

METHOD FOR TREATING ACIDIC GAS

TECHNICAL FIELD

[0001]

The present invention relates to a method for treating
5 harmful acidic gases such as hydrogen chloride and sulfur
oxides generated in combustion facilities such as municipal
solid waste incinerators, industrial waste incinerators,
electric power generator boilers, carbonizing furnaces and
private factories. In detail, it relates to a method of
10 efficiently controlling the addition amount of an alkali agent
to treat the acidic gas.

BACKGROUND ART

[0002]

Harmful exhaust gases containing hydrogen chloride or
15 sulfur oxides are treated with an alkali agent such as slaked
lime or sodium bicarbonate, and after subsequently suppressing
dust with a dust collector such as a bag filter (BF), are
discharged from a smokestack. On the other hand, the fly ash
collected by the dust collector contains harmful heavy metals
20 such as Pb and Cd, and after stabilization treating these
harmful heavy metals, are disposed by sanitary landfill.

[0003]

Sodium bicarbonate that has been fines processed to 5 to
30 μm , which is the alkali agent treating the acidic gas, has
25 high reactivity compared to slaked lime, and can stably treat

acidic gas along with having little unreacted portion, which can reduce the amount disposed by sanitary landfill and is an effective means for a reduction in the environmental burden. In addition, a method for insolubilization treating with a chelate such as diethyldithiocarbamate is common as a heavy metal treatment method, and although the heavy metal fixing effect is high in the short term, a problem remains in that heavy metals such as lead redissolve due to pH decline from acid rain at the final disposal site and oxidation autolysis of chelate. On the other hand, the heavy metal fixing by a phosphate compound such as phosphoric acid causes a change to hydroxyapatite form, which is an inorganic mineral; therefore, it is a treatment method that excels in long term stability at the final disposal site, and thus has extremely high value from the viewpoint of environmental protection. Furthermore, a method that treats fly ash that has been treated with the pulverized sodium bicarbonate with a heavy metal fixing agent such as phosphoric acid is an effective means having a great effect of environmental burden reduction.

20 [0004]

Incidentally, controlling the addition amount of an alkali agent such as slaked lime or sodium bicarbonate to treat an acidic gas such as hydrogen chloride or sulfur oxides not only can cut acidic gas treatment costs, but effects of reducing the unreacted amount of alkali agent and reducing the amount of fly ash disposed by landfill can be expected.

[0005]

The addition amount of alkali agent to treat an acidic gas such as hydrogen chloride or sulfur oxides is generally feedback controlled by way of a PID control device based on an HCl concentration measured by an ionization electrode-type hydrogen chloride measurement device installed at a later stage of the bag filter. However, the device measuring the acidic gas concentration of the inlet normally is not installed in burning facilities such as an incineration facility, and thus the parameters of PID control are set and the control output is adjusted in a state in which the fluctuating situation of the inlet is unknown. However, a PID control device requires much time to analyze suitable addition control due to there being the five setting items of P, I, D, addition amount (output) lower limit and addition amount (output) upper limit, and deciding the control output value by combining the setting values of each item. For this reason, there are many facilities conducting control in which, generally, when the setting by a PID control device exceeds a control target value (SV), the addition amount drastically increases.

20 [0006]

However, the control output of a normal PID control device can only set a single upper limit, for example, in a case of setting the control target value (SV) of the HCl concentration to 40 ppm, an addition of alkali agent will be made with the single upper limit of the control output at a concentration of at least 40 ppm as the limit, and will cause the alkali agent to be excessively added. In addition, the above-mentioned

feedback control is influenced by the measurement lag of the acidic gas measurement device. The HCl concentration at the bag filter outlet is normally measured by ionic electrometry (for example, HL-36 manufactured by Kyoto Electronics

5 Manufacturing Co., Ltd.), and the sulfur oxide concentration is measured by infrared absorbing analysis (for example, NSA-3080 manufactured by Shimadzu Corp.); however, when including the sampling time of sample exhaust gas and response time of the analyzer, there is a great measurement delay of 5 to 10
10 minutes. The present measurement delay becomes a cause inducing alkali agent addition lag, and along with leading to treatment failure of the acidic gas, inducing excessive addition of alkali agent.

[0007]

15 In order to solve the present problem, various control methods have been investigated. "P+PID control" that further adds P to normal PID control method has been proposed in Patent Document 1. The present proposal considers the handling of unexpected generation of acidic gas, which is difficult by
20 normal PID control. In addition, control schemes that combine feed-forward control to decide the addition amount of alkali agent based on the acidic gas concentration of the input, and feedback control that supplements the addition amount of alkali agent based on the acidic gas concentration after treating with
25 alkali agent has been proposed in Patent Documents 2 and 3. With the present control scheme, an effect of suppressing excessive addition of feedback control is anticipated, and it

is considered that stable treatment of acidic gas and an effect of curbing excessive addition of alkali agent will be obtained.

[0008]

[Patent Document 1] Japanese Unexamined Patent

5 Application, Publication No. 2002-113327

[Patent Document 2] Japanese Unexamined Patent

Application, Publication No. H10-165752

[Patent Document 3] Japanese Unexamined Patent

Application, Publication No. 2006-75758

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DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0009]

However, although the unexpected handling of the inlet is
15 possible to some extent in Patent Document 1, since the upper
limit value as well as the lower limit value of the control
output are single data input, in a facility in which the
fluctuation in the inlet acidic gas concentration dramatic,
hunting occurs depending on the agent; therefore, stable
20 treatment in which there are few peaks in the outlet acidic gas
concentration is difficult. In addition, the measurement delay
of the measurement device is not taken into account, and thus
it is not possible to deal with acidic gas treatment failure
due to the addition lag of the alkali agent from measurement
25 delay. Furthermore, with Patent Documents 2 and 3, facilities
that only measure the outlet acidic gas concentration account
for most combustion facilities such as incineration facilities,

and in order to conduct the present control scheme, it is necessary to newly introduce an expensive acidic gas measurement device to measure the inlet acidic gas concentration.

[0010]

Taking consideration of the above-mentioned state of the art, the present invention has an object of providing an acidic gas treatment method according to a new control scheme for performing stable acidic gas treatment that rarely causes the acidic gas concentration at the outlet to peak and for reducing the excessive addition of alkali agents in a feedback format that does not require the introduction of a new, expensive acidic-gas measurement device.

Summary

In an aspect, there is provided a method for treating acidic gas that adds an alkali agent to a combustion exhaust gas containing acidic gas, and feedback controls an addition amount of the alkali agent based on a measurement signal of an acidic-gas concentration measurement device that measures an acidic gas concentration after collecting dust, the method comprising: a step of calculating a basal addition amount by multiplying a coefficient of less than 1 by an average addition amount according to at least a predetermined time; and a step of calculating, through feedback computation, an addition amount output value of the alkali agent based on the basal addition amount thus calculated, and obtaining a value that is at least the basal addition amount thus calculated and

no greater than an upper limit established in advance, as an addition amount output value of the alkali agent.

Means for Solving the Problems

[0011]

According to a first aspect, in a method for treating acidic gas that adds an alkali agent to a combustion exhaust gas containing acidic gas, and feedback controls an addition amount of the alkali agent based on a measurement signal of an acidic-gas concentration measurement device that measures an acidic gas concentration after collecting dust, the method includes: a step of calculating a basal addition amount by multiplying a coefficient of no more than 1 (for example, 95%, 90%, 80%, 70%, 50%, etc. described later) by an average addition amount according to at least an average time (for example, 5 minutes, 15 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, etc. described later); and a step of calculating,

through feedback computation, an addition amount output value of the alkali agent based on the basal addition amount thus calculated.

[0012]

5 In PID control that is primarily being used currently, the addition output can only be set to simply the upper limit and lower limit. Therefore, when setting the control target value (SV) for the outlet HCl concentration to 40 ppm, for example, due to inappropriate addition (excess addition, insufficient
10 addition) of alkali agent repeatedly adding at the lower limit of the control output in order to decrease the addition of alkali agent at the actual outlet HCl concentration of 40 ppm or less, and setting the addition at the upper limit of the control output in order to increase the addition of alkali
15 agent at a control target value (SV) of 40 ppm or higher, the HCl concentration at the outlet greatly fluctuates, along with causing the excess addition of alkali agent.

