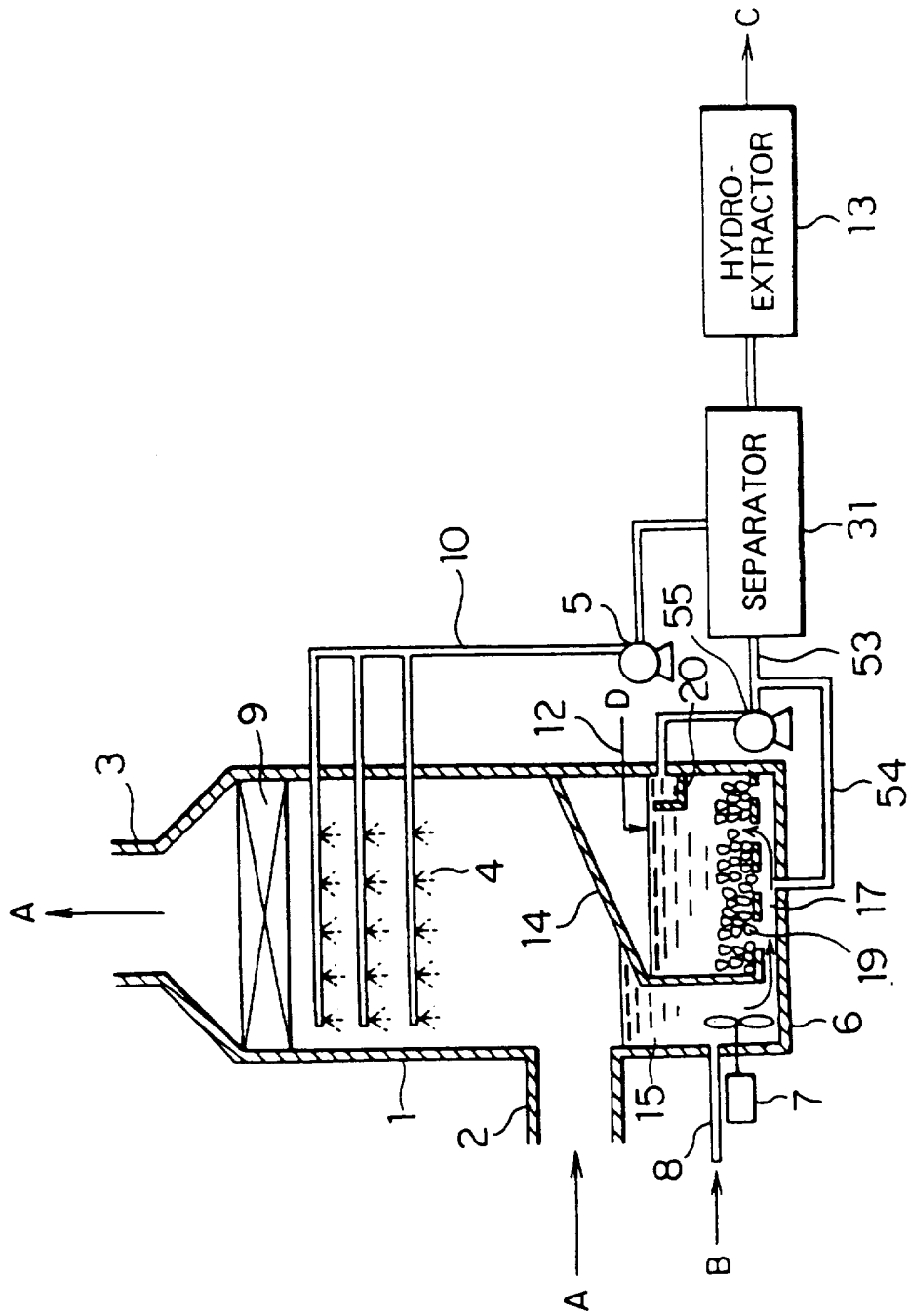


FIG. 35

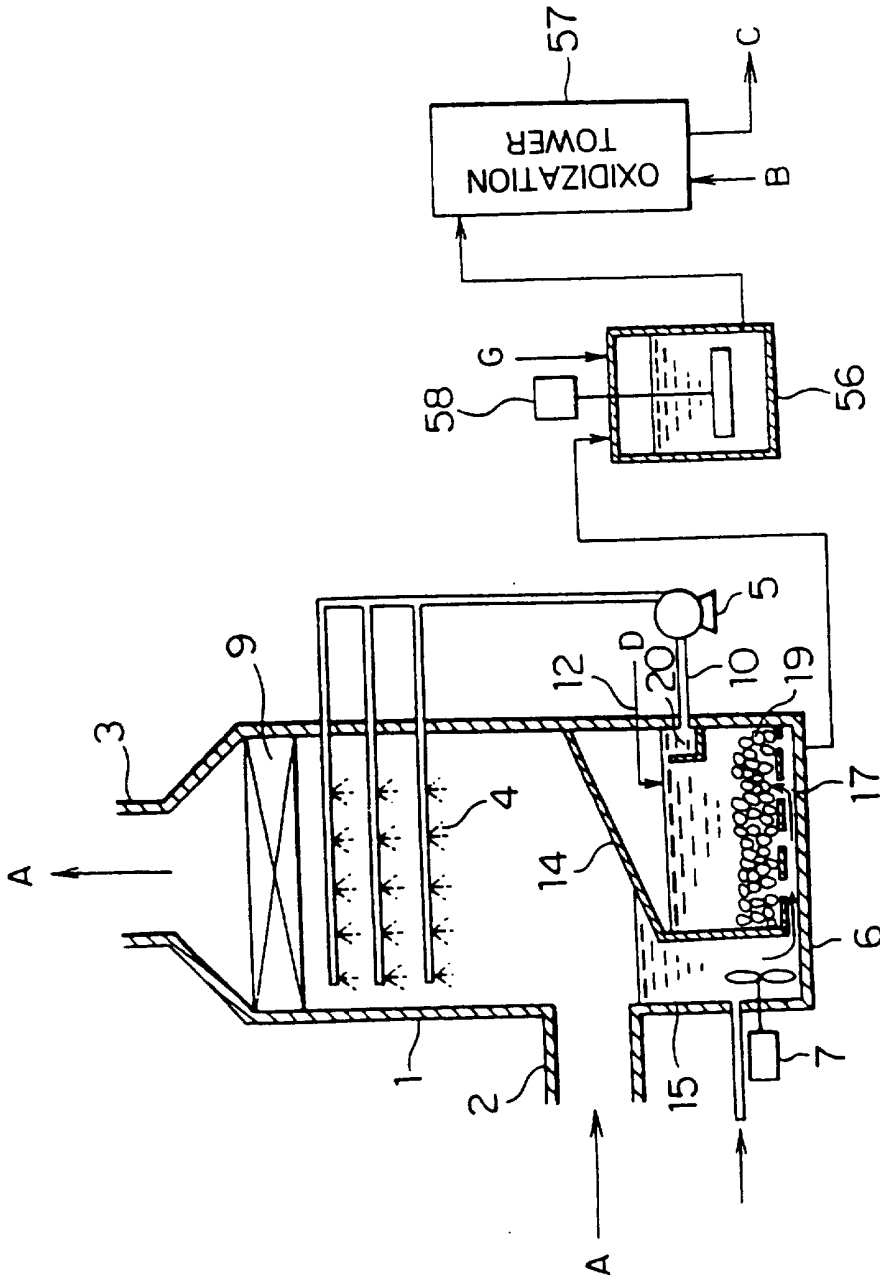


FIG. 36

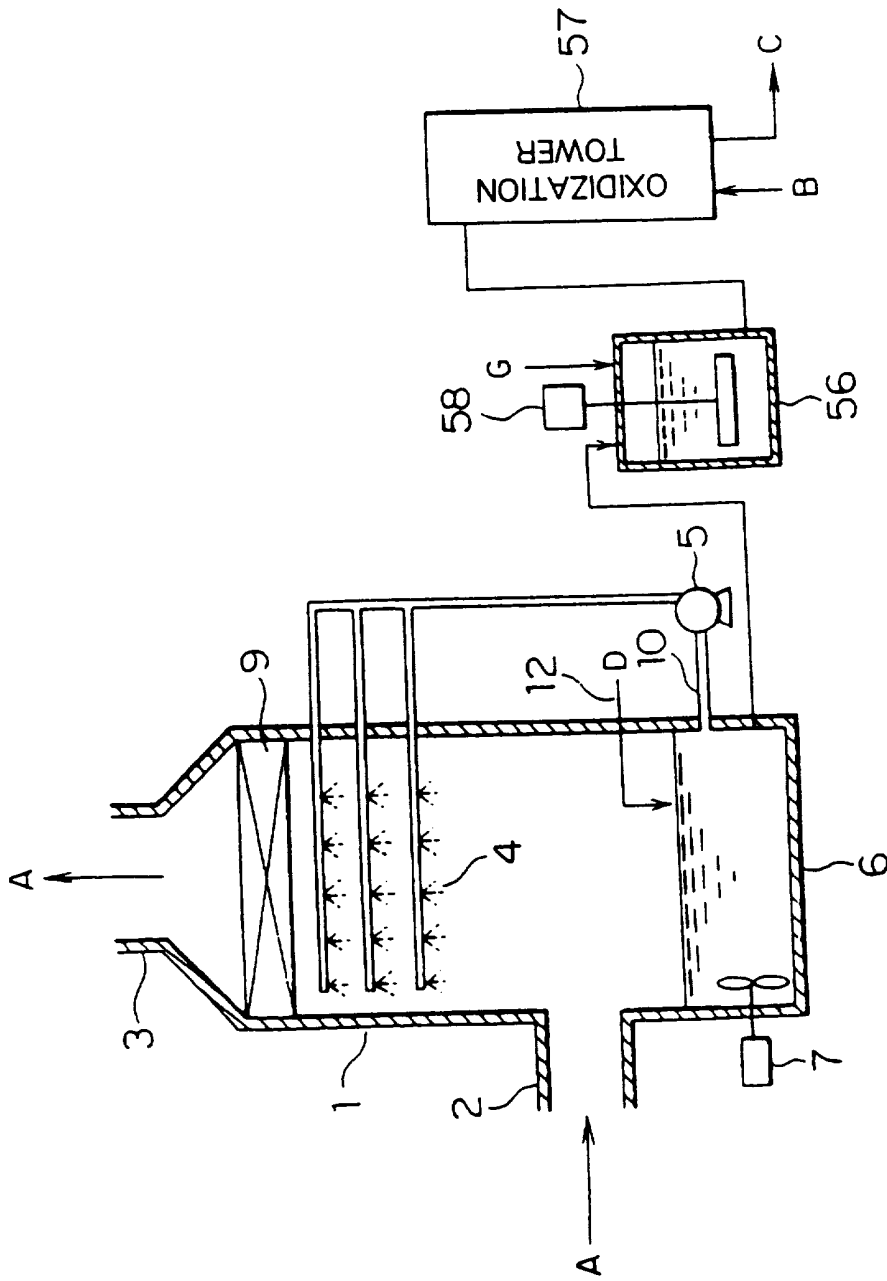


FIG. 37

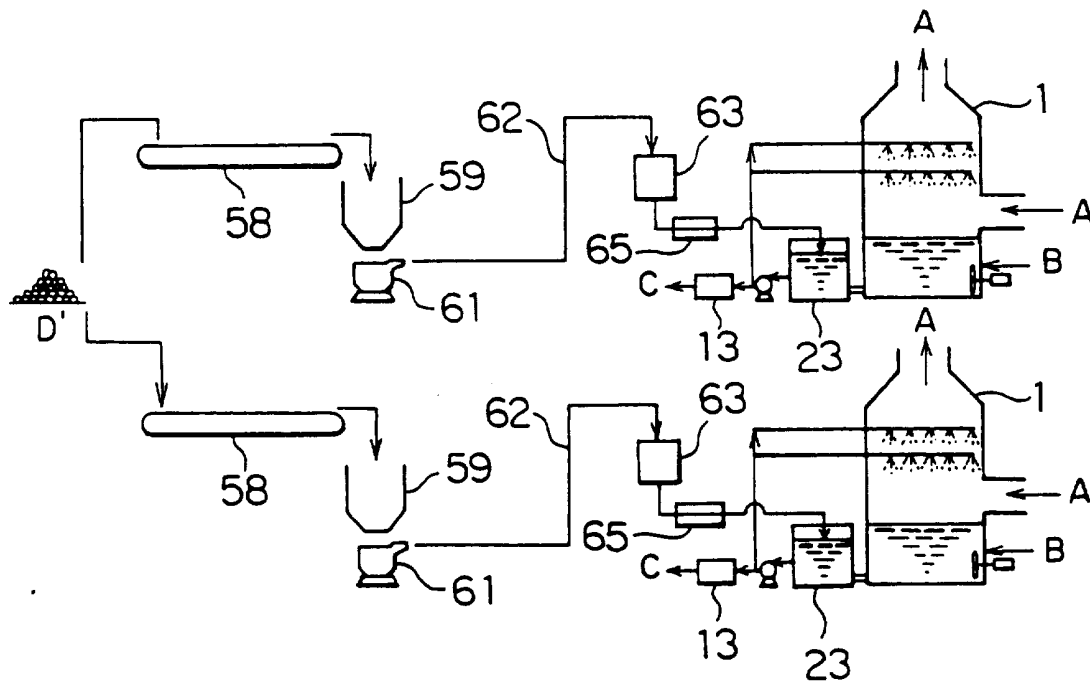


FIG. 38

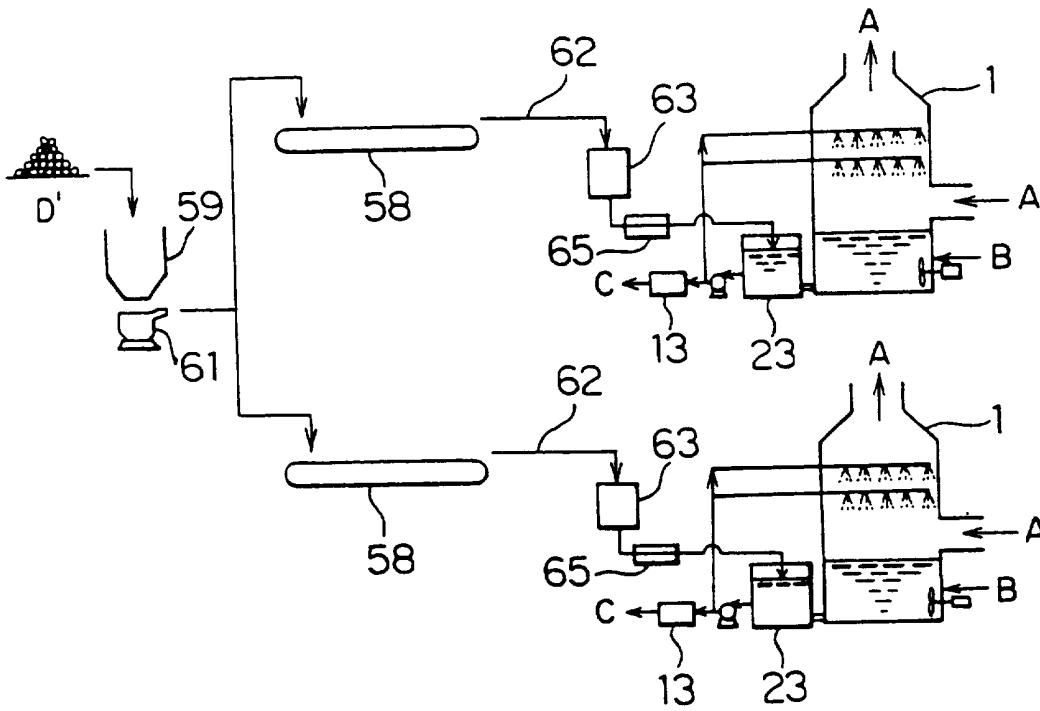
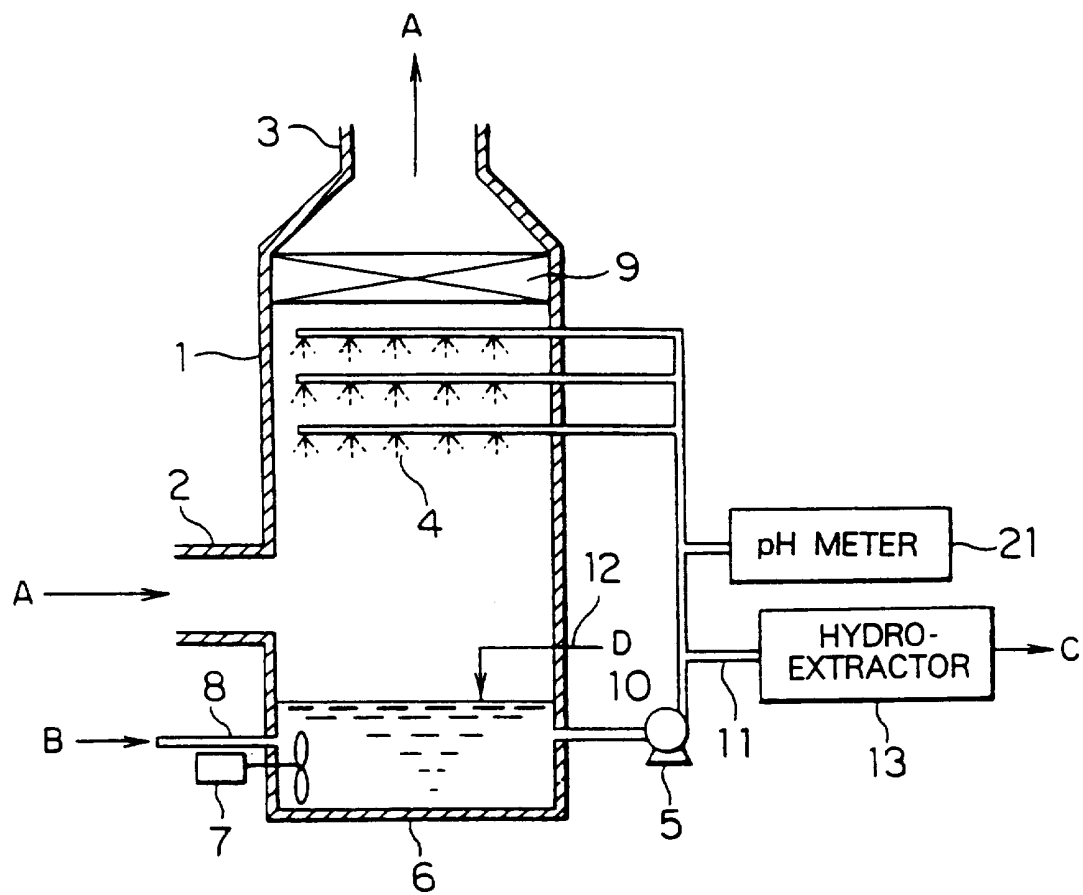


FIG. 39



SPECIFICATION

WET-TYPE FLUE GAS DESULFURIZATION PLANT AND METHOD

5 MAKING USE OF A SOLID DESULFURIZING AGENT

INDUSTRIAL FIELD

This invention relates to a wet-type flue gas desulfurization plant
10 and method making use of a solid desulfurizing agent, and more
particularly, to a wet-type flue gas desulfurization plant and method
making use of a solid desulfurizing agent for economically removing
sulfur oxides in flue gas exhausted from combustion equipment such as
boilers with higher desulfurization performance, decreased power for
15 grinding solid desulfurizing agents such as limestone and a lower
decrease in desulfurization performance due to aluminum and fluorine
components in an absorbent.

PRIOR ART

20

Sulfur oxides (hereinafter simply referred to as SO_2) in flue gas
generated as a result of combustion of fossil fuel in thermal power plants,
etc. is one of main origins to cause global environmental problems such
as air pollution, acid rain and the like. Thus, studies on flue gas
25 desulfurization methods to remove SO_2 therefrom and development of flue
gas desulfurization plants have been an important question.

Various processes have been proposed as such flue gas desulfurization methods although a wet-type is a major process. The wet-type process includes a sodium-, a calcium- and a magnesium methods using sodium-, calcium and magnesium compounds as an absorbent, respectively. The sodium method above all is excellent in reactivity between the absorbent and SO_2 , but the sodium compounds used are very expensive. This is because the calcium method using relatively cheaper calcium compounds such as calcium carbonate is most widely employed in a flue gas desulfurization system of large boilers in power plants.

The desulfurization method using such calcium compounds as absorbent liquid is generally classified into a spraying-, a wetted wall- and a bubbling systems depending on the difference in a gas-liquid contacting method. While each system has outstanding characteristic features independently, the spraying system is considerably popular and reliable, and is thus the most widely used in the world. A conventional spraying desulfurization system once comprised three towers, i.e., a cooling tower for cooling and dust-removing exhaust gas, a desulfurization tower for spraying absorbent liquid in the exhausted gas to react with SO_2 and a oxidation tower for oxidizing calcium sulfite formed in the desulfurization tower. Recently, a mono-tower desulfurization system (an in-tank oxidizing method) in which the desulfurization tower bears cooling and oxidation functions has been developed and is now getting the most popular method as the spraying system.

Fig. 39 shows an example of a conventional spraying mono-tower desulfurization plant. In general, such a mono-tower desulfurization system comprises a tower body 1, an inlet duct 2, an outlet duct 3, a spray nozzle 4, an absorbent pump 5, a circulation tank 6, a stirrer 7, an air blower 8, a mist eliminator 9, an absorbent draining pipe 10, a gypsum

draining pipe 11, a limestone supplying pipe 12, a hydroextractor 13 and the like. Several numbers of spray nozzles 4 are arranged to a horizontal direction and several stages thereof are loaded to a vertical direction. The stirrer 7 and the air blower 8 are connected to the circulation tank 6
5 allocated at an under portion of the desulfurization tower where the absorbing liquid resides, while the mist eliminator 9 is arranged at an uppermost portion of the desulfurization tower or in the outlet duct 3.

Exhaust gas A exhausted from a boiler is introduced to the desulfurization tower body 1 from the inlet duct 2 and exhausted through
10 the outlet duct 3. During such a process, the absorbing liquid is pumped from the absorbing liquid pump 5 through the absorbing liquid draining pipe 10 and is sprayed from a plurality of nozzles 4 to perform a gas-liquid contact of the absorbing liquid and the exhaust gas A. Upon spraying, SO₂ is selectively absorbed by the absorbing liquid from the exhaust gas A to
15 form calcium sulfite. The absorbing liquid containing the thus formed calcium sulfite resides in the circulation tank 6 where, with agitating by means of the stirrer 7, calcium sulfite in the absorbing liquids is oxidized by air B supplied by the air blower 8 to form gypsum C. A desulfurizing agent such as limestone D is added to the absorbing liquid in the
20 circulation tank 6 through the limestone supplying pipe 12. A portion of the absorbing liquid in the circulation tank 6 where limestone D and gypsum C are coexisting is once again pumped by the absorbing liquid pump 5 to the spray nozzle 4 through the absorbing liquid draining pipe 10, while an another portion thereof is pumped to the dehydrator 13
25 through the gypsum draining pipe 11. Smaller droplets of the absorbing liquid sprayed out of and atomized by the spray nozzle 4 are entrained with the exhaust gas A and collected by the mist eliminator 9 allocated on an upper portion of the desulfurization tower.

Problems inherent in the prior art as described above are as in the following.