[0013]

In contrast, in a case of calculating the basal addition
20 amount arrived at by multiplying a coefficient of no more than 1 by an average addition amount according at least to average time, and calculating the addition amount output value of alkali agent by way of a feedback computation based on the basal addition amount thus calculated as in the first aspect,
25 the inappropriate addition of alkali agent is prevented, and stable treatment with little fluctuation of the outlet HCl concentration to be treated is possible, as well as the

addition amount of alkali agent also being able to decrease as a result of appropriate addition according to the first aspect.
[0014]

The first aspect of the present invention focuses on the
5 past average addition amount as an element relating to the HCl concentration of the inlet that could not be taken into consideration with conventional feedback control, and has a characteristic of applying a basal addition amount arrived at by multiplying a coefficient of no more than 1 by the past
10 average addition amount. The addition amount of alkali agent is thereby calculated according to feedback control such as PID, for example, based on the basal addition amount arrived at by multiplying a coefficient of no more than 1 by a past average addition amount, which has validity as the base of the
15 addition amount, without performing the addition of alkali agent that repeatedly fluctuates greatly between the lower limit and upper limit as conventionally. Therefore, the addition fluctuation of alkali agent becomes small, thereby suppressing hunting caused by addition failure of the alkali
20 agent itself (excess addition, deficient addition), and an addition amount reduction becomes possible by performing appropriate addition, along with stable treatment of acidic gas with little fluctuation becoming possible.

[0015]

25 According to a second aspect, in the method for treating acidic gas as described in the first aspect, the basal addition amount thus calculated is defined as a lower limit value (for

example, LO: addition amount lower limit described later) for the addition amount output value of the alkali agent, in the step of calculating, through feedback computation, the addition amount output value.

5 [0016]

According to the second aspect, since the excess or deficiency in addition amount is adjusted by way of conventional feedback computation with the present basal addition amount as a base, by setting the basal addition amount
10 as the lower limit value of the addition amount output value, the addition of alkali agent is optimized, and the acidic gas can be efficiently treated.

[0017]

In addition, the average time of the average addition
15 amount is not particularly limited; however, applying the average value of a moving average of the addition amount or the like is effective, the average time being at least 5 minutes, and it is preferable to apply on the order of 15 to 24 hours. In addition, it is good for the coefficient defined by the
20 basal addition amount to be no more than 1. In the case of using a coefficient of at least 1, although stable treatment of the acidic gas is possible, it leads to excessive addition due to preventing a reduction in the addition amount accompanying a reduction in the inlet acidic gas concentration. Although it
25 is sufficient if the basal addition amount is no more than 1 times the average addition amount (coefficient no more than 100%), 0.5 to 0.95 (50 to 95%) is particularly preferable, and

0.7 to 0.9 (70 to 90%) is particularly preferable.

[0018]

According to a third aspect, in the method for treating acidic gas as described in the first or second aspect, the step
5 of calculating, through feedback computation, the addition amount output value further includes: a step of setting at least two ranges of slopes of the acidic gas concentration (for example, a range in which a 6-sec average of the slope of nearest HCl concentration is positive, a range of negative,
10 etc. described later); a step of setting a control target value (for example, 180 ppm, 220 ppm, etc. in Example 8 described later) for the acidic gas concentration in every range of the at least two ranges of slopes; and a step of calculating the addition amount output value of the alkali agent based on at
15 least the measurement signal and the control target value in each of the ranges of slope, in which a control target value set in a case of the range of slope of the acidic gas concentration being large (for example, case of 6-sec average of the slope of nearest HCl concentration being positive
20 described later (when acidic gas concentration ascends)) is smaller than a control target value set in a case of the range of slope of the acidic gas range being small (for example, case of 6-sec average of the slope of nearest HCl concentration being negative described later (when acidic gas concentration
25 descends)), in the step of setting a control target value.

[0019]

According to the third aspect, since the control target

value of the acidic gas concentration is made smaller in a case of the range of slope of the acidic gas concentration at the bag filter outlet being large (when acidic gas concentration ascends) than a case of the range of slope being small (when acidic gas concentration descends), it is possible to make the alkali agent addition amount output value larger when the acidic gas concentration ascends than when the acidic gas concentration descends. Therefore, the timing of adding alkali agent when the acidic gas concentration increases can be made fast compared to the current control, whereby treatment failure of the acidic gas due to measurement delay of the acidic gas measurement device can be improved.

In addition, since the alkali agent addition amount when the acidic gas concentration descends can conversely be made smaller than when the acidic gas concentration ascends, the alkali agent addition amount can be made to quickly decline when the acidic gas concentration reduces, and thus excess addition due to measurement delay of the acidic gas measurement device can be reduced.

[0020]

According to a fourth aspect, in the method for treating acidic gas as described in any one of the first to third aspects, the step of calculating, through feedback computation, the addition amount output value further includes a step of setting, between a lower limit value (for example, LO in FIG. 12, FIG. 15, FIG. 41 described later) and an upper limit value (for example, LH (control output upper limit) in FIG. 12, FIG.

15, FIG. 41 described later) for the addition amount output value calculated based on the measurement signal, at least one new upper limit value for the addition amount output value (for example, LM1 (output limit 1), LM2 (output limit 2) in FIG. 12, FIG. 15, FIG. 41 described later) to correspond with the acidic gas concentration (for example, BF outlet HCl concentration in FIG. 12, FIG. 15, FIG. 41 described later).

[0021]

There is only one output upper limit in normal feedback computation, and when the acidic gas concentration becomes at least the control target value, the alkali agent is addable at the upper limit value and excess addition occurs, irrespective of the magnitude of the acidic gas concentration at the inlet.

In contrast, according to the fourth aspect, suitable addition of alkali agent in response to the magnitude of the acidic gas concentration becomes possible by including a limitation of the control output according to the current acidic gas concentration, between the lower limit value and upper limit value for the addition amount output value, and thus a reduction in the addition amount becomes possible.

[0022]

According to a fifth aspect, in the method for treating acidic gas as described in any one of the first to fourth aspects, from 0.5 to 0.95 of the average addition amount when the average time is at least 5 minutes is defined as the basal addition amount in the step of calculating the basal addition amount.

[0023]

As mentioned above, the average time of the average addition amount is not particularly limited; however, applying the average value of a moving average of the addition amount or the like is effective, the average time being at least 5 minutes, and it is preferable to apply on the order of 15 to 24 hours. In addition, it is good for the coefficient defined by the basal addition amount to be no more than 1. In the case of using a coefficient of at least 1, although stable treatment of the acidic gas is possible, it leads to excessive addition due to preventing a reduction in the addition amount accompanying a reduction in the inlet acidic gas concentration. Although it is sufficient if the basal addition amount is no more than 1 times the average addition amount (coefficient no more than 100%), 0.5 to 0.95 (50 to 95%) is particularly preferable, and 0.7 to 0.9 (70 to 90%) is particularly preferable.

Therefore, according to the fifth aspect, it is possible to prevent excess addition of alkali agent, along with performing stable treatment of acidic gas.

20 [0024]

According to a sixth aspect, in the method for treating acidic gas as described in any one of the first to fifth aspects, the step of calculating, through feedback computation, the addition amount output value further includes a step of calculating an addition amount output value of the alkali agent using both outputs among a control output computed from a hydrogen chloride concentration and a control output computed

from a sulfur oxide concentration, in addition to the feedback computation.

[0025]

In an incineration facility of an industrial waste
5 incinerator or a private factory, hydrogen chloride and sulfur
oxides are often produced in high concentrations. On this
occasion, both the hydrogen chloride and sulfur oxides are
treatment targets, and it is possible to stably treat both
acidic gases of hydrogen chloride and sulfur oxides by adding a
10 control output obtained based on the sulfur oxide concentration
and a control output obtained based on the hydrogen chloride
concentration of a hydrogen chloride concentration measurement
device provided at a stage after the bag filter.

Therefore, according to the sixth aspect, it is possible
15 to stably treat both acidic gases of hydrogen chloride and
sulfur oxides.

[0026]

According to a seventh aspect, in the method for treating
acidic gas as described in any one of the first to sixth
20 aspects, the step of calculating, through feedback computation,
the addition amount output value further includes,

a step of calculating an addition amount output value of
the alkali agent based on an average value of hydrogen chloride
concentration and/or sulfur oxide concentration, in addition to
25 the feedback computation.

[0027]

However, there are facilities managing an emission

concentration control of acidic gas by a 1-hour average value of each acidic gas concentration (hydrogen chloride concentration, sulfur oxide concentration). Although generally controlling by providing a control target value (SV), the control target value is a target after all, and thus there are occasionally cases of being a concentration exceeding the target value as a result of control. Since stable treatment of acidic gas is a concept conflicting with an addition amount reduction in particular, the risk of the 1-hour average value exceeding the control value increases the more an addition amount reduction is obtained. In this case, control with a high degree of assurance in which both an addition amount reduction and stable treatment of acidic gas becomes possible by adding a great amount of alkali agent (defining a certain addition amount) when the acidic gas concentration has reached at least the 1-hour average control value or a concentration close thereto.

Therefore, according to the seventh aspect, since the addition amount output value of alkali agent is calculated based on the average value of the hydrogen chloride concentration and/or sulfur oxide concentration, control with a high degree of assurance that can achieve both an addition amount reduction and stable treatment of acidic gas becomes possible.

[0028]

According to an eighth aspect, in the method for treating acidic gas as described in any one of the first to seventh

aspects, the alkali agent is pulverized sodium bicarbonate having an average particle size of 5 to 30 μm .

[0029]

The alkali agent used in the present invention is not particularly limited. Pulverized sodium bicarbonate having an average particle size adjusted to 5 to 30 μm for which reaction with acidic gas is particularly fast has good control responsiveness and can effectively exhibit performance in the control technique of the present invention. In addition, slaked lime is also applicable. In this case, JIS special number slaked lime is applicable; however, using a slaked lime of high specific surface area, which is a specific surface area of at least 30 m^2/g at which the reactivity with acidic gas is high can better exhibit the performance of the present invention.

[0030]

According to a ninth aspect, the method for treating acidic gas as described in the eighth aspect jointly uses one other alkali agent different from the sodium bicarbonate.

[0031]

There are no particular limitations as the alkali agent exhibiting the effects of the present invention. Sodium carbonate, potassium bicarbonate, potassium carbonate, sodium sesquicarbonate, natural soda, sodium hydroxide, potassium hydroxide, magnesium oxide, magnesium hydroxide, etc. can be exemplified as alkali agents other than pulverized sodium bicarbonate. In addition, in the case of the alkali agent

being powder, the particle size is more preferably less than 30 μm , particularly fines of 5 to 20 μm , for which the reactivity with the acidic gas is high. An agent adjusted to a particle size in advance may be employed, or pulverization equipment may
5 be provided on site, and the alkali agent of coarse particle size may be added while pulverizing on site. In addition, each alkali agent can be implemented in a slurry or aqueous solution dissolved in water.

[0032]

10 According to a tenth aspect, in the method for treating acidic gas as described in the ninth aspect, the other alkali agent is at least one alkali agent selected from the group consisting of slaked lime, sodium hydroxide, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium
15 sesquicarbonate, natural soda and crude sodium bicarbonate.

[0033]

Jointly using a low-cost alkali agent differing from the alkali agent realizing the control according to the present invention is also an economically effective means. Although
20 there is no limitation in the alkali agent jointly used, slaked lime, sodium hydroxide, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium sesquicarbonate, natural soda and crude sodium bicarbonate can be exemplified as low-cost alkali agents that are generally used.

25 Effects of the Invention

[0034]

According to the present invention, it is possible to

provide an acidic gas treatment method according to a new control scheme for performing stable acidic gas treatment that rarely causes the acidic gas concentration at the outlet to peak and for reducing the excessive addition of alkali agents in a feedback format that does not require the introduction of a new, expensive acidic-gas measurement device.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035]

FIG. 1 is a block diagram representing the configuration of an acidic gas treatment system 1 that adds pulverized sodium bicarbonate to HCl, which is the exhaust gas of an incineration facility;

FIG. 2 is a basic configuration diagram of a simulation reaction system;

FIG. 3 is a graph showing a relationship between the added equivalents of pulverized sodium bicarbonate and HCl removal rate in the exhaust gas reaction;

FIG. 4 is a graph showing a relationship between the added equivalents of pulverized sodium bicarbonate and HCl removal rate in the reaction on the bag filter;

FIG. 5 is a graph showing the behavior of inlet HCl concentration;

FIG. 6 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and outlet HCl concentration as a result of actual equipment investigation;

FIG. 7 is a graph showing the behaviors of the added

amount of pulverized sodium bicarbonate and outlet HCl concentration as a result of a simulation investigation;

FIG. 8 is a table showing the added amount of alkali agent, etc. in every comparative example and example as a
5 result of the simulation investigation;

FIG. 9 is a graph showing the behavior of inlet HCl concentration;

FIG. 10 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl
10 concentration in Comparative Example 1;

FIG. 11 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 1;

FIG. 12 is a table of control settings of a step control
15 scheme in Comparative Example 2 and Examples 2 and 20;

FIG. 13 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Comparative Example 2;

FIG. 14 is a graph showing the behaviors of the added
20 amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 2;

FIG. 15 is a table of control settings of a step control scheme in Comparative Example 3 and Examples 3, 9, 10, 11, 17,
18, 21 and 22;

25 FIG. 16 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Comparative

Example 3;

FIG. 17 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 3;

5 FIG. 18 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 4;

FIG. 19 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl
10 concentration in Example 5;

FIG. 20 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 6;

FIG. 21 is a graph showing the behaviors of the added
15 amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 7;

FIG. 22 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 8;

20 FIG. 23 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 9;

FIG. 24 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl
25 concentration in Example 10;

FIG. 25 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl

concentration in Example 11;

FIG. 26 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 12;

5 FIG. 27 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 13;

10 FIG. 28 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 14;

FIG. 29 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 15;

15 FIG. 30 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 16;

FIG. 31 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 17;

20 FIG. 32 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 18;

FIG. 33 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Comparative Example 4;

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FIG. 34 is a graph showing the behaviors of the added

amount of pulverized sodium bicarbonate and the outlet HCl concentration in Example 19;

FIG. 35 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Example 20;

FIG. 36 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Example 21;

FIG. 37 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Example 22;

FIG. 38 is a block diagram representing the configuration of an acidic gas treatment system 2 that adds pulverized sodium bicarbonate to HCl, which is the exhaust gas of an incineration facility;

FIG. 39 is a table showing the added amount of alkali agent, etc. in every comparative example and example as a result of an actual equipment investigation;

FIG. 40 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Comparative Example 5;

FIG. 41 is a table of control settings of a step control scheme in Comparative Example 6, and Examples 23 and 24;

FIG. 42 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Comparative

Example 6;

FIG. 43 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Example 23;

5 and

FIG. 44 is a graph showing the behaviors of the added amount of pulverized sodium bicarbonate, the inlet HCl concentration and the outlet HCl concentration in Example 24.

10 EXPLANATION OF REFERENCE NUMERALS

[0119]

1 acidic gas treatment system

11 control device

12 pulverized sodium bicarbonate adding device

15 13 bag filter

14 HCl concentration measurement device

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0036]

20 Although the present invention will be more specifically explained by giving embodiments hereinafter, the present invention is not to be limited thereto.

[0037]

FIG. 1 is a block diagram representing the configuration
25 of an acidic gas treatment system 1 that adds pulverized sodium bicarbonate to HCl, which is the exhaust gas of an incineration facility.

[0038]

The acidic gas treatment system 1 is configured from a control device 11, a pulverized sodium bicarbonate adding device 12, a bag filter 13, and an HCl concentration measurement device 14. The control device 11 calculates an addition amount output value of pulverized sodium bicarbonate by way of feedback control (PID control scheme or step scheme) based on an HCl concentration measurement signal transmitted from the HCl concentration measurement device 14 and a basal addition amount calculated from a past average addition amount. The pulverized sodium bicarbonate adding device 12 adds pulverized sodium bicarbonate to the HCl in the exhaust gas, based on the addition amount output value of pulverized sodium bicarbonate calculated by the control device 11.

It should be noted that the basal addition amount is calculated by multiplying a coefficient of no more than 1 by a past average addition amount according to an average time (for example, moving average time).

[0039]

The bag filter 13 removes dust after the reaction between HCl in the exhaust gas and pulverized sodium bicarbonate. The HCl concentration measurement device 14 measures the HCl concentration (bag filter outlet HCl concentration described later) after the pulverized sodium bicarbonate accumulated on the bag filter 13 (pulverized sodium bicarbonate remaining from reaction with HCl in exhaust gas is accumulated on bag filter 13) and HCl after exhaust gas reaction has reacted, and

transmits an HCl concentration measurement signal to the control device 11.

[0040]

The acidic gas treatment system 1 performs feedback
5 control by repeating such a cycle, whereby the control device 11 performs control to make the control output value of pulverized sodium bicarbonate addition amount an appropriate value.

It should be noted that the HCl concentration measurement
10 device 14 is an ionization electrode-type HCl concentration measurement device, for example.

[0041]

In addition, as shown in FIG. 1, it is preferable to install the HCl concentration measurement device 14 so as to
15 measure the HCl concentration after the pulverized sodium bicarbonate accumulated on the bag filter 13 and HCl after exhaust gas reaction have reacted (bag filter outlet HCl concentration described later). This is because more accurate measurement of HCl concentration is possible since the
20 pulverized sodium bicarbonate remaining from reaction with HCl in the exhaust gas is accumulated on the bag filter 13, and this accumulated pulverized sodium bicarbonate reacts with the HCl after exhaust gas reaction.

[0042]

25 In addition, the control device 11 performs feedback control with the calculated basal addition amount as a lower limit value for the addition amount output value of pulverized

sodium bicarbonate (for example, LO: addition amount lower limit described later).