(1) The absorbing liquid contains not only calcium carbonate (limestone) which absorbs SO_2 but a considerable amount of gypsum
5 which makes no contribution to the absorption. When proportion of the limestone in the absorbing liquid is increased so as to improve the desulfurization performance, then quality of gypsum is decreased to a useless level.

(2) Considerable power energy is consumed to grind the limestone.

10 (3) When components of aluminum and fluorine component coexist in the absorbing liquid, inactive compounds containing aluminum and fluorine are formed on a surface of limestone particles, which decreases the desulfurization performance.

Accordingly, it is an object of the present invention to provide an
15 flue gas desulfurization plant and method in order to solve conventional problems as described above and to economically achieve higher desulfurization performance.

An another object of the present invention is to provide a flue gas desulfurization plant and method capable of increasing desulfurization
20 performance without decreasing quality of solid products made from a solid desulfurizing agent.

A still another object of the present invention is to provide a flue gas desulfurization plant and method with higher desulfurization performance capable of reducing a power cost for grinding a solid
25 desulfurizing agent.

Further object of the present invention is to provide a flue gas desulfurization plant and method with higher desulfurization performance capable of easily separating a solid desulfurizing agent

contained in absorbing liquid and solid products formed from the solid desulfurizing agent.

These and other objects of the present invention will be described in the following.

5

DISCLOSURE OF THE INVENTION

To achieve the above described objects, according to a first aspect and feature of the present invention, there is provided a wet-type flue gas desulfurization method making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid followed by neutralization of the absorbing liquid containing the sulfur oxide thus absorbed, which comprises selectively leaving the solid desulfurizing agent in an absorbing liquid neutralizing zone and selectively draining the absorbing liquid containing water as a main constituent and solid products formed by the sulfur oxide from said neutralizing zone.

Further, there is provided a wet-type flue gas desulfurization method making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid, which comprises oxidizing the absorbing liquid after the exhaust gas is absorbed therein, neutralizing thus oxidized absorbing liquid by a solid desulfurizing agent which is selectively left in a neutralizing zone, selectively draining solid products formed from sulfur oxide and the absorbing liquid containing water as a main

constituent and once again contacting thus drained absorbing liquid containing water as a main constituent with the exhaust gas.

There is also provided a wet-type flue gas desulfurization plant making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid followed by neutralization of the absorbing liquid containing the sulfur oxide thus absorbed, which comprises an absorbing liquid neutralizing zone for selectively leaving the solid desulfurizing agent and selectively draining the absorbing liquid containing water as a main constituent and solid products formed by the sulfur oxide.

Furthermore, there is provided a wet-type flue gas desulfurization plant making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid, which comprises an absorbing zone for contacting the absorbing liquid with the exhaust gas to absorb the sulfur oxide from the exhaust gas to the absorbing liquid, an oxidizing zone for oxidizing the absorbing liquid containing the sulfur oxide thus absorbed, a neutralizing zone for neutralizing said oxidized absorbing liquid by a desulfurizing agent, selectively leaving the solid desulfurizing agent and selectively draining the absorbing liquid containing water as a main constituent and solid product formed from the sulfur oxide and a circulation channel of the absorbing liquid for supplying the absorbing liquid containing water and the solid products formed from the sulfur oxide to the absorbing zone.

A solid desulfurizing agent used in the present invention preferably has a weight-average particle diameter (hereinafter simply referred to as average particle diameter) of more than 0.5 mm. Those having an

average particle diameter less than 0.5 mm would make it uneasy to separate the desulfurizing agent from oxidization reaction products such as gypsum and result in a particle size reduction of the solid desulfurizing agent such as limestone during a conveying process after grinding thereof to a flue gas desulfurization plant. More preferably, the solid desulfurizing agent has an average particle diameter more than 1.0 mm. The solid desulfurizing agent having an average particle diameter more than 10 mm would decrease in a reactivity to neutralize the absorbing liquid which absorbed SO₂ in the exhaust gas and, in addition, wear a solid desulfurizing agent supplying pipe which is connected to a neutralizing zone of the flue gas desulfurization plant, Accordingly, the solid desulfurizing agent used in the present invention desirably has an average particle diameter of 0.5 mm to 10 mm. However, the present solid desulfurizing agent may contain those of 0.5 mm or less, because this desirable average particle diameter is a kind of standard which is not so strictly restricted.