Therefore, since the excess or deficiency in the addition amount is adjusted by way of conventional feedback computation with the present basal addition amount as a base, the addition of alkali agent is optimized, and the acidic gas can be efficiently treated.

[0043]

In addition, the average time of the average addition amount is not particularly limited; however, applying the average value of a moving average of the addition amount or the like is effective, the average time being at least 5 minutes, and it is preferable to apply on the order of 15 to 24 hours.

In addition, it is good for the coefficient defined by the basal addition amount to be no more than 1. In the case of using a coefficient of at least 1, although stable treatment of the acidic gas is possible, it leads to excessive addition due to preventing a reduction in the addition amount accompanying a reduction in the inlet acidic gas concentration. Although it is sufficient if the basal addition amount is no more than 1 times the average addition amount (coefficient no more than 100%), 0.5 to 0.95 (50 to 95%) is particularly preferable, and 0.7 to 0.9 (70 to 90%) is particularly preferable.

[0044]

Furthermore, the control device 11 provides the two ranges of a range in which the slope of the HCl concentration (time rate of change in concentration) is a positive and a range in

which it is negative. Then, the control target value of the HCl concentration is set in each of these two ranges.

[0045]

Herein, setting of the control target value for the HCl concentration may be set so that a control target value at which the slope of the HCl concentration falls in the positive range is smaller than a control target value for a negative range. By configuring in this way, it is possible to make the pulverized sodium bicarbonate addition amount when the HCl concentration ascends greater than when the HCl concentration descends. In addition, it is possible to conversely make the pulverized sodium bicarbonate addition amount when the HCl concentration descends smaller than when the HCl concentration ascends. Consequently, it is possible to conduct addition output of pulverized sodium bicarbonate ahead of schedule by way of feedback computation, and the influence from measurement delay can be further reduced.

[0046]

Furthermore, the control device 11 may perform feedback control according to a step scheme. Herein, step scheme is a control scheme that sets the control output step-wise according to the HCl concentration. More specifically, in addition to the upper limit value for the control output value being set in PID control scheme, a new upper limit value for the control output value is set in correspondence with the HCl concentration.

[0047]

Herein, there is only one output upper limit in normal PID control, and when the acidic gas concentration becomes at least the control target value, the alkali agent is addable at the upper limit value and excess addition occurs, irrespective of the magnitude of the acidic gas concentration. Therefore, by adopting the step control scheme, suitable addition of pulverized sodium bicarbonate in response to the magnitude of the HCl concentration becomes possible by including a new control output upper limit value according to the current HCl concentration, between the lower limit value and upper limit value for the addition amount output value, and thus suppression of excessive addition in the addition amount is possible.

[0048]

Furthermore, although the new control output upper limit value is set correspondence with the HCl concentration (for example, LM1 (output limit 1) and LM2 (output limit 2") in FIG. 12, FIG. 15 and FIG. 41 described later), the new control output upper limit value is also set to higher as the HCl concentration increases. However, in order for suppression of excessive addition of alkali agent, it is preferable to make a smaller value than the upper limit value of the control output value being set in PID control scheme (for example, LH (control output upper limit) in FIG. 12, FIG. 15 and FIG. 41 described later).

[0049]

The measurement device of the acidic gas used in the

present embodiment can be implemented irrespective of the measurement system. The hydrogen chloride concentration can be measured by an ionization electrode system, single absorption linear absorption spectroscopy by laser, etc., and the sulfur
5 oxides can be measured by infrared absorption spectroscopy, ultraviolet fluorescence method, etc. It should be noted that, since advantageous effects are obtained in the present embodiment by applying a valid basal addition amount that had not been taken into account by conventional feedback control,
10 the effects of the present invention will be obtained irrespective of the measurement delay speed.

[0050]

In an incineration facility of an industrial waste incinerator or a private factory, hydrogen chloride and sulfur
15 oxides are often produced in high concentrations. On this occasion, both the hydrogen chloride and sulfur oxides are treatment targets, and it is possible to stably treat both acidic gases of hydrogen chloride and sulfur oxides by adding a control output obtained in the control scheme based on the
20 sulfur oxide concentration and a control output obtained in the control scheme based on the hydrogen chloride concentration of a hydrogen chloride concentration measurement device provided at a stage after the bag filter.

[0051]

25 Furthermore, there are facilities managing an emission concentration control of acidic gas by a 1-hour average value of each acidic gas concentration (hydrogen chloride and sulfur

oxide concentrations). Although generally controlling by providing a control target value (SV), the control target value is a target after all, and thus there are occasionally cases of being a concentration exceeding the target value as a result of control. Since stable treatment of acidic gas is a concept conflicting with an addition amount reduction in particular, the risk of the 1-hour average value exceeding the control value increases the more an addition amount reduction is obtained. In this case, control with a high degree of assurance in which both an addition amount reduction and stable treatment of acidic gas becomes possible by adding a great amount of alkali agent (defining a certain addition amount) when at least the 1-hour average control value or having reached a concentration close thereto.

[0052]

The alkali agent used in the present embodiment is not particularly limited. Pulverized sodium bicarbonate having an average particle size adjusted to 5 to 30 μm for which reaction with acidic gas is particularly fast has good control responsiveness and can effectively exhibit performance in the present control technique. In addition, for the slaked lime, it is also possibly JIS special number slaked lime; however, using a slaked lime of high specific surface area, which is a specific surface area of at least 30 m^2/g at which the reactivity with acidic gas is high can better exhibit the performance of the present invention. As the other alkali agents, sodium carbonate, potassium bicarbonate, potassium

carbonate, sodium sesquicarbonate, natural soda, sodium hydroxide, potassium hydroxide, magnesium oxide, magnesium hydroxide, etc. can be exemplified.

[0053]

5 In addition, in the case of the alkali agent being powder, the particle size is more preferably less than 30 μm , particularly fines of 5 to 20 μm , for which the reactivity with the acidic gas is high. An agent adjusted to a particle size in advance may be employed, or pulverization equipment may be
10 provided on site, and the alkali agent of coarse particle size may be added while pulverizing on site. In addition, each alkali agent can be implemented in a slurry or aqueous solution dissolved in water.

[0054]

15 Furthermore, jointly using a low-cost alkali agent differing from the alkali agent realizing control according to the present embodiment is also an economically effective means. Although there is no limitation in jointly used alkali agents, slaked lime, sodium hydroxide, magnesium hydroxide, magnesium
20 oxide, sodium carbonate, sodium sesquicarbonate, natural soda and crude sodium bicarbonate can be exemplified as low-cost alkali agents generally being used.

EXAMPLES

25 [0055]

A simulation reaction system will be explained.

[0056]

(Simulation reaction system): complex reaction in exhaust gas and on bag filter

In the simulation reaction system, the reaction between pulverized sodium bicarbonate and hydrogen chloride (HCl) was constituted by the two reactions of a reaction occurring instantly in the exhaust gas, and between unreacted pulverized sodium bicarbonate accumulated on the bag filter and HCl (refer to FIG. 2). In addition, the residence time of the collected substance on the bag filter is normally on the order of 2 hours. Therefore, the present simulation is configured so that the pulverized sodium bicarbonate on the bag filter disappears at a stipulated time (set to about 2 hours).

[0057]

The basic configuration of the simulation reaction system will be explained while referencing FIG. 2.

First, with the injection control of an incineration facility, an agent addition amount (pulverized sodium bicarbonate addition amount (Ag)) is determined by computation of a control scheme such as PID based on an HCl concentration (post treatment) signal of an ionization electrode-type hydrogen chloride measurement device installed at the bag filter outlet (formula (1) below), and pulverized sodium bicarbonate (acidic gas treatment agent) of the determined addition amount is added to the exhaust gas (inlet HCl concentration (Hi)). The pulverized sodium bicarbonate added to the flue reacts with acidic gas such as HCl in the exhaust gas, whereby HCl in the exhaust gas is eliminated.

[0058]

$$Ag = Ag1 + LO \quad (1)$$

Ag: pulverized sodium bicarbonate addition amount (kg/h)

Ag1: addition amount (kg/h) defined from outlet of HCl

5 concentration measurement device (for case of step scheme,
refer to FIGS. 12, 15 and 41)

LO: addition amount lower limit (kg/h)

The LO set in advance is used when normal (case of not
applying basal addition amount according to present invention).

10 In the case of applying the basal addition amount
according to the present invention, an output is calculated
with LO as the basal addition amount arrived at by multiplying
a predetermined coefficient by the moving average addition
amount of a specified time.