Exhaust gas contains many kinds of fine particle components and, especially in a case of coal fired boilers, a large amount of combustion ashes. Such combustion ashes are substantially removed by means of a dust collector in front of desulfurization plant but partially took into the desulfurization plant and captured by the sprayed absorbing liquid. The combustion ashes contain an aluminum component (Al), a part of which dissolves in the absorbing liquid when SO₂ is absorbed therein to decrease pH thereof. On the other hand, hydrogen fluoride (HF) contained in the exhaust gas is captured by the sprayed absorbing liquid and, in the presence of the Al component described above, reacted with limestone to form aluminum-fluorine containing compounds, for example, typically represented by a chemical formula: $\text{CaAlF}_3(\text{OH})_2 \cdot \text{CaF}_2$. Such

compounds are deposited on a surface of limestone particles to decrease the reactivity of the limestone. The inventors have found that this reaction has no connection with a particle diameter of the limestone particle. It has been also found, however, that the aluminum-fluorine containing
5 compound can be removed by the limestone having an average particle diameter of more than 0.5 mm when each limestone is mutually contacted and abraded in a neutralizing zone of the limestone. Finer limestone particles suspend in the absorbing liquid because of smaller particle diameter thereof and never result in such a phenomenon.

10 It is desirable in the present invention to supply the solid desulfurizing agent in a form of slurry or by an air-conveying method a dried condition to the neutralizing zone.

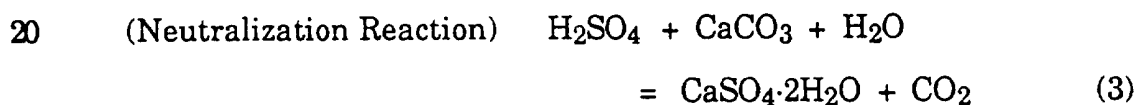
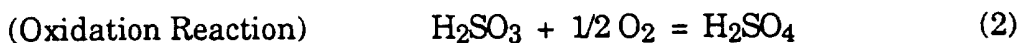
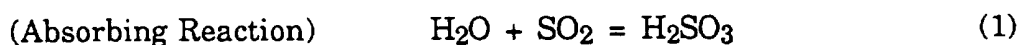
An amount of the solid desulfurizing agent to be supplied to the neutralizing zone is controlled by a fixed quantity feeder or an on-off
15 operation of a grinder for the solid desulfurizing agent, while a particle size of the solid desulfurizing agent is controlled by regulating a speed of the grinder, etc.

The limestone is a typical example of the solid desulfurizing agent used in the present invention. So called limestone used herein means
20 sedimentary rock containing calcium carbonate as a main component and further includes such rock which contains magnesium carbonate as the limestone in the present invention. Accordingly, dolomite which contains CaCO_3 and MgCO_3 as main components is also included in the limestone used herein. While the limestone contains impurities which
25 affects reactivity of desulfurization, it is desirable that CaCO_3 having higher reactivity is exposed on the solid surface by grinding limestone. However, as the solid desulfurizing agent of finer particle size is easily included in the solid products such as gypsum, such finer particles

should be separated and removed previously even though they have higher reactivity. On the other hand, excessively larger particles would damage the solid desulfurizing agent supplying zone and it is desirable that the supplying zone is provided with a filter or a cyclone to classify the solid desulfurizing agent.

Principal reactions occurred in the flue gas desulfurization plant according to the present invention proceed as in the following. The following reaction formulas (1) to (3) are shown as typical reactions for better understanding of the present invention and it is considered that all reactions occurred in the present flue gas desulfurization plant may or may not always conform to the formulas (1) to (3).

The reactions following to these formulas (1) to (3) will be described in an example in which limestone (CaCO_3) is used as a solid absorbing agent. The absorbing liquid (which contains water as a main constituent) absorbs SO_2 in the exhaust gas to form H_2SO_3 which is then oxidized by air to yield H_2SO_4 (dilute sulfuric acid). H_2SO_4 is neutralized by CaCO_3 to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).



Gypsum thus formed is collected and used as an industrial material such as a gypsum board. A considerable inclusion of limestone in gypsum inconveniently deteriorates quality of the product. Thus, in conventional flue gas desulfurization plants, it has been necessary that concentration of limestone in the absorbing liquid at a level where the neutralization reaction occurs is kept under a predetermined value (e.g., about 1/100 of gypsum). It is possible to treat the absorbing liquid

containing gypsum and limestone by means of a classifier such as wet cyclone in order to selectively collect gypsum in the absorbing liquid. However, such a classification is not so effective because difference in a diameter between limestone and gypsum particles used in the
5 conventional flue gas desulfurization plant is small and, in addition, classifying devices are expensive.

According to the present invention, the limestone particles are selectively left in a neutralizing zone where pH value of the absorbing liquid is decreased due to an absorption of sulfur oxide in the flue gas
10 desulfurization plant, and water and gypsum formed by sulfur oxide are selectively drained out of the system. This enables to improve the desulfurization performance while keeping the quality of gypsum. In a practical process of the present invention, limestone used to neutralize the absorbing liquid which absorbs SO_2 in the exhaust gas has a larger
15 weight-average diameter of 0.5 mm, and preferably 1.0 mm or more, thereby easily separating limestone and gypsum (having a normal weight-average diameter of 30 to 100 μm).

Further, according to the present invention, as there is used limestone of a relatively larger particle diameter, finer grinding thereof is
20 not necessary, thereby eliminating fine grinders and saving power for grinding.

It is possible in the present invention to load limestone in the neutralizing zone in an amount sufficient to provide what is spent during a continuous run for about 20 hours under a standard condition. It is
25 thus a feature of the present invention that a precise supply control of limestone in the neutralizing zone is not required even when load of the exhaust gas increases and a pH value of the absorbing liquid absorbed the exhaust gas markedly decreases.

The reaction of formula (3) proceeds on a surface of the limestone particles in the neutralizing zone. A continuous contact of the absorbing liquid containing H_2SO_4 with the limestone particles promotes the reaction (3) and increases the desulfurizing performance. When the
5 absorbing liquid is flowed from top to down of a limestone layer in a limestone loading zone, the limestone layer is tightened to form regions where the absorbing liquid flows slowly and never flow, while the desulfurizing performance decreases. In order to solve such a tightening problem of the limestone layer, for example, the absorbing liquid is flowed
10 at a certain speed of flow or faster than it from the bottom to upward of the limestone layer in the neutralizing zone to fluidize the limestone particles, thereby the desulfurizing performance being increased.

As it is difficult to determine height of the limestone layer and a fluidized condition of limestone at a level of neutralization of the present
15 invention although a fluidized bed of the limestone layer is formed, there is the possibility that the absorbing liquid selectively flows to a portion of lower height in the layer. Further, when an amount of the absorbing liquid circulating in an area contacted with the exhaust gas is unchanged, if the absorbing liquid is flowed mainly to the portion of lower
20 height in the limestone layer (a portion containing lesser amount of limestone), the proportion of limestone to the absorbing liquid is decreased extremely. This results in a decrease not only in a pH value of the absorbing liquid fed to the area contacted with the exhaust gas but in the desulfurizing performance.

25 It is possible to substantially level (or make even) the height of the limestone layer as a whole in the neutralizing zone and thus to prevent the decrease in the desulfurizing performance by employing more than one of the following manners: blowing gas such as air into the limestone

layer in the neutralizing zone, jetting liquid such as water into the limestone layer or stirring limestone by means of a stirring equipment. It is also possible to level (or make even) the height of the limestone layer as a whole in the neutralizing zone by, instead of simply blowing gas into the limestone layer, blowing the gas toward a portion where the absorbing liquid is jetted from the bottom to upward in the neutralizing zone to feed the gas together with the absorbing liquid into the limestone layer. A stirring device for the limestone layer used herein includes a stirrer provided with stirring blades or rakes in the neutralizing zone, an equipment to rotate the neutralizing zone itself and the like.

More preferably, leveling of the height of the limestone layer as a whole in the neutralizing zone is conducted by employing more than one of the following manners: first of all, detecting a fluidizing condition of limestone in plural spots by determining more than one factor selected from a group consisting of pressure loss of the limestone layer in plural fluidizing spots, solid concentration, specific gravity and viscosity of the absorbing liquid (the pressure loss decreases in poorly fluidizing spots), followed by blowing gas such as air or jetting liquid such as water into the limestone layer in spots where the fluidizing condition is poor, or stirring limestone by means of a stirring device.

Presser loss P in a portion of fluidized bed is generally expressed by the following formula:

$$P = (\text{gravity of limestone} - \text{gravity of absorbing liquid}) \\ \times (\text{height of limestone layer}) \times (1 - \text{void})$$

The void in the above formula is a value under a fluidizing condition, however, the product of (height of limestone layer) \times (1 - void) is equivalent under a stationary and a fluidizing conditions, and accordingly, height of the limestone layer under a stationary condition

can be determined by the formula above. That is, while gravity of limestone is known (about 2.7) and the void under a stationary condition is about 0.4 although it depends on a particle shape, the height of the limestone layer is obtainable from determination of pressure loss P and
5 gravity of the absorbing liquid. Further, as gravity of the absorbing liquid correlates with a particle concentration (substantially gypsum particle concentration) or viscosity of the absorbing liquid, such concentration or viscosity may be determined instead of the gravity.

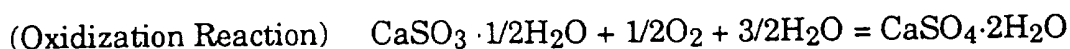
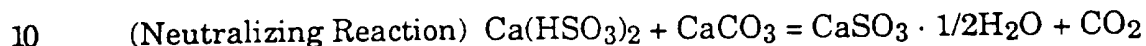
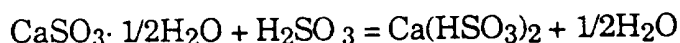
Mixing of the limestone particles in the absorbing liquid is
10 promoted and a contacting effect of these components is increased by employing more than one of the following manners: blowing gas such as air into the limestone layer, jetting liquid such as air into the limestone layer or stirring limestone by means of a stirring equipment.

Further, a part of CO₂ dissolved in the absorbing liquid is expelled to
15 promote the neutralizing reaction and improve the desulfurizing performance by blowing gas except CO₂, such as air, into the limestone layer.

The present invention is also applicable to a flue gas desulfurization plant provided with an external oxidizing tower. This type of flue gas
20 desulfurization plant comprises a cooling tower for cooling and dust removing exhaust gas, a desulfurizing tower for spraying an absorbing liquid to react with SO₂ in the exhaust gas and an oxidizing tower for oxidizing calcium sulfite formed in the desulfurizing tower. Principal reactions occurred in the desulfurization plant provided with an external
25 oxidizing tower according to the present invention are as in the following.

The absorbing liquid (containing water as a main constituent) absorbs SO₂ in the exhaust gas to form sulfurous acid (H₂SO₃), followed by reaction with calcium sulfite (CaSO₃ · 1/2 H₂O) to yield calcium

hyposulfite ($\text{Ca}(\text{HSO}_3)_2$). Then, calcium hyposulfite is reacted with limestone in a neutralizing zone to form calcium sulfite. The product calcium sulfite is recycled to an absorbing zone to react with H_2SO_3 which has been formed by absorbing SO_2 in the exhaust gas. On the other hand, 5 a part of calcium sulfite is fed to the oxidizing tower, where sulfuric acid is subsequently added thereto to adjust a pH value thereof. Finally, sulfurous acid is oxidized to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).



BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of a mono-tower wet-type flue gas 15 desulfurization plant according to Example 1 of the present invention;

Fig. 2 is a sectional view taken on line a - a in Fig. 1;

Fig. 3 is an enlarged view of a limestone supplying pipe in Fig. 1;

Fig. 4 is an enlarged view of a modified neutralizing zone in Fig. 1;

Fig. 5 is a modification taken on line b - b in Fig. 4;

20 Fig. 6 is a graph illustrating the relationship between pH of absorbing liquid and desulfurizing percentage or limestone concentration in gypsum in Example 1 (full line) and Comparative Example 1 (broken line);

Fig. 7 is a graph illustrating the relationship between flow velocity 25 of an upward flow of absorbing liquid in a limestone layer and a desulfurizing percentage in Example 1;

Fig. 8 is a graph illustrating the relationship between concentration of components A1 and F in absorbing liquid and a desulfurizing rate in Example 1 (full line (a)) and Comparative Example (broken line (b));

Fig. 9 is a flow-sheet of a desulfurizing plant of Example 2;

5 Fig. 10 is a graph illustrating a change in a desulfurizing rate with time in Example 2, a full line showing a result obtained when a limestone layer is allowed to stand in a neutralizing device and a broken line showing that obtained when limestone is stirred in the neutralizing device;

10 Fig. 11 is a schematic view of a neutralizing device provided with a stirrer used in Example 2;

Fig. 12 is a schematic view of a rotary wet process kiln used as a neutralizing device in Example 2;

15 Fig. 13 is a schematic view of a desulfurization plant in which a rake is arranged under a circulation tank used as a neutralizing device in Example 2;

Fig. 14 is a schematic view of a desulfurization plant used in Example 3;

20 Fig. 15 is a graph illustrating the relationship between concentration of dissolved oxygen in an absorbing liquid after neutralization and desulfurizing rate in Example 3;

Fig. 16 is a schematic view of a desulfurization plant having a grid tower used in Example 4 according to the present invention;

25 Fig. 17 is a schematic view of a jet bubbling desulfurization plant used in Example 5 according to the present invention in which exhaust gas is jetted into absorbing liquid through a pipe;

Fig. 18 is a schematic view of a horizontal (or crosswise) desulfurization plant used in Example 6 according to the present invention;

Fig. 19 is a schematic view of a desulfurization plant used in Example 7 in which a carboxylic acid or a salt thereof is supplied to absorbing liquid;

Fig. 20 is a graph illustrating the relationship between liquid-gas ratio (L/G) (i.e., ratio in amount of sprayed absorbing liquid to exhaust gas) and a desulfurizing rate when concentration of sodium formate in absorbing liquid is changed in Example 7;

Fig. 21 is a graph illustrating a change in a desulfurizing rate when pH of absorbing liquid at an exit of a neutralizing device is adjusted by an amount of limestone in Example 8;

Fig. 22 is a flow-sheet of a flue gas desulfurization plant provided with a pH meter to a dispersing pipe used in Example 9;

Fig. 23 is a graph illustrating the relationship between an operation time of a desulfurization plant and a desulfurizing rate, a full line (a) and a broken line (b) showing the relationship between the operation time and the desulfurizing rate in Example 9 and Comparative Example 3, respectively;

Fig. 24 is a graph illustrating the relationship between an operation time of a desulfurization plant and a desulfurizing rate, a full line (a) and a broken line (b) showing the relationship between the operation time and the desulfurizing rate in Example 10 and Comparative Example 4, respectively;

Fig. 25 is a schematic view of a desulfurization plant in which air is blown into a limestone layer used in Example 11;

Fig. 26 is an enlarged view of a neutralizing device shown in Fig. 25;

Fig. 27 is a graph illustrating a change in a desulfurizing rate of a desulfurization plant with time, a full line (a) showing the change when an desulfurization plant used in Example 11 is halted to operate for a certain period of time and then restarted, a broken line (b) showing a similar change in a conventional plant (shown in Fig 39) used in Comparative Example 5 and a chain dash (c) showing a similar change in Example 12 when air is continuously blown into an limestone layer through an air blowing hole;

Fig. 28 is a schematic view of a desulfurization plant used in Example 13 in which a neutralizing device is provided besides a main desulfurizing tower body and a limestone layer in the neutralizing device is stirred by a stirrer so as to level layer height;

Fig. 29 is an enlarged bottom portion of a circulation tank used in Example 14 in which cone baffle plates are arranged below downward extending vertical pipes fixed to a dispersing pipe;

Fig. 30 is a graph illustrating the relationship between an angle X of baffle plates to a bottom plane of a circulation tank and a desulfurizing rate in Example 14;

Fig. 31 is a modification of Example 14 in which cone baffle plates are arranged above upward extending vertical pipes fixed to a dispersing pipe;

Fig. 32 is sectional views of an apex portion of vertical pipes in Examples 30 or 31;

Fig. 33 is a schematic view of a desulfurization plant used in Example 15 in which a neutralizing device is provided independently besides a circulation tank, only a part of absorbing liquid in the

circulation tank being circulated to spray nozzles and the rest being circulated to the neutralizing device;

Fig. 34 is a schematic view of a desulfurization plant used in Example 16 in which a by-pass line of absorbing liquid connecting to an under portion of a circulation tank is provided besides a circulation line of the absorbing liquid to spray nozzles;

Fig. 35 is a schematic view of a desulfurization plant provided with an external oxidization tower used in Example 17 according to the present invention;

Fig. 36 is a schematic view of a conventional flue gas desulfurization plant provided with an external oxidizing tower;

Fig. 37 is an example of a starting limestone supplying system according to the present invention;

Fig. 38 is an another example of a starting limestone supplying system according to the present invention; and

Fig. 39 is a schematic view of a conventional mono tower wet-type flue gas desulfurization plant.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will now be described in detail by way of embodiments but is not intended to be limited to the embodiments.

Example 1.

This example is shown in Figs. 1 and Fig. 2, a sectional view taken on line a - a in Fig. 1. Similarly as a conventional desulfurization tower as shown in Fig. 39, the present plant in this Example comprises a tower body 1, an inlet duct 2, an outlet duct 3, a spray nozzle 4, an absorbing

liquid pump 5, a circulation tank 6, a stirrer 7, an air blower 8, a mist eliminator 9 and the like, and is further provided with a liquid collecting pipe 14, an introducing pipe 15, a branch pipe 16 shown in Fig. 2 and a dispersing pipe 17 in the circulation tank 6 for collecting dropped absorbing liquid, generating an upward flow thereof from the bottom portion to the top of a layer 19 of limestone particles loaded in a lower portion of the circulation tank 6 and fluidizing the limestone particles in the absorbing liquid.

Exhaust gas A exhausted from a boiler (not shown) is introduced from the inlet duct 2 to the desulfurization tower body 1 and drained from the outlet duct 3. During this process, the absorbing liquid pumped by the absorbing liquid pump 5 is sprayed in the desulfurization tower through plural spray nozzles 4 to conduct a gas-liquid contact between the absorbing liquid and the exhaust gas A. Thereby, droplets of the absorbing liquid selectively absorb SO_2 from the exhaust gas A to form sulfurous acid. The droplets of absorbing liquid containing sulfurous acid thus formed drop on the liquid collecting plate 14 arranged on the circulation tank 6. The absorbing liquid dropped on the collecting plate 14 is collected and led to the bottom of the circulation tank 6 through the introducing pipe 15. On the way, sulfurous acid in the absorbing liquid is oxidized to sulfuric acid by oxidizing air blown from the air blowing device 8.

A dispersing 17 is connected to the bottom of the introducing pipe 15, which allows the absorbing liquid to go upward in the existing absorbing liquid in the circulation tank 6 homogeneously throughout a plane thereof. In Fig. 2, structure of the dispersing pipe 17 is illustrated. Fig. 2 is a bottom plane view of the circulation tank 6 provided with the dispersing pipe 17 which has structure for allowing the absorbing liquid

to go upward from the bottom of the circulation tank 6 homogeneously throughout a bottom plane thereof.

The dispersing pipe 17 is arranged to uniformly spread all over the bottom plane of the circulation tank 6, while the absorbing liquid led from the introducing pipe 15 enters to the branch pipe 16 and is then led to the dispersing pipe 17. The dispersing pipe 17 has plural dispersing holes 18 through which the absorbing liquid and air are homogeneously and vigorously jetted out all over the bottom plane of the circulation tank 6 to generate an upward flow thereof. Sulfuric acid and limestone are reacted to form gypsum in the limestone layer 19 which is fluidizing in the absorbing liquid in the circulation tank 6. A pH value of the circulating absorbing liquid is always measured by a pH meter 21.

The absorbing liquid thus neutralized in the limestone layer 19 in the circulation tank 6 and followed by recovery of a certain pH value is again fed to the spray nozzles 4 from an outlet 20 allocated at an upper portion of the circulation tank 6 through an absorbing liquid draining pipe 10 to selectively absorb SO₂ in the exhaust gas A. A part of the absorbing liquid is fed to a hydroextractor 13 to collect gypsum C.

Limestone D is supplied in the circulation tank 6 through a limestone supplying pipe 12. Limestone particles are supplied as a slurry or in a dried form from the limestone supplying pipe 12. When the dried limestone is supplied pneumatically to the tower through the limestone supplying pipe 12, the limestone is wetted and adhered as a deposition F on an inner wall surface of the supplying pipe 12 in consequence of vapor of the absorbing liquid as shown in Fig. 3, because a temperature thereof in the circulation tank 6 is about 50 °C. As a large quantity of the wetted limestone adhered on the wall would cause clogging of the limestone supplying pipe 12, it is desirable to provide a wash-water spray nozzle 22

for periodically washing the inner wall of the limestone supplying pipe 12 to remove the limestone deposition F. Such a wash -water spray nozzle 22 for periodically washing the inner wall of the limestone supplying pipe 12 to remove the limestone deposition F is desirably applied in all Examples
5 which will be described bellow although it is not shown in the drawings.

While sulfuric acid and limestone is reacted in the fluidizing limestone layer 19 to form gypsum, only gypsum particles and water are drained out of the circulation tank 6 through the outlet 20 allocated at the upper portion thereof because the gypsum particles are smaller than the
10 limestone particles, and limestone is selectively left in the circulation tank 6.

When the circulation tank 6 has a curb shape, those introducing-, branch- and dispersing pipes 15, 16 and 17 as shown in Figs. 4 and 5, respectively, may be applied. Fig. 4 is a side view of the circulation tank 6
15 and Fig. 5 is a sectional view taken on line b - b in Fig. 4. The branch pipe 16 is connected to a side surface close to the bottom of the introducing pipe 15, while there are arranged plural dispersing pipes 17 extending from the branch pipe 16 throughout the bottom of the circulation tank 6. Jetting speed of the absorbing liquid from the dispersing holes 18 of each branch
20 pipe 17 are designed to keep above a predetermined rate.

A spray header used in the spraying zone for spraying the absorbing liquid may be used as the dispersing pipe 17 having dispersing holes 18 after the nozzles 4 are demounted.

In the desulfurization plant according to Example 1, a
25 desulfurizing test was conducted using limestone having a weight-average diameter of 2 mm. SO₂ concentration of the exhaust gas at the inlet of the desulfurization plant was 1,000 ppm. An amount of air to be blown into the circulation tank 6 was 30 times that of SO₂ in the exhaust

gas based on the molar ratio. The relationship between a pH value after neutralization and a desulfurization percentage as well as limestone concentration in gypsum is shown in by a full line (a) in Fig. 6. Adjustment of the pH value after neutralization was done by an amount of
5 limestone. While the desulfurizing percentage increases with an increase in the pH value of the absorbing liquid, the limestone concentration in gypsum shows little increase with an increase in the pH value after neutralization and is very low as 0.1 % or less. This demonstrates the gypsum drained out of the circulation tank 6 from the
10 outlet 20 allocated at the upper portion thereof has higher quality.

Upward flow velocity of the absorbing liquid was controlled by changing a sectional area of the limestone layer 19 (an amount of limestone being kept constant).

Fig. 7 is a graph illustrating the relationship between upward flow
15 velocity of the absorbing liquid in the limestone layer 19 and the desulfurizing percentage. With an increase in the upward flow velocity of the absorbing liquid, the desulfurizing percentage is improved and remains nearly constant at the upward flow velocity of 6 cm/sec. The upward flow velocity is a value obtained by dividing an amount of liquid
20 flow by a sectional area of the limestone layer 19.

When the SO₂ concentration in the exhaust gas at the inlet duct 2 of the desulfurization tower was changed from 100 to 5,000 ppm, the desulfurizing percentage increases with an increase in the upward flow velocity of the absorbing liquid in the limestone layer 19 under a condition
25 of any concentration above, and remains nearly constant at the upward flow velocity of 6 cm/sec. Preferably, the upward flow velocity of the absorbing liquid is 3 to 15 cm/sec. depending on a particle diameter of limestone. The desulfurizing performance decreases at lower velocity

and the pressure loss increases at higher velocity than the preferred range described above.

When an equimolar AlCl_3 and NaF are added together as a reagent to the absorbing liquid to change concentration of Al and F components in the absorbing liquid under a condition of predetermined height of the limestone layer and particle diameter of limestone, the desulfurizing percentage changes as shown by a full line (a) in Fig. 8. Little decrease in the desulfurizing percentage is observed even when concentration of Al and F components is 5 mmol/L.

Although the absorbing liquid drained from the circulation tank 6 is directly fed to the spray nozzles 4 and the hydroextractor 13 in this Example, limestone in the drained absorbing liquid from the circulation tank 6 may be separated by means of a separator, which is not shown. The resulted absorbing liquid in which limestone is removed is dehydrated to collect gypsum of high quality.

While an operation of the desulfurization plant is stopped upon periodical inspection of various units and devices included therein, limestone in the circulation tank 6 is removed and replaced by new one if necessary, thereby used limestone being easily removed after the limestone layer 19 is fluidized. That is, pumping limestone in a static condition is quite difficult but is easy in a fluidized condition together with the liquid. However, a part of limestone still remains in the neutralizing zone by simply removing thereof in such a condition because the absorbing liquid is easily drained than limestone. Accordingly, in order to remove limestone completely from the neutralizing zone, it is possible that the absorbing liquid and limestone are allowed to stand to sediment limestone and to recycle only the liquid to the neutralizing zone. Limestone thus removed is not wastefully discarded but ground to reduce

a particle diameter to some extent so as to expose considerably reactive components on the particle surface for a reuse thereof.

Comparative Example 1.

5 In the same desulfurization plant as that in Example 1, the desulfurizing performance was tested using limestone having an average particle diameter of 10 μm . Because of a smaller particle diameter of limestone, limestone is suspended in the absorbing liquid in this Comparative Example and does not form any fluidized bed thereof as that
10 observed in Example 1. The relationship between pH of the absorbing liquid after neutralization and the desulfurizing percentage as well as concentration of limestone in gypsum is shown by a broken line (b) in Fig. 6. When a pH value after neutralization is the same, then the desulfurizing percentage is the same as that of Example 1. However, it
15 seems that the concentration of limestone in gypsum is higher than that of Example 1, and with an increase in the pH value, such concentration increases and the quality of gypsum obtained is deteriorated.

Comparative Example 2.

 When an equimolar AlCl_3 and NaF are added together as reagents
20 to the absorbing liquid to change concentration of Al and F components in the absorbing liquid under a condition of predetermined concentration of limestone in the absorbing liquid etc., the desulfurizing percentage changes as shown by a broken line (b) in Fig. 8. The desulfurizing percentage is considerably low as compared with that of Example 1.