15 [0059]

In addition, the HCl removal rate of inlet HCl
concentration by the pulverized sodium bicarbonate was
preliminarily calculated from a relationship between the
exhaust-gas-reaction pulverized sodium bicarbonate addition
20 equivalents (J_g) and the exhaust-gas-reaction HCl removal rate
(α_g) (FIG. 3), and the relationship between the reaction-on-
bag-filter pulverized sodium bicarbonate addition equivalents
(J_s) and the reaction-on-bag-filter HCl removal rate (α_s) (FIG.
4) from applied knowledge of our company's pulverized sodium
25 bicarbonate. In addition, the reaction between HCl and
pulverized sodium bicarbonate was defined as instantaneous.
First, the HCl concentration (H_g) after reaction in the exhaust

gas is derived from the pulverized sodium bicarbonate addition equivalents (Jg) of the exhaust gas reaction and the exhaust-gas-reaction HCl removal rate (αg) (formula (2) below). It should be noted that the pulverized sodium bicarbonate addition equivalents (Jg) of the exhaust gas reaction are calculated according to formula (3) below.

[0060]

$$H_g = H_i \times (1 - \alpha g / 100) \quad (2)$$

H_i : inlet HCl concentration (ppm)

10 H_g : HCl concentration after exhaust gas reaction (ppm)

αg : HCl removal rate in exhaust gas reaction (%)

(Setting from relationship between exhaust-gas-reaction pulverized sodium bicarbonate addition equivalents and HCl removal rate (FIG. 3))

15 [0061]

$$J_g = A_g / (H_i / 0.614 / 1000 / M_1 \times M_2 \times F / 1000) \quad (3)$$

J_g : exhaust-gas-reaction pulverized sodium bicarbonate addition equivalents

A_g : pulverized sodium bicarbonate addition amount (kg/h)

20 H_i : inlet HCl concentration (ppm)

M_1 : HCl molecular weight (set at 36.5)

M_2 : sodium bicarbonate molecular weight (set at 84)

F : exhaust gas amount (Nm³/h) (set at 55,000 Nm³/h)

[0062]

25 In addition, the pulverized sodium bicarbonate remaining from the exhaust gas reaction accumulates at all times on the bag filter. The pulverized sodium bicarbonate accumulated on

the BF reacts with HCl after exhaust gas reaction, whereby the HCl concentration at the bag filter outlet (Ho) is decided. On this occasion, the pulverized sodium bicarbonate amount accumulated on the BF (As) is arrived at by deducting the

5 pulverized sodium bicarbonate amount reacted with HCl on the BF from the sodium bicarbonate having accumulated in the exhaust gas reaction. In addition, the HCl removal rate on the bag filter (α_s) was decided from the pulverized sodium bicarbonate addition equivalents on the bag filter (Js) calculated from the

10 present accumulated pulverized sodium bicarbonate amount on the bag filter (As) and the HCl concentration after exhaust gas reaction (Hg) (formula (5) below), and the HCl concentration at the bag filter outlet (Ho) was determined (formula (4) below).

[0063]

15
$$Ho = Hg \times (1 - \alpha_s / 100) \quad (4)$$

Hg: HCl concentration after exhaust gas reaction (ppm)

Ho: HCl concentration at bag filter outlet (ppm)

α_s : HCl removal rate of reaction on bag filter (%)

(Setting from relationship between pulverized sodium

20 bicarbonate addition amount on bag filter and HCl removal rate (FIG. 4))

[0064]

$$Js = As / (Hg / 0.614 / 1000 / M1 \times M2 \times F / 1000) \quad (5)$$

Js: pulverized sodium bicarbonate addition amount on bag

25 filter

As: pulverized sodium bicarbonate amount on bag filter

(kg/h)

Hg: HCl concentration after exhaust gas reaction (ppm)

M1: HCl molecular weight (set at 36.5)

M2: sodium bicarbonate molecular weight (set at 84)

F: exhaust gas amount (Nm³/h) (set at 55,000 Nm³/h)

5 [0065]

$$As = Z_n / Ts \times 3600 \quad (6)$$

Z_n: pulverized sodium bicarbonate accumulated amount on bag filter (kg)

Ts: unit simulation time (= data sampling time) (sec)

10 (0.5 sec setting)

[0066]

$$Z_n = Z_{n'} \times (1 - 2.3 / T4 \times Ts) \quad (7)$$

Z_{n'}: unreacted pulverized sodium bicarbonate (kg)

T4: accumulated pulverized sodium bicarbonate on bag

15 filter 90% disappearance time constant (sec)

(7,200 sec setting)

Ts: unit simulation time (= data sampling time) (sec)

(0.5 sec setting)

[0067]

20
$$Z_{n'} = (Ag / 3600 \times Ts - Rg) + (Z_{n-1} - Rs) \quad (8)$$

Ag: pulverized sodium bicarbonate addition amount (kg/h)

Ts: unit simulation time (= data sampling time) (sec)

(0.5 sec setting)

Rg: sodium bicarbonate reacted amount in exhaust gas

25 reaction (kg/h)

Z_{n-1}: pulverized sodium bicarbonate accumulated amount (kg) on bag filter before Ts (sec)

Rs: sodium bicarbonate reacted amount in reaction on bag filter (kg/h)

[0068]

$$R_g = (H_i / 0.614 / 1000 / M_1 \times M_2 \times F / 1000) / 3600 \times T_s$$

5 $\times \alpha_g / 100$ (9)

H_i : inlet HCl concentration (ppm)

M_1 : HCl molecular weight (set at 36.5)

M_2 : sodium bicarbonate molecular weight (set at 84)

F : exhaust gas amount (Nm^3/h) (set at 55,000 Nm^3/h)

10 α_g : HCl removal rate in exhaust gas reaction (%)

[0069]

$$R_s = (H_g / 0.614 / 1000 / M_1 \times M_2 \times F / 1000) / 3600 \times T_s$$

$\times \alpha_s / 100$ (10)

H_g : HCl concentration after exhaust gas reaction (ppm)

15 M_1 : HCl molecular weight (set at 36.5)

M_2 : sodium bicarbonate molecular weight (set at 84)

F : exhaust gas amount (Nm^3/h) (set at 55,000 Nm^3/h)

α_s : HCl removal rate of reaction on bag filter (%)

[0070]

20 The HCl concentration at the bag filter outlet after the present reaction is measured by the ionization electrode-type hydrogen chloride measurement device 14. However, with the ionization electrode-type hydrogen chloride measurement device 14, there is a measurement delay time due to the facility (T_1),

25 a measurement delay time due to exhaust gas sampling ($T_{2\alpha}$), and a measurement delay time due to ionization electrode-type measurement ($T_{2\beta}$, response time), and thus feedback

characteristic control lag occurs.

[0071]

Therefore, the delay time (T) of the HCl concentration measurement device 14 in the present simulation is defined as the sum of the delay time due to the facility (T_1) and the measurement delay time of the HCl concentration measurement device 14 (T_2) (formula (11) below). It should be noted that the measurement delay time of the HCl concentration measurement device 14 (T_2) is arrived at by setting the measurement delay time of sampling exhaust gas after HCl treatment from the flue and the measurement delay time of the ionization electrode-type HCl concentration measurement device ($T_{2\beta}$) (response time), and summing these (formula (12) below). For the 90% response time (measurement delay) of an ionization electrode system generally used, diffusion of HCl gas into absorbing liquid has an influence; therefore, $T_{2\beta}$ was defined as (formula (13) below). In the present simulation, for the ionization electrode system having long measurement delay time, it was defined as a total of 600 sec (10 min: $T_1 = 0.5$ min, $T_2 = 9.5$ min) for $T_1 = 30$ sec, $T_{2\alpha} = 390$ sec (sampling delay 210 sec + bromine scrubber passing delay 180 sec), and $T_{2\beta} = 180$ sec, based on the conditions of an actual equipment facility.

[0072]

It should be noted that, for the case of using an HCl concentration measurement device having a short measurement delay time according to an ionization electrode system, the behavior was confirmed by varying the measurement delay time.

[0073]

(HCl concentration measurement device (simulating low speed response, ionization electrode system))

$$T = T1 + T2 \quad (11)$$

5 T: delay time of simulation reaction system of HCl concentration measurement device (sec)

 T1: delay time of facility (sec) (30 sec setting)

 T2: measurement delay time of HCl concentration measurement device (sec)

10 $T2 = T2\alpha + T2\beta \quad (12)$

 T2 α : exhaust gas sampling time of HCl concentration measurement device (sec)

 (390 sec setting)

 T2 β : 90% response time of HCl concentration measurement device (sec) (180 sec setting)

$$T2\beta = 2.3 \times \tau \quad (13)$$

$$Y_n = Y_{n-1} + (X_n - Y_{n-1}) / \tau \times Ts \quad (14)$$

τ : time constant (sec)

 Ts: unit simulation time (= data sampling time) (sec)
20 (0.5 sec setting)

 Xn: current measurement device inlet HCl concentration (ppm)

 Yn current measurement device outlet HCl concentration (ppm)

25 Y_{n-1}: previous (Ts (sec) before) measurement device outlet HCl concentration (ppm)

[0074]

In addition, the addition amount of alkali agent treating the acidic gas is defined based on the addition output obtained from feedback operated based on the concentration measured by the HCl measurement device (above formula (1)). The basal
5 addition amount according to the present invention was calculated with the moving average addition amount x coefficient (no more than 1) as the lower limit of feedback control.