25

Example 2.

 A flow-sheet of a desulfurization plant used in Example 2 is shown in Fig. 9. As is different from Example 1 in which the absorbing liquid is

neutralized in the circulation tank 6, a neutralizing unit 23 may also be arranged outside of the absorbing liquid in the circulation tank 6 as used in this Example 2. Similarly as a conventional desulfurization tower as shown in Fig. 39, the present plant in this Example comprises a tower
5 body 1, an inlet duct 2, an outlet duct 3, a spray nozzle 4, an absorbing liquid pump 5, a circulation tank 6, a stirrer 7, an air blower 8, a mist eliminator 9 and the like, and is further provided with the neutralizing unit 23 for increasing a pH value of the absorbing liquid the pH valve of which has been decreased due to absorption of SO₂ in the exhaust gas A.

10 Similarly as Example 1, the absorbing liquid selectively absorbs SO₂ in the exhaust gas A to form sulfurous acid, which is then oxidized in the circulation tank 6 to yield sulfuric acid. The absorbing liquid containing sulfuric acid is fed to the neutralizing unit 23 by means of a pump (not shown) and neutralized therein by limestone to form gypsum. A part of
15 the absorbing liquid after neutralization is fed to a dehydrator 13 and dehydrated to collect gypsum C. On the other hand, the absorbing liquid thus neutralized is recycled to spray nozzles 4 to selectively absorb SO₂. Limestone D is fed to the neutralizing unit 23 through a limestone supplying pipe 12.

20 Similarly as Example 1, when the dried limestone is supplied pneumatically to the tower through the limestone supplying pipe 12, in order to prevent a deposition of wetted limestone in the supplying pipe 12, it is also desirable in this Example to provide a wash-water spray nozzle
22 for periodically washing the inner wall of the limestone supplying pipe
25 12 to remove the limestone deposition.

Using the desulfurization plant of this Example, a desulfurizing test was conducted. The SO₂ concentration in the exhaust gas A at the inlet of the desulfurization tower was 1,000 ppm. Limestone (having an

average particle diameter of 5 mm) was loaded in advance in the neutralizing unit 23 in an equimolar amount of SO₂ in the exhaust gas, i.e., an amount enough to desulfurize for two hours, and further supplied thereto in an amount of 0.97 molar ratio corresponding to SO₂ in the exhaust gas A through the supplying pipe 12. An amount of air blown into the circulation tank 6 was 30 times that in mol ratio of SO₂ in the exhaust gas.

A change in the desulfurizing percentage with time is shown by a full line (a) in Fig. 10 when the limestone layer 19 is allowed to stand in the neutralizing unit 23. Higher desulfurizing performances were observed in the beginning, which decreased with the elapse of time. As a reason for this, it has been found that gypsum particles are scaled on the surface of the limestone particles in the neutralizing unit 23 thereby decreasing the reactivity of limestone. Then, structure of the neutralizing unit 23 was reformed to agitate limestone loaded therein by means of a stirrer 25 as shown in Fig. 11. A change in the desulfurizing percentage with time after such reforming is shown by a curve b in Fig. 10. It was observed that the desulfurizing performance did not decrease but remained a higher level over a long period of time. When the SO₂ concentration in the exhaust gas A at the outlet of the desulfurization tower was changed from 100 to 5,000 ppm., the desulfurizing performance was kept at a higher level over a long period of time under any condition of such concentration by using the stirrer 25.

Any structure in which limestone having an average diameter of 1 mm or so is agitated in the absorbing liquid may be used as the structure of the neutralizing unit 23. In the neutralizing unit 23 shown in Fig. 11, the absorbing liquid containing sulfuric acid is fed from the circulation tank 6 to the neutralizing unit 23 through a pipe line 10 and neutralized by

limestone D with stirring by means of the stirrer 25. Because of a smaller particle diameter of the gypsum compared with that of limestone, only the gypsum particles and water are fed from an upper portion of the neutralizing unit 23 to the spray nozzles 4 and hydroextractor 13, while
5 the limestone D is selectively left in the neutralizing unit 23. As the neutralizing unit 23 is an equipment for reacting limestone and the absorbing liquid, any structure in which a substantial flow of the limestone particles to downstream does not occur may be used.

Further, prevention of scaling of the gypsum particles on the
10 surface of the limestone particles other than making use of the stirrer 25 may be conducted by bubbling gas such as air among the limestone particles to control scaling thereof.

A rotary wet kiln 26 shown in Fig. 12 may also be used as the neutralizing unit 23. In this case, loaded limestone (not shown) is
15 agitated due to rotation of the wet kiln 26. On the other hand, Fig. 13 is a schematic view of a desulfurization plant in which a rake 27 is arranged as the neutralizing unit on the bottom of the circulation tank 6.

When the kiln 26 shown in Fig. 12 is used, it is possible to control a residence time of the absorbing liquid in the kiln 26 by changing rotation
20 velocity of the kiln 26 instead of adjusting that of the stirrer 25, or by recycling a part of the absorbing liquid to the inlet of the kiln 26 through a pipe line 30 by means of a dispenser 29 allocated at the outlet of the kiln 26 instead of adjusting an amount of the absorbing liquid (tank level) in the neutralizing unit 23 shown in Fig. 11.

25 Further, when the rake 27 is arranged on the bottom of the circulation tank 6 as shown in Fig. 13 instead of the neutralizing unit 23 allocated outside of the desulfurization tower, the limestone particles (not shown) are loaded in the circulation tank 6, while the concentration of SO₂

at the outlet of the desulfurization tower may be controlled by stirring velocity of the rake 27. Fig. 13 shows an example in which a limestone-gypsum separator 31 is arranged outside of the desulfurization tower.

5 Example 3.

While the neutralizing unit 23 is arranged outside of the desulfurization tower in Example 2, it is also possible to load limestone D in an under portion of the circulation tank 6 and the absorbing liquid drained therefrom is neutralized through a layer 19 of limestone D to supply to the separator 31 as shown in Fig. 14. Oxidized absorbing liquid is neutralized by the layer 19 of limestone D and fed to the separator 31 to separate gypsum and limestone, thereby the absorbing liquid of a lower limestone content being fed to the hydroextractor 13 to dehydrate and collect gypsum C. On the other hand, the absorbing liquid of a higher limestone content is recycled to the spray nozzles 4 in the tower body 1 to selectively absorb SO₂.

It is preferable to remove scaled gypsum on the surface of limestone even when the desulfurization plant has structure described above.

While changing an amount of air B blown into the circulation tank 6 shown in Fig. 14 in a range of 10 to 100 times that of SO₂ in the exhaust gas A and determining dissolved oxygen concentration in the separator 31 by a dissolved oxygen meter 33, the desulfurizing performance was checked. The relationship between the dissolved oxygen and the desulfurizing percentage is illustrated in Fig. 15, in which the desulfurizing percentage decreases when the dissolved oxygen concentration falls drops less than 1 ppm. As a reason for this, it is presumed that H₂SO₃ is left in the liquid as a result of an incomplete oxidation reaction ($H_2SO_3 + 1/2 O_2 = H_2SO_4$) if an amount of air blown into

the circulation tank 6 is small, thereby retarding an absorbing reaction ($\text{H}_2\text{O} + \text{SO}_2 = \text{H}_2\text{SO}_3$). It is thus preferred to control an amount of oxidizing air to keep the dissolved oxygen concentration in the absorbing liquid more than 1 ppm by determining such concentration.

5 While the dissolved oxygen concentration in the absorbing liquid is determined in the separator 31 in this example, the dissolved oxygen determination in absorbing liquid may also be conducted at other sites such as in the neutralizing unit 23, etc. if the absorbing liquid has been oxidized.

10 If the required quality of gypsum is low or the concentration of limestone particles in the absorbing liquid is low, the separator 31 may be omitted and further it is possible to combine the neutralizing unit 23 and the separator 31 to provide these functions as an equipment. Any equipment in which the gypsum particles and water can be separated,
15 such as a thickener, a centrifugal hydroextractor and the like may be used as the separator 31.

Desulfurization plants having a characteristic feature a flow direction of the exhaust gas or a contacting system of the exhaust gas and
20 the absorbing liquid will be described in the following Examples 4 to 6.

Example 4.

Fig. 16 shows a desulfurization plant provided with a grid tower according to the present invention. The desulfurization plant shown in
25 Fig. 16 is a modification of that of shown in Fig. 1 in which the desulfurizing process is similarly carried out as in the spraying desulfurization tower in Example 1 except that absorption of SO_2 in the exhaust gas is conducted through the grid 34 arranged in the

desulfurization tower and the flow direction of the exhaust gas is different.

The exhaust gas A exhausted from a boiler is introduced in the desulfurization tower body 1 from an inlet duct 2 arranged at the top thereof and exhausted from an outlet duct 3 arranged at a lower position thereof. During this process, the absorbing liquid pumped by means of an absorbing liquid pump 5 is fed dropwise on the top of the grid 34 through plural spray nozzles 4 or openings (not shown) opened on a pipe for the spray nozzle 4, thereby a gas-liquid contact between the absorbing liquid and the exhaust gas A being conducted on the grid 34. Thus, SO₂ in the exhaust gas A is selectively absorbed by the absorbing liquid to form sulfurous acid.

Absorbing droplets containing sulfurous acid thus formed are collected in a circulation tank 6 and sulfuric acid contained in the absorbing liquid is neutralized by limestone through a limestone layer 19 to form gypsum similarly as the process in Example 1.

Example 5.

Fig. 17 shows a desulfurization plant used in this example according to the present invention in which the exhaust gas is blown into the absorbing liquid through a pipe. In Fig. 17, equipments and parts similarly functioning as those shown in Fig. 1 are numbered as the same numerals and a further description thereof is omitted.

The exhaust gas A exhausted from a boiler is introduced in a desulfurization tower body 1 from an inlet duct 2 and exhausted from an outlet duct 3. During this process, the exhausted gas A is blown into the absorbing liquid in a storing tank 37 thereof arranged at the bottom of the desulfurization tower body 1 through an exhaust gas blowing pipe 35

connected to the inlet duct 2, thereby a gas-liquid contact between the absorbing liquid and the exhaust gas A being conducted.

Thus, SO_2 in the exhaust gas is selectively absorbed by the absorbing liquid in the tank 37 to form sulfurous acid. With agitating with a stirrer 5 38, sulfurous acid is oxidized to sulfuric acid by oxidizing air B blown into the absorbing liquid in the tank 37 from a blower 8 and neutralized by a limestone layer 19 loaded in the tank 37 to form gypsum. Limestone D is agitated in the tank 37 by means of the stirrer 38. A part of the absorbing liquid in the tank 37 is fed from an outlet 20 arranged to the tank 37 to a 10 hydroextractor 13 through a gypsum draining pipe 11 by means of a pump 39 to collect gypsum C. Limestone D is supplied in the tank 37 through a limestone supplying pipe 12.

While the absorbing liquid is neutralized in the circulation tank 6 and the tank 37 in Examples 4 and 5, respectively, the neutralizing unit 15 may be arranged outside of the desulfurization tower similarly as in Example 2. For example, in a case of Example 5, a part of the absorbing liquid may be drained from the tank 37 to neutralize in the neutralizing unit and then recycled to the desulfurization tower as shown in Fig. 33.

20 Example 6.

Although upright structure of the desulfurization plant in which the exhaust gas is introduced from a lower or upper portion of the desulfurization tower and exhausted from the upper or lower portion thereof is used in Examples 1 to 5, a horizontal (crosswise) type flue gas 25 desulfurization plant in which a flow path of the exhaust gas is arranged to a not vertical direction as shown in Fig. 18 is also effectively used in the present invention. A desulfurization tower in this example comprises a desulfurization tower body 1, an inlet duct 2 and an outlet duct 3 in which

spray nozzles 4 for the absorbing liquid are arranged to the inlet duct 2 to spray the absorbing liquid to the introduced exhaust gas to absorb SO₂ therein, followed by dropping the absorbing liquid containing SO₂ in a circulation tank 6 arranged at the bottom of the desulfurization tower to
5 subject to oxidation. The outlet duct 3 is provided with a mist eliminator 9 so as not to exhaust flying mist outside of the desulfurization tower.

The exhaust gas A exhausted from a boiler (not shown) is introduced in the desulfurization tower body 1 from the inlet duct 2 and exhausted from the outlet duct 3. During this process, the absorbing
10 liquid pumped by means of an absorbing liquid pump 5 is sprayed in the desulfurization tower through the plural spray nozzles 4, thereby a gas-liquid contact between the absorbing liquid and the exhaust gas A being conducted. Thus, SO₂ in the exhaust gas A is selectively absorbed by the absorbing liquid to form sulfurous acid. Absorbing droplets containing
15 sulfurous acid thus formed is allowed to drop on a collecting plate 14 arranged on the circulation tank 6. The absorbing liquid dropped on the collecting plate 14 is collected and fed to the bottom of the circulation tank 6 through an introducing pipe 15. On the way, sulfurous acid is oxidized by oxidizing air B blown from an air blower 8 to form sulfuric acid.

20 A dispersing pipe 17 is connected to the bottom of the introducing pipe 15, which allows the absorbing liquid to go upward in the existing absorbing liquid in the circulation tank 6 homogeneously throughout a plane thereof. The absorbing liquid led from the introducing pipe 15 enters to the branch pipe 16 and is then led to the dispersing pipe 17. The
25 dispersing pipe 17 has plural dispersing holes (not shown) through which the absorbing liquid and air are homogeneously and vigorously jetted out all over the bottom plane of the circulation tank 6 to generate an upward flow thereof. Sulfuric acid and limestone are reacted to form gypsum in a

limestone layer 19 which is fluidizing in the absorbing liquid in the circulation tank 6. The absorbing liquid neutralized in the limestone layer 19 is pumped to the spray nozzles 4 by means of the absorbing liquid pump 5 through an absorbing liquid draining pipe 10. After neutralization, a part of the absorbing liquid is fed to a hydroextractor 13 to hydrate and collect gypsum C.