[0075]

10 In addition, using the inlet HCl concentration, which fluctuates as shown in FIG. 5, the reaction efficiencies of the exhaust gas reaction and HCl reaction on BF were set from the addition behavior of PID in actual equipment as well as the HCl generation situation (FIG. 6), and the results of the present
15 simulation reaction system (FIG. 7). The present investigation results are shown in FIG. 6 and FIG. 7. In the present facility, at the HCl removal efficiency from the exhaust gas of 80% and the removal efficient of reaction on the BF of 65%, the behaviors of the actual equipment and simulation agreed (FIG. 6
20 and FIG. 7). Therefore, the following simulations were performed at the present conditions. It should be noted that, in order to clarify the control responsiveness according to the control method, an inlet HCl concentration (H_i) of a time period having large comparative fluctuation was used to conduct
25 the present simulation.

[0076]

Hereinafter, the present invention will be more

specifically explained by giving examples; however, the present invention is not to be limited thereto.

The investigation in the following examples was done by producing a simulation reaction system from actual equipment investigation results, and investigating the control results by each control method. It should be noted that, since there is a condition of long average time for the average addition amount in the basal addition amount (3 hours, 6 hours), the inlet HCl concentration was repeatedly used, and evaluation was done with the results during the 6 to 9 hour elapse.

[0077]

Comparative Example 1

Using the inlet HCl concentration shown in FIG. 9, the control target value (SV) of the outlet HCl concentration in PID control scheme "P (proportional gain) = 100%, I = 0.1 sec, D = 0.1 sec, addition amount output lower limit 200 kg/h, addition amount output upper limit 480 kg/h" based on the HCl concentration measured with an HCl measurement device (9.5- min measurement device measurement delay total time) in the simulation was set to 200 ppm, and was feedback controlled.

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration (average, 1-hour average maximum, instantaneous maximum, 1-hour average minimum, instant minimum) after treatment with pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration during the present control are shown in FIG.

10.

[0078]

The maximum value of the 1-hour average value for the outlet HCl concentration often used as the emission control value of acidic gas was 212 ppm, and the instantaneous maximum was 384 ppm.

[0079]

Example 1

Except for multiplying a coefficient of 80% by the 30-minute moving average addition amount (kg/h) to define the basal addition amount, and applying as the addition amount output lower limit, it was operated at the same setting conditions shown in Comparative Example 1, and feedback controlled.

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIG. 11.

[0080]

According to Example 1, with the maximum value of HCl for the 1-hour average value of 189 ppm and the instantaneous maximum of 309 ppm, the acidic gas treatment performance improved compared to Comparative Example 1, as well as the addition amount being reduced from 330 kg/h to 315 kg/h.

[0081]

Herein, an outline of the step control scheme will be explained. Control was performed according to step control scheme in place of the PID control scheme in Comparative Examples 2, 3 and 6, and Examples 2, 3, 9 to 11, 17, 18 and 20 to 24.

[0082]

Contrary to PID control scheme, the step scheme was defined as a control scheme that stipulates the output in a step-wise manner in response to the HCl concentration of the outlet. When explaining with Comparative Example 2 and Examples 2 and 20 (FIG. 12), while the HCl concentration is between SV control target value (control output initial concentration (at least output lower limit)) and SM1, the control output is outputted in a step-wise manner between LO and LM1. It defines a format that outputs a control output set at LM2 while the HCl concentration is between SM1 and SM2, and outputs LH (control output upper limit) at SM2 or higher. It should be noted that there is no output limit in a normal PID control method, and there is only setting of LO and LH. In addition, correction of the table deciding the HCl concentration and control output used in the control operation according to the HCl slope was performed with SVA1 and SVA2, and when the HCl slope was positive, SVA1 was subtracted from the HCl concentration used in the operation, and when the HCl slope was negative, SVA2 was added to the HCl concentration used in the operation. The control output calculated upon inputting the same HCl concentration is thereby defined in a

format in which the control output value when the value of the HCl slope is large (acidic gas concentration increasing trend) is larger than the control output value when the value of the HCl slope is small.

5 It should be noted that the pulverized sodium bicarbonate addition amount (Ag) is obtained with the above formula (1).

[0083]

Comparative Example 2

10 In the simulation, the control target value (concentration at which control output of alkali agent in present scheme is added at output lower limit or higher defined as SV) in control of the step scheme based on the HCl concentration measured by the HCl measurement device (9.5-min measurement device measurement delay time) was set to 200 ppm, and feedback
15 controlled (refer to FIG. 12).

 The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate
20 addition amount and bag filter outlet HCl concentration during the present control are shown in FIG. 13.

[0084]

 The maximum value for the 1-hour average value of the outlet HCl concentration according to the step scheme was 212
25 ppm, and the instantaneous maximum was 383 ppm.

[0085]

Example 2

Except for multiplying a coefficient of 80% by the 30-min moving average addition amount (kg/h) to define the basal addition amount, and applying as the addition amount output lower limit, it was operated at the same setting conditions of the step scheme shown in Comparative Example 2, and feedback controlled.

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIG. 14.

[0086]

According to Example 2, with the maximum value of the 1-hour average value of the output HCl concentration in the step scheme being 195 ppm and the instantaneous maximum being 320 ppm, the acidic gas treatment performance improved compared to Comparative Example 2, as well as the addition amount also being reduced from 295 kg/h to 289 kg/h.

[0087]

Comparative Example 3

In the step scheme control based on the HCl concentration measured by the HCl measurement device (9.5-min measurement device measurement delay time) in the simulation, it was feedback controlled with the control target value (SV) of 180 ppm (SV - 20 ppm) when the 6-sec average of the slope of the nearest HCl concentration is positive, and the control target

value (SV) of 220 ppm (SV + 20 ppm) when the 6-sec average of the slope of the nearest HCl concentration is negative (refer to FIG. 15).

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIG. 16.

10 [0088]

The maximum value of the 1-hour average value of the outlet HCl concentration according to the present feedback control in which the control target value was changed according to the slope of the HCl concentration (hereinafter referred to as SV change), in addition to the present step scheme, was 216 ppm, and the instantaneous maximum was 381 ppm.

[0089]

Example 3

Except for multiplying a coefficient of 80% by the 30-min moving average addition amount (kg/h) to define the basal addition amount, and applying as the addition amount output lower limit, it was operated at the same setting conditions of the feedback format shown in Comparative Example 3, and feedback controlled.

25 The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In

addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIG. 17.

[0090]

5 According to Example 3, with the maximum value of the 1-hour average value of the output HCl concentration in the feedback scheme being 198 ppm and the instantaneous maximum being 283 ppm, the acidic gas treatment performance improved compared to Comparative Example 3, as well as the addition
10 amount also being reduced from 301 kg/h to 289 kg/h.

[0091]

Examples 4 to 8

Except for multiplying a coefficient of 80% by the moving average addition amounts (kg/h) of varying average time
15 (Example 4: 5 min, Example 5: 15 min, Example 6: 1 hour, Example 7: 3 hours, Example 8: 6 hours) to define the basal addition amount, and applying as the addition amount output lower limit, it was operated at the same setting conditions shown in Comparative Example 1, and feedback controlled.

20 The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during
25 the present control are shown in FIGS. 18 to 22.

[0092]

According Examples 4 to 8, by applying the basal addition

amount arrived at by multiplying a coefficient of 1 or less by the average addition amount as an element of feedback control, and calculating the addition amount of alkali agent, stable treatment of acidic gas becomes possible.

5 [0093]

The results of Examples 4 to 8 are obtained by applying the element of the average addition amount in feedback, and there are no particular limitations in the average time. For 5-min addition amount average time (Example 4), at the same
10 addition amounts, a stable treatment effect on acidic gas is obtained with 186 ppm as the outlet HCl concentration 1-hour average value maximum, and 369 ppm as the instantaneous maximum. Furthermore, with a 1-hour average value maximum for the outlet HCl concentration of 194 ppm, and instantaneous
15 maximum of 308 ppm for the 6-hour addition amount average time (Example 8), a stable treatment effect is obtained, as well as the addition amount being reduced to 311 kg/h. The average time of the addition amount is preferably at least 5 min, and 15 min to 6 hours is particularly preferable.

20 [0094]

Examples 9 to 11

Except for multiplying a coefficient of 80% by the moving average addition amounts (kg/h) of varying average time (Example 9: 15 min, Example 10: 1 hour, Example 11: 3 hours) to
25 define the basal addition amount, and applying as the addition amount output lower limit, it was operated at the same setting conditions shown in Comparative Example 3, and feedback

controlled.