A horizontal absorbing tower of the present invention includes those in which a gas path in the tower extends not only to the horizontal direction as shown in Fig. 18 but to a slightly declined or not vertical direction.

Example 7.

The problem accompanied by Example 2 as shown in Fig. 9 is improved by this example.

While the absorbing liquid is neutralized by limestone D in the neutralizing unit 23 in Fig. 9, the neutralizing velocity slows down when gypsum particles are deposited on the surface of limestone particles and accordingly it is preferably that the surface of the limestone particles are renewed by the liquid in the neutralizing unit 23.

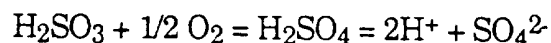
The absorbing liquid containing limestone should be agitated slowly but continuously, for example, in a tank provided with a wet kiln 26 (Fig. 12) or a stirrer 25 (Fig. 11), or by fluidizing limestone in the liquid. Further, according to the process shown in Fig. 9, the absorbing liquid in the neutralizing unit 23 is neutralized by rough limestone D of relatively large particle diameters, while the limestone D content in the absorbing liquid sprayed through the spray nozzles 4 is low. It has been thus a problem in Example 2 that a pH value of the absorbing droplets dropping in the desulfurization tower decreases with an increase in the SO₂ concentration

at the inlet of the desulfurization plant, thereby decreasing the desulfurizing percentage.

According to this example, in a wet-type desulfurization plant in which the absorbing liquid of decreased pH is neutralized by a solid desulfurizing agent such as rough and not finely ground limestone having relatively larger diameters, economical and higher desulfurizing performance is achieved even when the SO₂ concentration increases at the outlet of the desulfurization plant.

A flow of the desulfurization plant according to this example is shown in Fig. 19, in which equipments and parts similarly functioning as those shown in Fig. 9 are numbered as the same numerals. The desulfurization plant of this example is further provided with, other than those shown in Fig. 9, a pipe 41 for supplying a carboxylic acid or a salt thereof E (formic acid being used in this example).

The exhaust gas A exhausted from a boiler is introduced in a desulfurization tower body 1 from an inlet duct 2 and exhausted from an outlet duct 3. During this process, the absorbing liquid pumped by means of an absorbing liquid pump 5 is sprayed in the desulfurization tower through the plural spray nozzles 4, thereby a gas-liquid contact between the absorbing liquid and the exhaust gas A being conducted. Thus, SO₂ in the exhaust gas A is selectively absorbed by the absorbing liquid to form sulfurous acid (H₂O + SO₂ = H₂SO₃). The absorbing droplets containing sulfurous acid thus formed are allowed to drop toward a circulation tank 6. Sulfurous acid is then oxidized in the circulation tank 6 to form sulfuric acid following to a chemical formula:

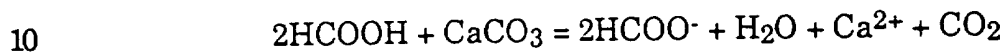


According to the above chemical reaction formula, hydrogen ion (H⁺) concentration in water temporarily increases (i.e., a pH value of the

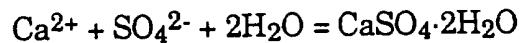
absorbing liquid decreases), but when formic acid E is supplied thereto through the pipe 41, HCOO^- and H^+ are combined together following to a chemical reaction formula below to cause a decrease in the hydrogen ion concentration in water (or an increase in pH):



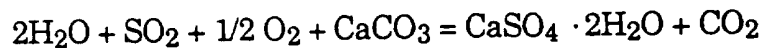
The absorbing liquid containing formic acid thus formed is pumped to a neutralizing unit 23 by means of a pump 42 followed by a reaction HCOOH with limestone D (CaCO_3) to form HCOO^- again in the neutralizing unit 23 following to a chemical reaction formula below:



When the concentration of Ca^{2+} and SO_4^{2-} in water exceeds a saturated solubility thereof, gypsum C is crystallized following to a chemical reaction formula below:



15 The reaction as a whole is expressed by the following formula in which formic acid E is not consumed except when the acid is decomposed or evaporated it self, or dissolved in water in which gypsum is deposited.



20 While gypsum is contained in the absorbing liquid which has been neutralized in the neutralizing unit 23, both can be easily separated because a particle diameter of the limestone particles is about 10 to 50 μm and that of limestone in the neutralizing unit 23 is about 10 mm on the average. In order to prevent run-off of rough limestone particles, for example, it is possible to arrange a wire mesh finer than the limestone
25 particles at an outlet of the neutralizing unit 23 or drain an upper portion of the absorbing liquid in the neutralizing unit 23. The absorbing liquid drained from the neutralizing unit 23, however, contains not only gypsum C but sometimes a slight amount of limestone and, if necessary, is fed to a

separator 31 to separate gypsum C and limestone D. A part of thus separated absorbing liquid having a lower limestone content is then fed to a hydroextractor 13 to hydrate and collect gypsum C, and the other part thereof having a higher limestone content is recycled to the spray nozzles 4 to selectively absorb SO₂. Limestone D is supplied to the neutralizing unit 23 through a limestone supplying pipe 12. The separator 31 may be omitted if the quality of collected gypsum is not important.

According to this process, while the absorbing liquid is neutralized by the limestone particles in the neutralizing unit 23, the neutralizing velocity of limestone D would decrease if the gypsum particles are deposited on the surface of the limestone particles. Accordingly, the surface of the limestone particles in the neutralizing unit 23 is preferably renewed by the liquid. The absorbing liquid containing limestone D should be agitated slowly but continuously, for example, by means of the wet kiln 26 (Fig. 12) or a tank provided with the stirrer 25 (Fig. 11) or by fluidizing limestone D with the liquid or gas.

Using the desulfurization plant of this example shown in Fig. 19, a desulfurizing test was carried out. The SO₂ concentration in the exhaust gas A at the inlet of the desulfurization tower was 1,000 ppm. Limestone (having an average particle diameter of 1 mm) was loaded in advance in the neutralizing unit 23 in an equimolar amount of SO₂ in the exhaust gas, i.e., an amount enough to desulfurize for five hours, and further supplied thereto in an amount of 0.97 molar ratio corresponding to SO₂ in the exhaust gas through the supplying pipe 12. An amount of air B blown into the circulation tank 6 was 30 times in mol ratio of SO₂ in the exhaust gas. Sodium formate was supplied to the absorbing liquid through a pipe 41 for supplying a carboxylic acid or a salt thereof so as to yield predetermined concentration in the liquid.

Fig. 20 shows the relationship between liquid-gas ratio (i.e., ratio in amount of sprayed absorbing liquid to exhaust gas; hereinafter referred to as L/G) and the desulfurizing percentage when the sodium formate concentration in the absorbing liquid is changed. At constant L/G ratio, the desulfurizing percentage increases with an increase in the sodium formate concentration.

Example 8.

A desulfurizing test was carried out under the same condition as Example 7 except that a pH value of the absorbing liquid at the outlet of the neutralizing unit 23 was adjusted by an amount of limestone in the neutralizing unit 23. Fig. 21 shows the relationship between a pH value and the desulfurizing percentage when the L/G ratio and the sodium formate concentration are constant. An effect of sodium formate is little observed at a pH value less than 3.2. As a test result of sodium formate and other carboxylates, it is apparent that higher desulfurizing percentage can be obtained by controlling an amount of limestone and the liquid flow velocity in the neutralizing unit 23 to keep pH of the absorbing liquid at the outlet of the unit 23 at a higher value than an acid dissociation constant pK_a of supplied carboxylates.

Although the neutralizing unit 23 is arranged outside of the desulfurization tower in Example 7, the absorbing liquid dropping in the desulfurization tower may be introduced to the bottom of the circulation tank 6 arranged at a lower portion of an absorbing zone to generate an upward flow from the bottom of a limestone layer as shown in Figs. 1 and 2 (Example 1) so as to fluidize the limestone particles in the absorbing liquid, followed by neutralization thereof. There may arrange a pipe for supplying a carboxylic acid or a salt thereof to the absorbing liquid at an

upper portion of the limestone layer 19 (Fig. 1, etc.) so as to yield predetermined concentration of sodium formate in the absorbing liquid. Further, sodium formate may be supplied to the absorbing liquid in an introducing pipe 15 as shown in Figs. 1 and 2. An upward flow of the
5 absorbing liquid in the limestone layer 19 is thus generated in the circulation tank 6, which is a characteristic feature of this example because the stirrer 25 shown in Fig. 11 and facilities required for instrumentation thereof as well as power related thereto are not necessary.

10 Although upright structure of the desulfurization plant in which the exhaust gas is introduced from a lower or upper portion of the desulfurization tower and exhausted from the upper or lower portion thereof is used in this example, a horizontal (crosswise) type flue gas
15 desulfurization plant in which a flow path of the exhaust gas is arranged to a not vertical direction as shown in Fig. 18 is also effectively used in the present invention. In this case, there may arrange a pipe for supplying a carboxylic acid or a salt thereof to the absorbing liquid at an upper portion of a layer of the limestone particles (corresponding to the limestone layer
20 19 in Fig. 18) so as to yield predetermined concentration of sodium formate in the absorbing liquid.

A solid desulfurizing agent is not required to be ground because coarse limestone, etc. is used herein as such an agent, is easily separated
25 from solid product particles such as gypsum (usually, average particle diameter of 20 to 100 μm) because of coarseness thereof (average particle diameter of 0.5 mm or more), contributes to increase the desulfurizing performance because a large amount thereof can be loaded in the neutralizing unit and yields a solid product of improved quality because of less contamination thereof in the product particles. Further, the

desulfurizing performance is improved by an addition of carboxylates. Carboxylic acids and/or salts thereof used herein include acids such as formic acid, acetic acid, etc. and/or salts thereof.

5 Example 9.

This example is an improvement of the plant of Example 1 shown in Figs. 1 and 2.

According to a desulfurizing flow of the plant shown in Fig. 1, a characteristic feature thereof resides in that no finely grinding facilities
10 for limestone D nor grinding power is required and gypsum C produced has high quality. However, when an operation of the desulfurization plant is stopped and then restarted, it has been a problem that the desulfurizing performance is deteriorated for a certain period of time (several tens minutes to several hours) after the stoppage of operation.

15 A flow in a flue gas desulfurization plant of this example is shown in Fig. 22, in which equipments and parts similarly functioning as those shown in Fig. 1 are numbered as the same numerals and descriptions thereof are omitted. The desulfurization plant of this example is further provided with a pH meter 21 for determining a pH value of the absorbing
20 liquid in a dispersing pipe 17. In this example, the absorbing liquid is allowed to circulate in a desulfurization tower even after a feed of exhaust gas from a boiler is ceased and the operation of the desulfurization plant is stopped when an indication of pH 5.5 is confirmed by means of the pH meter 21 arranged in the dispersing pipe 17.

25 Using limestone having an average particle diameter of 2 mm, a desulfurizing test was carried out in the plant according to this example. The SO₂ concentration in the exhaust gas A at an inlet of the desulfurization tower was 1,000 ppm.

A change in the desulfurizing percentage with time is shown by a full line (a) in Fig. 23, wherein the absorbing liquid was allowed to circulate in the desulfurization tower even after a feed of exhaust gas A from a boiler was ceased, while the operation of the desulfurization plant was stopped when the pH meter 21 arranged in the dispersing pipe 17 indicated a value of pH 5.5 and restarted again after 24 hours passed. It is observed that stable desulfurizing performance is obtained even after the restart of operation.

10 Comparative Example 3.

Using the same plant as Example 9, the desulfurizing performance after the restart of operation was tested. In this comparative example, circulation of the absorbing liquid in the desulfurization tower was stopped immediately after a feeding of the exhaust gas A from the boiler was ceased. A change in the desulfurizing performance with time is shown by a broken line (b) in Fig. 23, wherein the operation was restarted after 24 hours passed. It is observed that a condition of lower desulfurizing percentage continues for one hour or more after the restart of operation.

20

Example 10.

A desulfurizing test was carried out using the same plant and conditions as Example 9 except that the SO₂ concentration in the exhaust gas A at the inlet of the desulfurization tower was 3,000 ppm. The result obtained is shown by a full line (a) in Fig. 24. It is observed that stable desulfurizing performance is obtained even after the restart of operation.

Comparative Example 4

A desulfurizing test was carried out using the same plant and conditions as Comparative Example 3 except that the SO₂ concentration in the exhaust gas A at the inlet of the desulfurization tower was 3,000 ppm. The result obtained is shown by a broken line (b) in Fig. 24. It is observed
5 that a condition of lower desulfurizing percentage continues for two hours or more after the restart of operation.

The desulfurizing performance was further tested under different conditions other than those described above. As a result, it is confirmed that the higher the SO₂ concentration in the exhaust gas A at the inlet of
10 the desulfurization tower is, the longer a recovery of the desulfurizing performance after the restart of operation takes in the conventional technology, while stable desulfurizing performance is obtained even after the restart of operation in Examples 9 and 10.

When the operation of the desulfurization plant used in Example 1
15 (Fig. 1) is stopped, H₂SO₃ and H₂SO₄ left in the absorbing liquid are reacted with limestone as a neutralization reaction, during a stoppage of the operation, following to a reaction formula (3) previously described or a reaction formula below:



20 It is considered that CaSO₃ (calcium sulfite) and gypsum C thus formed are deposited on the surface of limestone D to lower the reactivity thereof, thereby deteriorating the desulfurizing performance upon the restart of operation. It is also anticipated that calcium sulfite and gypsum C are removed from the surface of limestone D by fluidization of limestone in the
25 absorbing liquid or mutual collision thereof presently after the operation is restarted, thereby the desulfurizing performance being recovered. On the other hand, in examples 9 and 10, the absorbing liquid is allowed to circulate even after the exhaust gas from the boiler is ceased and then the

operation of the desulfurization plant is stopped, for example, after a pH value of the absorbing liquid entering to a neutralizing zone (absorbing liquid in the dispersing pipe 17 in Fig. 22) reaches a predetermined level (usually 4.0 to 6.0 or more). Accordingly, stable desulfurizing performance can be obtained without deposition of calcium sulfite and gypsum C on the surface of limestone D or a deterioration in the desulfurizing performance after the restart of operation because H_2SO_3 or H_2SO_4 does not exist in the absorbing liquid during stoppage of the operation.

10 In examples 9 and 10, limestone is selectively left in the neutralizing zone depending on a difference in rate of settle caused by different particle diameters of limestone and gypsum, but both component may also be separated, for example, by means of mesh or by applying a difference in inertia force and the like.

15

Example 11.

The desulfurization plant used in this example is shown in Figs. 25 and 26 (the latter is an enlarged view of a zone for neutralizing the absorbing liquid by limestone). In Figs. 25 and 26, equipments and parts 20 similarly functioning as those described in Example 1 and shown in Fig. 1 are numbered as the same numerals and descriptions thereof are omitted. The desulfurization plant of this example is further provided with a pressure gauge 43 for measuring pressure loss of a fluidizing limestone layer 19, an air blower 45 for blowing gas such as air into the 25 limestone layer 19 and air blowing holes 46.

The absorbing liquid which absorbed SO_2 in the exhaust gas is allowed to drop on a absorbing liquid collecting plate 14 and led to the bottom of a circulation tank 6 through an introducing pipe 15. On the

way, sulfurous acid contained in the absorbing liquid is oxidized to sulfuric acid. The absorbing liquid dispersed from plural dispersing holes 18 arranged on a dispersing pipe 17, which is connected to the bottom of the introducing pipe 15, and air blown from the air blowing holes 46 are jetted together homogeneously and vigorously through all supplying holes to generate an upward flow. Limestone and sulfuric acid are reacted in the fluidizing limestone layer 19 to form gypsum.

The absorbing liquid thus neutralized followed by recovery of a predetermined pH value is recycled from an outlet 20 at an upper portion of the circulation tank 6 to spray nozzles 4 through an absorbing liquid draining pipe 10 to selectively absorb SO₂. A difference in pressure at the bottom and the top in the circulation tank 6 are measured at plural portions by means of the pressure gauge 43. Air is blown into portions where the difference pressure is smaller than a predetermined value through the air blowing holes 46 of the air blower 45 to accelerate fluidization of less fluidizing portion of the limestone layer 19. Water may be blown thereinto instead of air.

When partitions (not shown) are arranged between each dispersing pipe 17 to a vertical direction to the limestone layer 19 to separate each dispersing pipe 17 so as to form a fluidized bed of the limestone layer 19 within each of plurally divided neutralizing zones, such independent formation of fluidized bed in each division makes it easy to fluidize less fluidizing portion of the limestone layer 19.

Further, when a gravimeter 47 for measuring specific gravity of the absorbing liquid is arranged in the introducing pipe 15, height of the limestone layer 19 can be obtained from the following formula by measuring both pressure loss (P) in the fluidizing limestone layer 19 and

specific gravity of the absorbing liquid by means of the gravimeter 47 together with the pressure gauge 43:

$$P = (\text{specific gravity of limestone} - \text{specific gravity of absorbing liquid}) \\ \times (\text{height of limestone layer}) \times (1 - \text{porosity})$$

5 Using limestone having an average particle diameter of 2 mm in the plant of this example, a desulfurizing test was carried out. The SO₂ concentration in the exhaust gas A at an inlet of a desulfurization tower was 1,000 ppm. A difference in depth of liquid was 2 m when a difference in pressure was measured between the bottom and the top of a circulation
10 tank 6. Air was blown from the air blower 45 through the air blowing holes 46 to portions where the difference in pressure due to the fluidization of limestone D was 0.05 kg/cm² or less after the difference in pressure due to the difference in liquid depth of 0.2 kg/m² was subtracted therefrom so as to improve the difference in pressure due to the
15 fluidization of limestone D to an extent of 0.1 kg/cm² or more.

A change in the desulfurizing percent with time is shown by a full line (a) in Fig. 27 when an operation of the desulfurization plant is stopped for a certain period of time and then restarted. While the desulfurizing percentage is low because a fluidizing condition of limestone D is not
20 homogeneous throughout the limestone layer 19 immediate after the restart of operation, the desulfurizing percentage is improved when such fluidization is homogenized throughout the layer by blowing air thereinto (height of the limestone layer is rendered nearly even), and kept stably after that. Further, the air blow results in the fluidization of limestone D
25 after the restart of operation which contributes to increase reactivity thereof. A similar effect is obtainable when water is introduced through the blowing holes 46 instead of the air blow.

Instead of direct blowing of gas such as air into the limestone layer 19, it is also possible to supply gas together with the absorbing liquid into the limestone layer 19 by blowing gas to an introducing pipe 15, a branch pipe 16 or a dispersing pipe 17 so as to render the height of the limestone layer 19 nearly even as a whole.

Comparative Example 5.

Using a conventional plant shown in Fig. 39, the desulfurizing performance after the restart of operation was tested under the same condition as Example 11. A change in the desulfurizing percentage with time is shown by a broken line (b) in Fig. 27. The desulfurizing percent is substantially low and decreases with the elapse of time. As a reason for this, it is assumed that the height of the limestone layer is rendered increasingly uneven throughout the layer with the elapse of time.

15

Example 12.

The desulfurizing performance was tested using the same plant and under the same condition as Example 11 except that air was blown therein continuously over a period of testing through air blowing holes 46 arranged evenly all over the bottom of the circulation tank 6. An amount of blown air was 1 vol. % of the exhaust gas. A change in the desulfurizing percentage with time is shown by a chain line (c) in Fig. 27. The desulfurizing percentage under a normal condition is 94 % which is higher than that achieved by Example 11. It is considered that CO₂ in the absorbing liquids is expelled by air to promote the neutralization reaction of $(\text{H}_2\text{SO}_4 + \text{CaCO}_3 + \text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2)$.

25

Example 13.

In Example 12, the height of the limestone D layer is rendered nearly even as a whole because of structure in which limestone is fluidized in the circulation tank 6 and the air blow thereinto. On the other hand, it is also possible to render the height of the limestone D layer
5 nearly even as a whole by means of a neutralizing unit 31 arranged independently from a tower body 1 and connected to a circulation tank 6 through a connecting pipe 10 while agitating a limestone layer 19 in the neutralizing unit 31 by a stirrer 25 and flowing the absorbing liquid fed from the circulation tank 6 upward from the bottom of the neutralizing
10 unit 31 as shown in Fig. 28.

Example 14.

A flue gas desulfurization plant shown in Fig. 1 was used in this example. However, as shown in Fig. 29 of a partial sectional view of a
15 bottom portion of the circulation tank 6 in which a dispersing pipe 17 is arranged, this plant is further provided with vertical pipes 49 extending downward, connecting to the dispersing pipe 17, which is shown in Figs. 2 and 4, and having a dispersing hole 18 at each end thereof. A cone battle plate 50 is arranged under each vertical pipe 49 to rectify the absorbing
20 liquid jetted out of the dispersing hole 18. Because of a vertical velocity distribution of the absorbing liquid (the velocity increases to the downward direction), the velocity of the absorbing liquid is kept large at a bottom portion in the circulation tank 6 by the existence of the cone battle plate 50 even if the velocity of the absorbing liquid jetting out of the dispersing hole
25 18 is decreased, thereby easily fluidizing the limestone particles.

Using limestone having an average particle diameter of 2 mm in the plant according to this example, a desulfurizing test was carried out. The SO₂ concentration in the exhaust gas A at an inlet of an

desulfurization tower was 1,000 ppm. The relationship between an angle X of the cone battle plate 50 to a bottom plane of the circulation tank 6 and the desulfurizing percentage is shown in Fig. 30. The angle X is preferably fallen in a range of 30 to 70° according to the desulfurizing percentage in the graph.

It is also possible to arrange vertical pipes 49 extending upward on the dispersing pipe 17 as shown in Fig. 31 in which each vertical pipe 49 is provided with a dispersing hole 18 on the top thereof and a cone battle plate 51 above thereof, which is arranged upside down with respect to those shown in Fig. 29, to prevent flow back of the limestone particles to the dispersing pipe 17 and homogeneously flow the absorbing liquid jetting out of the dispersing holes 18 to a neutralizing zone. Further, the vertical pipe 49 may be provided with an apex of various shapes as shown in Fig. 32.

15

Example 15.

In a desulfurization plant used in this example, a neutralizing unit 23 is arranged independently from a circulation tank 6 in which only a part of the absorbing liquid therein is circulated to spray nozzles 4 and the other part thereof is circulated to the neutralizing unit 23 as shown in Fig. 33. In this case, it is possible to independently maintain and control each of absorbing liquid circulation systems to the neutralizing unit 23 and to the spray nozzles 4. Accordingly, if one of these circulation systems is broken down, the other working system can be used to continue operation for a while. As has been described in Examples 9 and 10, pH control of the absorbing liquid in the neutralizing zone is easy when the operation of the flue gas desulfurization plant is stopped. That is, when only the neutralizing unit 23 is continuously operated for a while after the

operation of the flue gas desulfurization plant is stopped, the neutralizing unit 23 can be easily stopped after a pH meter 21 indicates pH 5.5 in the absorbing liquid at an outlet of the neutralizing unit 23. When the flue gas desulfurization plant is started to operate, it is also possible to operate the absorbing circulation system to the spray nozzles 4 after a pH value of the absorbing liquid in the neutralizing unit 23 is sufficiently increased.

Further, when a pipe in which the absorbing liquid is circulated through a wet cyclone (not shown) is connected to the neutralizing unit 23 from an absorbing liquid flow path allocated just upstream side of a dehydrator 13, limestone D of larger particle diameter can be collected in the neutralizing unit 23 without flowing out thereof to the hydroextractor 13.

Example 16.

A desulfurizing process flow of this example is shown in Fig. 34. In this example, there is arranged a by-pass line 54, other than a circulation line 10 to spray nozzles 4 for the absorbing liquid, for connecting the bottom of a circulation tank 6 and a circulation line 53. The by-pass line 54 is used to fluidize a limestone layer 19 when a desulfurization plant is started to operate, thereby the absorbing liquid being pumped from a pump 55 to the circulation tank 6 directly without passing through the spray nozzles 4. Since the limestone layer 19 is hydrostatically pressed until the operation of the desulfurization plant is stopped, higher pressure is required to fluidize the layer 19 when the plant is restarted. Pressure loss required to pump the absorbing liquid to the spray nozzles 4 is canceled off by arranging the by-pass line 54, thereby easily fluidizing limestone D upon the restart. Once limestone D is fluidized, a circulation line of the absorbing liquid is changed from the by-pass line 54 to the

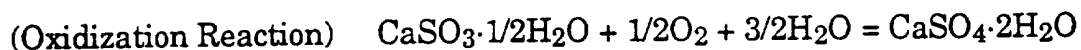
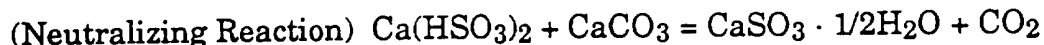
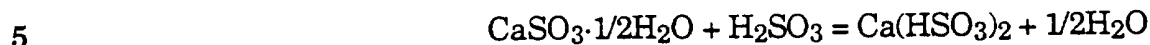
circulation line 53 and operation may be continued, for example, following to the process described in Example 1. According to this example, limestone D in the absorbing liquid is separated by means of a separator 31 followed by dehydration of the absorbing liquid from which limestone D is thus separated off by means of a hydroextractor 13 to collect gypsum C.

Example 17.

The present invention is applicable to a flue gas desulfurization plant provided with an external oxidization tower as shown in Fig. 35. The present desulfurization plant comprises three towers, i.e., a cooling tower for conducting cooling and dust-removing of the exhaust gas (not shown), a desulfurization tower body 1 for spraying the absorbing liquid to react with SO₂ in the exhaust gas and an oxidation tower 57 for oxidizing calcium sulfite formed in the desulfurization tower body 1. Substantial reactions occurred in the flue gas desulfurization plant provided with the external oxidization tower shown in Fig. 35 are as in the following. A flow-sheet of a conventional flue gas desulfurization plant provided with an external oxidization tower is shown in Fig. 36.

SO₂ in the exhaust gas A is absorbed by the absorbing liquid (main constituent: water) in the desulfurization tower body 1 to form H₂SO₃ which is then reacted with calcium sulfite (CaSO₃ · 1/2H₂O) contained in the absorbing liquid to form calcium hyposulfite (Ca(HSO₃)₂). Calcium hyposulfite is reacted with limestone in a neutralizing zone during a step passing through a limestone layer 19 to form calcium sulfite. Calcium sulfite thus formed is recycled to spray nozzles 4 and reacted with H₂SO₃ which has been formed by absorption of SO₂ in the exhaust gas A. On the other hand, a part of calcium sulfite is fed to a tank 56, where a pH value thereof is adjusted by adding sulfuric acid G with agitation by means of a

stirrer 58, and then fed to the oxidization tower 57. Air is supplied to the oxidation tower 57, thereby sulfurous acid is oxidized to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) following to chemical reaction formulas:



A large amount of limestone may be loaded as the limestone layer 19 in the neutralizing zone and generally, limestone D is loaded in an amount sufficient to cover about 20 hour-continuous operation. Such an amount limestone is applicable to every example described above. Accordingly, if limestone D is loaded in the neutralizing zone all at once during night when the operation of the desulfurization plant is stopped, it is not necessary to supply limestone D in the daytime or to maintain a grinder for limestone, etc. in the nighttime. In particular, as limestone is loaded when the operation of the desulfurization plant is stopped, it is not necessary to take measures for preventing deposition of wetted limestone D in a limestone supplying pipe 12 of the desulfurization tower body 1 simultaneously when limestone D is loaded.