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In

5 addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIGS. 23 to 25.

[0095]

According to Examples 9 to 11 when varying with 15-min to
10 3-hour addition amount average times in feedback control according to a Step + SV variable scheme, an acidic gas stable treatment effect and addition amount reduction effect are obtained irrespective of the addition amount average time. The present scheme is a control scheme particularly excelling in
15 addition amount reduction effect with the addition amount of 288 to 292 kg/h.

[0096]

Examples 12 to 16

Except for varying the coefficient (Example 12: 95%,
20 Example 13: 90%, Example 14) 80%, Example 15: 70%, Example 16: 50%) multiplying by the 1-hour moving average addition amount (kg/h) to define the basal addition amount, and applying as the addition amount output lower limit, it was operated at the same setting conditions shown in Comparative Example 1, and feedback
25 controlled.

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with

pulverized sodium bicarbonate are shown in FIG. 8. In addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIGS. 26 to 30.

5 [0097]

The effects of Examples 12 to 16 are obtained due to applying the element of the average addition amount to feedback, and the coefficient multiplying by the average addition amount upon calculating the basal addition amount is
10 not particularly limited so long as being no more than 1. In a case of multiplying a coefficient of 1 (100%) or more by the present coefficient, the average addition amount used in the present basal addition amount will not be reduced leading to excess addition, even if the inlet HCl concentration decreases.

15 For the coefficient calculating the present basal addition amount of 95% (Example 12) to 70% (Example 15), both the 1-hour average value maximum and instantaneous maximum value of the outlet HCl concentration declined compared to Comparative Example 1, and a stable treatment effect of acidic gas was
20 obtained, along with an addition amount reduction effect being obtained. In addition, with a coefficient of 50% (Example 16), although the addition amount increases somewhat, the acidic gas stable treatment effect is obtained. The coefficient multiplying the average addition amount upon calculating the
25 basal addition amount is sufficient so long as no more than 1. 50 to 95% is preferable, and 70 to 90% is particularly preferable.

[0098]

Examples 17 and 18

Except for varying the coefficient (Example 17: 90%,
Example 18: 70%) multiplying by the 1-hour moving average
5 addition amount (kg/h) to define the basal addition amount, and
applying as the addition amount output lower limit, it was
operated at the same setting conditions shown in Comparative
Example 3, and feedback controlled.

The pulverized sodium bicarbonate addition amount and the
10 bag filter outlet HCl concentration after treating with
pulverized sodium bicarbonate are shown in FIG. 8. In
addition, the behaviors of the pulverized sodium bicarbonate
addition amount and bag filter outlet HCl concentration during
the present control are shown in FIGS. 31 and 32.

15 [0099]

According to Examples 17 and 18 when varying at 70 to 90%
the coefficient multiplied when calculating the basal addition
amount in feedback control according to the Step + SV variable
scheme, an acidic gas stable treatment effect and addition
20 amount reduction effect are obtained irrespective of the factor
calculating the basal addition amount. In addition, the
present scheme is a control scheme particularly excelling in
the addition amount reduction effect with the addition amount
of 289 to 297 kg/h.

25 [0100]

Comparative Example 4

In the simulation, the control target value (SV) of the

outlet HCl concentration in PID control scheme "P (proportional gain) = 100%, I = 0.1 sec, D = 0.1 sec, addition amount output minimum 200 kg/h, addition amount output maximum 480 kg/h" based on the HCl concentration measured with an HCl measurement device (2-sec minute measurement device measurement delay total time) was set to 200 ppm, and feedback controlled.

The pulverized sodium bicarbonate addition amount and the bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate are shown in FIG. 8. In

addition, the behaviors of the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration during the present control are shown in FIG. 33.

[0101]

The influence from the measurement delay time of the measurement device was investigated. When feedback controlling using a fast-response HCl measurement device with little measurement delay, the addition amount change of alkali agent and the change in outlet HCl concentration occur instantly, and was predicted that an improvement would be made. However, addition failure due to alkali agent addition fluctuations were predicted to occur, and the maximum value of the 1-hour average value of the outlet HCl concentration often used as the emission control value of acidic gas was 209 ppm, and the instantaneous maximum was 385 ppm.

[0102]

Example 19

Feedback control was done at the same conditions as

Example 1, except for PID control operating based on the HCl concentration measured by an HCl measurement device (2-sec measurement device total measurement delay time) in the simulation.

5 FIG. 8 shows the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate. In addition, FIG. 34 shows the behaviors of pulverized sodium bicarbonate addition amount during the present control and the bag filter outlet HCl
10 concentration.

[0103]

Example 20

Feedback control was done at the same conditions as Example 2, except for operation according to the step scheme
15 being done based on the HCl concentration measured by an HCl measurement device (2-sec measurement device total measurement delay time) in the simulation.

FIG. 8 shows the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration after treating
20 with pulverized sodium bicarbonate. In addition, FIG. 35 shows the behaviors of pulverized sodium bicarbonate addition amount during the present control and the bag filter outlet HCl concentration.

[0104]

25 Example 21

Feedback control was done at the same conditions as Example 3, except for operation according to the Step + SV

variable scheme being done based on the HCl concentration measured by an HCl measurement device (2-sec measurement device total measurement delay time) in the simulation.

FIG. 8 shows the pulverized sodium bicarbonate addition amount and bag filter outlet HCl concentration after treating with pulverized sodium bicarbonate. In addition, FIG. 36 shows the behaviors of pulverized sodium bicarbonate addition amount during the present control and the bag filter outlet HCl concentration.

10 [0105]

According to Example 21, the effects are exhibited irrespective of the length of the measurement delay time of the measurement device. In addition, so long as the control format is a feedback format, the effects are exhibited with either.

15 Examples 19 to 21 are results assuming a 2-sec measurement delay time; however, addition failure in alkali agent were suppressed by feedback, and thus both a stable treatment effect of acidic gas and addition amount reduction effect were obtained.

20 [0106]

Example 22

Feedback control was done at the same conditions (9.5 min delay time, Step + SV variable) as Example 10, except for conducting addition of 480 kg/h of alkali agent in the case of the 1-hour average value of the outlet HCl concentration exceeding 190 ppm in the simulation. FIG. 8 shows the pulverized sodium bicarbonate addition amount and bag filter

25

outlet HCl concentration after treating with pulverized sodium bicarbonate. In addition, FIG. 37 shows the behaviors of pulverized sodium bicarbonate addition amount during the present control and the bag filter outlet HCl concentration.

5 [0107]

There are facilities in which the emission concentration control of acidic gas is managed by the 1-hour average value of each acidic gas (hydrogen chloride, sulfur oxide concentration). Although it is common to control by providing the control target value (SV) in control, the control target value is consistently the target, and there are cases reaching a concentration exceeding the target value as a result of controlling.

The present example is an example of conducting 1-hour average management (190 ppm or higher, 480 kg/h added) in Example 10 in which the 1-hour average value of the outlet HCl concentration exceeded 200 ppm. In a case of the 1-hour average value at the outlet approaching the concentration to be managed, by conducting control to abundantly add the alkali agent, a further stable treatment effect of acidic gas and efficient use of alkali agent become possible.

[0108]

Hereinafter, upon explaining Comparative Examples 5 and 6 and Examples 23 and 24, which are actual equipment investigation results, the configuration of the acidic gas treatment system 2 that is used in Comparative Examples 5 and 6 and Examples 23 and 24 will be explained.

[0109]

FIG. 38 is a block diagram representing the configuration of the acidic gas treatment system 2 that adds pulverized sodium bicarbonate to HCl, which is the exhaust gas of an incineration facility.

[0110]

The acidic gas treatment system 2 is configured from a control device 21, a pulverized sodium bicarbonate adding device 22, a pulverized sodium bicarbonate adding device 26, a bag filter 23 and an HCl concentration measurement device (ionization electrode system) 24. The control device 21 calculates an addition amount output value of pulverized sodium bicarbonate by way of feedback control (PID control scheme or step scheme) based on an HCl concentration measurement signal transmitted from the HCl concentration measurement device (ionization electrode system) 24 and a basal addition amount calculated from a past average addition amount. The pulverized sodium bicarbonate adding device 22 adds pulverized sodium bicarbonate to the HCl in the exhaust gas, based on the addition amount output value of pulverized sodium bicarbonate calculated by the control device 21. In addition, the pulverized sodium bicarbonate adding device 26 adds a fixed amount of pulverized sodium bicarbonate that is unrelated to the addition amount output value of pulverized sodium bicarbonate calculated by the control device 21, to the HCl in the exhaust gas.

It should be noted that the basal addition amount is

calculated by multiplying a coefficient of no more than 1 by a past average addition amount according to an average time (for example, moving average time).

[0111]

5 The bag filter 23 removes dust after the reaction between HCl in the exhaust gas and pulverized sodium bicarbonate. The HCl concentration measurement device (ionization electrode system) 24 measures the HCl concentration (bag filter outlet HCl concentration described later) after the pulverized sodium bicarbonate accumulated on the bag filter 23 (pulverized sodium bicarbonate remaining from reaction with HCl in exhaust gas is accumulated on bag filter 23) and HCl after exhaust gas reaction has reacted, and transmits an HCl concentration measurement signal to the control device 21.

15 It should be noted that the inlet HCl concentration of the bag filter is measured by an HCl concentration measurement device (laser system) that is not illustrated.

[0112]

20 The acidic gas treatment system 2 performs feedback control by repeating such a cycle, whereby the control device 21 performs control to make the control output value of pulverized sodium bicarbonate addition amount an appropriate value.

[0113]

25 Comparative Example 5

 In an industrial waste incinerator, a laser-type HCl measurement device (KLA-1 manufactured by Kyoto Electronics

Manufacturing Co., Ltd.) was installed between a reduced-temperature tower outlet and bag filter, and the inlet HCl concentration was measured. In addition, feedback control was conducted with an oxygen equivalent value to manage an emission reference value based on a signal measured by an ionization electrode-type HCl measurement device (HL-36N manufactured by Kyoto Electronics Manufacturing Co., Ltd.) for the bag filter outlet. It should be noted that, although conducted by adding the filter bag addition output (SV 180 ppm) according to the SOx concentration signal at the outlet to the addition output according to the HCl concentration, since SOx was not generated in the present facility, it is omitted from the present report.

In addition, for the alkali agent treating the acidic gas, 8- μ m pulverized sodium bicarbonate (HIPERSAR B-200 manufactured by Kurita Water Industries Ltd.) was added according to the above-mentioned feedback control. Two alkali agent adding devices were applied due to a problem with the maximum addition amount, one making the fixed amount addition of 180 kg/h, and one being feedback controlled based on the outlet HCl concentration signal at "lower limit of 20 kg/h, upper limit of 300 kg/h, PID control settings P (proportional gain) = 100%, I = 0.1 sec, D= 0.1 sec".

FIG. 39 shows the bag filter inlet HCl concentration and bag filter outlet HCl concentration with the addition amount of pulverized sodium bicarbonate (sum of two adding devices). In addition, FIG. 40 shows the behaviors of the pulverized sodium bicarbonate addition amount and the HCl concentrations at the

bag filter inlet and outlet during the present control execution.

[0114]

Comparative Example 6

5 In the same facility, feedback control was conducted with the HCl concentration signal (oxygen equivalent value) measured by an ionization electrode-type HCl measurement device (HL-36N manufactured by Kyoto Electronics Manufacturing Co., Ltd.) for the bag filter outlet. It should be noted that, it was
10 similarly conducted by adding the filter bag addition output (SV 180 ppm) according to the SOx concentration signal at the outlet to the addition output according to the HCl concentration.

15 In addition, for the adding devices, similarly one was a fixed amount addition of 180 kg/h, and one was the "Step + SV variable scheme (refer to FIG. 41 for details)".

20 FIG. 39 shows the bag filter inlet HCl concentration and bag filter outlet HCl concentration with the addition amount of pulverized sodium bicarbonate (sum of two adding devices). In addition, FIG. 42 shows the behaviors of the pulverized sodium bicarbonate addition amount and the HCl concentrations at the bag filter inlet and outlet during the present control execution.

[0115]

25 Example 23

 In the same facility, feedback control was conducted at the same settings as Comparative Example 6, except for applying

the basal addition amount (30-min moving average addition amount, 70% coefficient) in the feedback control of "Step + SV variable system", and adding 300 kg/h at the outlet HCl concentration 1-hr average value of 213 ppm or higher (present facility HCl control value no more than 215 ppm). It should be noted that, it was similarly conducted by adding the filter bag addition output (SV 180 ppm) according to the SOx concentration signal at the outlet to the addition output according to the HCl concentration.

In addition, for the adding devices, similarly one was a fixed amount addition of 180 kg/h, and one was the "Step + SV variable scheme (refer to FIG. 41 for details)". FIG. 39 shows the bag filter inlet HCl concentration and bag filter outlet HCl concentration with the addition amount of pulverized sodium bicarbonate (sum of two adding devices). In addition, FIG. 43 shows the behaviors of the pulverized sodium bicarbonate addition amount and the HCl concentrations at the bag filter inlet and outlet during the present control execution.

[0116]

The present example is the application result of the present invention according to actual equipment. Compared to Comparative Examples 5 and 6, the fluctuation in inlet HCl concentration decreased. According to the present example, the added equivalents indicating the addition amount of alkali agent relative to the inlet HCl concentration by the efficient addition of alkali agent according to the present invention could be reduced compared to Comparative Examples 5 and 6, and

thus efficient control was possible.

[0117]

Example 24

In the same facility, feedback control was conducted at
5 the same settings as Example 23, except for jointly applying
high reactivity slaked lime with a specific surface area of at
least 30 m²/g (Tamakalk ECO manufactured by Okutama Kogyo Co.,
Ltd.) in the feedback control of the "Step + SV variable
system". It should be noted that, it was similarly conducted
10 by adding the filter bag addition output (SV 180 ppm) according
to the SOx concentration signal at the outlet to the addition
output according to the HCl concentration.

In addition, one of the adding devices was a fixed amount
addition of 170 kg/h of high reactivity slaked lime, and the
15 other one was a "Step + SV variable system (refer to FIG. 41
for details)".

FIG. 39 shows the bag filter inlet HCl concentration and
bag filter outlet HCl concentration with the addition amount of
pulverized sodium bicarbonate (sum of two adding devices). In
20 addition, FIG. 44 shows the behaviors of the pulverized sodium
bicarbonate addition amount and the HCl concentrations at the
bag filter inlet and outlet during the present control
execution.

[0118]

25 The present example is a case example of applying by
jointly using comparatively low-cost industrially slaked lime
with pulverized sodium bicarbonate. A stable treatment effect

of acidic gas is obtained stably in the present technique. Due to applying low-cost slaked lime and thus the acidic gas treatment cost being reduced, it is a technique that is effective industrially.

CLAIMS

1. A method for treating acidic gas that adds an alkali agent to a combustion exhaust gas containing acidic gas, and feedback controls an addition amount of the alkali agent based on a measurement signal of an acidic-gas concentration measurement device that measures an acidic gas concentration after collecting dust, the method comprising:

a step of calculating a basal addition amount by multiplying a coefficient of less than 1 by an average addition amount according to at least a predetermined time; and

a step of calculating, through feedback computation, an addition amount output value of the alkali agent based on the basal addition amount thus calculated, and obtaining a value that is at least the basal addition amount thus calculated and no greater than an upper limit established in advance, as an addition amount output value of the alkali agent.

2. The method according to claim 1, wherein the basal addition amount thus calculated is defined as a lower limit value for the addition amount output value of the alkali agent, in the step of calculating, through feedback computation, the addition amount output value.

3. The method according to claim 1 or 2, wherein the step of calculating, through feedback computation, the addition amount output value further includes

a step of setting, between a lower limit value and an upper limit value for the addition amount output value calculated based on the measurement signal; at least one new upper limit value for the addition amount output value to correspond with the acidic gas concentration.

4. The method according to any one of claims 1 to 3, wherein the step of calculating the basal addition amount includes setting, as a basal addition amount, from 0.5 to 0.95 of a moving average addition amount defined by an average value of the acidic gas concentration when continuously measuring for a predetermined time the acidic gas concentration every time established in advance that is selected from at least 5 minutes.

5. The method according to any one of claims 1 to 4, wherein the step of calculating, through feedback computation, the addition amount output value further includes

a step of calculating an addition amount output value of the alkali agent using both outputs among a control

output computed from a hydrogen chloride concentration and a control output computed from a sulfur oxide concentration, in addition to the feedback computation.

- 5 6. The method according to any one of claims 1 to 5, wherein the step of calculating, through feedback computation, the addition amount output value further includes

10 a step of calculating an addition amount output value of the alkali agent based on an average value of hydrogen chloride concentration and/or sulfur oxide concentration, in addition to the feedback computation.

- 15 7. The method according to any one of claims 1 to 6, wherein the alkali agent is pulverized sodium bicarbonate having an average particle size of 5 to 30 μm .

- 20 8. The method according to claim 7, jointly using other alkali agent than the sodium bicarbonate.

- 25 9. The method according to claim 8, wherein the other alkali agent is at least one alkali agent selected from the group consisting of slaked lime, sodium hydroxide, magnesium hydroxide, magnesium oxide, sodium carbonate, sodium sesquicarbonate, natural soda and crude sodium bicarbonate.