20 In order to supply limestone D of a predetermined particle diameter to the flue gas desulfurization plant, original rocks thereof as a raw material is ground by means of a grinder such as jaw-, hammer-, roller-crushers and the like and conveyed to the plant. However, such original limestone D' are generally available at a site far from, for example, several kilometers away from the plant. Accordingly, there is employed a raw material conveying system in this example in which a grinder 61 is placed either in the vicinity of the site of original limestone D' or the desulfurization tower body 1 itself to connect between original limestone

D' and the tower body 1 by means of a belt conveyor as shown in Figs. 37 and 38.

A raw material supplying system in which original limestone D' is supplied to a hopper 59 and then a grinder 61 placed near to the flue gas desulfurization plant by means of a belt conveyor 58 and, after grinding, fed from a limestone delivery pipe 62 to a neutralizing unit 23 through a hopper 63 and a fixed quantity feeder 65 is shown in Fig. 37. An another raw material supplying system in which original limestone D' is supplied to a hopper 59 and then a grinder 61 placed near the site of original limestone D' by means of a belt conveyor 58 and, after grinding, fed to a neutralizing unit 23 through a hopper 63 and a fixed quantity feeder 65 placed near to the desulfurization tower body 1 is shown in Fig. 38. In either delivery systems, it is not necessary to provide grinders 61 corresponding to a total number of the desulfurization tower bodies 1 each to each, but is possible to allow one grinder 61 to serve a plurality of desulfurization tower bodies 1. Particularly in the system shown in Fig. 38, limestone D can be supplied to all desulfurization tower bodies 1 by placing only one grinder 61 near to the site of original limestone D'.

While Figs. 37 and 38 show examples in which the neutralizing unit 23 is arranged independently from the desulfurization tower body 1, it is apparent that the present invention is not restricted by these examples. The exhaust gas A is thus absorbed by the absorbing liquid in the desulfurization tower body 1, the absorbing liquid is then oxidized by air B and finally gypsum C is collected by means of a hydroextractor 13.

An amount of limestone D to be supplied to the neutralizing unit 23 is controlled by the fixed quantity feeder 65 or an on-off operation of the grinder 61, and particle size of limestone is controlled by changing speed of the grinder.

In above examples, limestone is selectively left in the neutralizing zone depending on a difference in rate of settle caused by different particle diameters of limestone D and gypsum C, but both component may also be separated, for example, by means of mesh or by applying a difference in inertia force and the like.

Although most of examples described above provide structure in which the exhaust gas A is introduced from a bottom or lower portion of the desulfurization tower body 1 and exhausted from an upper portion thereof and a desulfurization tower body in which the absorbing liquid is sprayed in the exhaust gas A by spray nozzles, the present invention is effective independently of a flow direction of the exhaust gas A or a contacting manner between the exhaust gas A and the absorbing liquid (such as a wetted-wall absorbing unit, a system for bubbling the exhaust gas into the absorbing liquid through a pipe dipped therein, etc.).

According to the present invention, coexistence of Al and F in the absorbing liquid seldom deteriorates the desulfurizing performance as has been described above.

Further, grinding of a solid desulfurizing agent is not necessary because such an agent as limestone of a coarse particle diameter is used; gypsum particles (20 to 100 μm in general) are easily separated from the solid desulfurizing agent because of a coarse particle diameter thereof (more than 0.5 mm, preferably more than 1 mm): higher desulfurizing performance can be obtained because of an increased amount of the solid desulfurizing agent in a neutralizing zone; and quality of solid products is improved because the solid desulfurizing agent is not mixed with particles of solid products such as gypsum.

WHAT IS CLAIMED IS:

1. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to
5 absorb sulfur oxide from the exhaust gas to the absorbing liquid followed by neutralization of the absorbing liquid containing the sulfur oxide thus absorbed,

which comprises selectively leaving the solid desulfurizing agent in an absorbing liquid neutralizing zone and selectively draining the
10 absorbing liquid containing water as a main constituent and solid products formed by the sulfur oxide from said neutralizing zone.

2. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to
15 absorb sulfur oxide from the exhaust gas to the absorbing liquid,

which comprises oxidizing the absorbing liquid after the exhaust gas is absorbed therein, neutralizing thus oxidized absorbing liquid by a solid desulfurizing agent which is selectively left in a neutralizing zone, selectively draining solid products formed from the sulfur oxide and the
20 absorbing liquid containing water as a main constituent and once again contacting thus drained absorbing liquid containing water as a main constituent with the exhaust gas.

3. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2 in which scaling of reaction
25 products particles around a solid desulfurizing agent is prevented in a neutralizing zone.

4. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 3 in which a flow of absorbing

liquid from a bottom portion to an upper portion of a neutralizing zone is generated, or together with said flow of the absorbing liquid or otherwise a flow of air or gas from the bottom portion to the upward portion of the neutralizing zone is generated to prevent scaling of reaction products particles around a solid desulfurizing agent, and the absorbing liquid is neutralized.

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5. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 3 in which inside of a neutralizing zone is agitated to prevent scaling of reaction products particles around a solid desulfurizing agent.

6. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2 in which a neutralizing zone is plurally divided to prevent scaling of reaction products particles around a solid desulfurizing agent independently in each division.

7. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2 in which a carboxylic acid and/or salt thereof is supplied to an absorbing liquid.

8. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 7 in which at least either amount of a solid desulfurizing agent or flow velocity of absorbing liquid is controlled to raise a pH value of the absorbing liquid before absorbing sulfur oxide in exhaust gas higher than dissociation constant pK_a of a carboxylic acid.

9. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2 in which concentration of dissolved oxygen in absorbing liquid in a neutralizing zone is determined to control an amount of air for oxidizing the absorbing liquid which absorbed sulfur oxide in exhaust gas.

10. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2 in which a solid desulfurizing agent is limestone and a reaction product is gypsum.

11. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2 in which a solid desulfurizing agent has a particle diameter larger than a particle diameter of a solid product produced by a neutralizing reaction.

12. A wet-type flue gas desulfurization method making use of a solid desulfurizing agent claimed in claim 1 or 2, wherein an upright-type exhaust gas flow path in which exhaust gas is introduced from a lower portion and exhausted from an upper portion or the exhaust gas is introduced from the upper portion and exhausted from the lower portion, or a horizontal-type exhaust gas flow path in which exhaust gas does not flow vertically, is arranged.

13. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid followed by neutralization of the absorbing liquid containing the sulfur oxide thus absorbed,

which comprises an absorbing liquid neutralizing zone for selectively leaving the solid desulfurizing agent and selectively draining the absorbing liquid containing water as a main constituent and solid products formed by the sulfur oxide.

14. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid,

which comprises a absorbing zone for contacting the absorbing liquid with the exhaust gas to absorb the sulfur oxide from the exhaust gas to the absorbing liquid,

an oxidizing zone for oxidizing the absorbing liquid containing the sulfur oxide thus absorbed,

a neutralizing zone for neutralizing said oxidized absorbing liquid by a desulfurizing agent, selectively leaving the solid desulfurizing agent and selectively draining the absorbing liquid containing water as a main constituent and solid product formed from the sulfur oxide, and

a circulation channel of the absorbing liquid for supplying the absorbing liquid containing water as a main constituent and the solid products formed from the sulfur oxide.

15. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 14 in which an absorbing zone comprises a gas-liquid contacting region between exhaust gas and sprayed absorbing liquid.

16. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 15 in which a grid for gas-liquid contacting between exhaust gas and absorbing liquid is arranged in a liquid contacting region.

17. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14 in which a pipe for introducing exhaust gas into absorbing liquid is arranged in a neutralizing zone by a bubbling system.

18. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14 in which a means is provided to prevent scaling of reaction products particles around a solid desulfurizing agent in a neutralizing zone.

19. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 18 in which a means for preventing scaling of reaction products particles around a solid desulfurizing agent in a neutralizing zone comprises

5 a branched dispersing flow path of absorbing liquid which is branched all over a bottom portion of a layer consisting of a solid desulfurizing agent to generate a jet flow of the absorbing liquid dispersing from said bottom portion to an upward portion, and

10 a branched dispersing flow path of air or water which is branched, together with said branched dispersing flow path of the absorbing liquid or independently, all over the bottom portion of said solid desulfurizing agent layer to generate a jet flow of air or water dispersing.

20. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 19 in which a branched dispersing
15 flow path of absorbing liquid comprises a vertical pipe provided with a dispersing hole at an end thereof for jetting out the absorbing liquid upward or downward, and a baffle plate is arranged in a neutralizing zone at an opposite position to said dispersing hole.

21. A wet-type flue gas desulfurization plant making use of a solid
20 desulfurizing agent claimed in claim 18 in which a means for preventing scaling of reaction products particles around a solid desulfurizing agent in a neutralizing zone comprises an agitating blade or a rake arranged in a neutralizing zone or the neutralizing zone comprises a rotator.

22. A wet-type flue gas desulfurization plant making use of a solid
25 desulfurizing agent claimed in claim 13 or 14 in which a solid desulfurizing agent is loaded in each of plurally divided neutralizing zone.

23. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14 in which a supplying zone for supplying a solid desulfurizing agent to a neutralizing zone is provided, and said supplying zone is provided with a washing unit for preventing the solid desulfurizing agent from depositing on a wall surface thereof.

24. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14 in which a solid desulfurizing agent is limestone and a reaction product is gypsum.

25. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14 in which a solid desulfurizing agent has a weight-average particle diameter of 0.5 mm or more.

26. A wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14, wherein an upright-type exhaust gas flow path in which exhaust gas is introduced from a lower portion and exhausted from an upper portion or the exhaust gas is introduced from the upper portion and exhausted from the lower portion or a horizontal-type exhaust gas flow path in which exhaust gas does not vertically flow is arranged.

27. A method for stopping an operation of a wet-type flue gas desulfurization plant making use of a solid desulfurizing agent in which an operation of the wet-type flue gas desulfurization plant is stopped after a detected pH value of absorbing liquid absorbed sulfur oxide goes up to over a predetermined value when an operation of the wet-type flue gas desulfurization plant claimed in claim 13 or 14 is stopped.

28. A method for stopping an operation of a wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed

in claim 27 in which the wet-type flue gas desulfurization plant is stopped to operate when a detected pH value of the absorbing liquid which absorbed sulfur oxides is more than 4.0.

29. A method for operating a wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 13 or 14 in which a solid desulfurizing agent in a neutralizing zone is agitated to render height of the solid desulfurizing agent nearly even throughout the neutralizing zone when the wet-type flue gas desulfurization plant making use of the solid desulfurizing agent claimed in claim 13 or 14 is started to operate or during operation thereof.

30. A method for operating a wet-type flue gas desulfurization plant making use of a solid desulfurizing agent claimed in claim 29 in which one or more than two values of pressure loss of a solid desulfurizing agent layer in a neutralizing zone, torque of a stirring device, solid concentration in absorbing liquid, specific gravity of absorbing liquid and viscosity of absorbing liquid are determined to detect an agitated condition of solid desulfurizing agent, and when it is observed that height of the solid desulfurizing agent layer is uneven throughout the neutralizing zone, the absorbing liquid, gas or water is blown into the solid desulfurizing agent layer or the solid desulfurizing agent layer is agitated with the stirring device.

ABSTRACT OF THE DISCLOSURE

A wet-type flue gas desulfurization method and plant making use of a solid desulfurizing agent in which exhaust gas exhausted from a combustion equipment such as boilers is brought into contact with absorbing liquid to absorb sulfur oxide from the exhaust gas to the absorbing liquid followed by neutralization of the absorbing liquid containing the sulfur oxide thus absorbed, which comprises selectively leaving the solid desulfurizing agent in an absorbing liquid neutralizing zone and selectively draining the absorbing liquid containing water as a main constituent and solid products formed by the sulfur oxide from said neutralizing zone.

In the neutralizing zone, an upward flow of the absorbing liquid is generated or, together with said upward flow or independently therefrom, an upward flow of air or water to form a fluidized bed of limestone particles, thereby preventing scaling of gypsum particles around limestone and keeping reactivity of limestone.

According to the present invention, coexistence of Al and F in the absorbing liquid seldom deteriorates the desulfurizing performance. Further, it is possible to reduce a power cost required to grind limestone and to achieve higher desulfurizing performance.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/00921

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ B01D53/34

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ B01D53/34

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

Jitsuyo Shinan Koho 1926 - 1995
Kokai Jitsuyo Shinan Koho 1971 - 1995

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Microfilm of the specification and drawings annexed to the written application of Japanese Utility Model Application No. 93314/1991 (Laid-open No. 33828/1993) (Ishikawajima-Harima Heavy Industries Co., Ltd.), May 7, 1993 (07. 05. 93) (Family: none) Claim, Fig. 1	1
X	Lines 3 to 4, paragraph No. 0023, page 8	2
A	Lines 1 to 2, paragraph No. 0008, page 5	5

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

* Special categories of cited documents:

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

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Date of the actual completion of the international search
July 3, 1995 (03. 07. 95)

Date of mailing of the international search report
July 25, 1995 (25. 07. 95)

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