(12) UK Patent Application (19) GB (11) 2 234 232 (13) A

(43) Date of A publication 30.01.1991

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(54) Desulphurizing flue gas with calcium salts

(57) A furnace desulfurization process uses a desulfurizing agent in a furnace or flue to absorb SO_2 from the exhaust gas. The agent may be a salt obtained by a least partly neutralizing a Ca desulfurizing agent with an acid. A Ca desulfurizing agent can be used to effect a first-stage desulfurization reaction. Ash collected from the exhaust gas and containing a waste of the agent having an unreacted substance enclosed therein can be reacted with an acid to at least partly neturalize the unreacted portion of the agent. Ash containing the resulting salt is recycled to effect a second-stage desulfurization reaction. A denitrating reducing agent can be added to the collected ash, to effect a denitration reaction when recycled.

GB 2 234 232 A

FIG.1

(%)

DESULFURIZATION EFFICIENCY

100

50

0

C

B

A

0   1   2   3   4

Ca/S EQUIVALENT RATIO

FIG.2

(%)

FURNACE DESULFURIZATION EFFICIENCY

100

50

0

D

C

B

A

0   1   2   3   4

Ca/S EQUIVALENT RATIO

FIG.3

(%)

EFFECTIVE Ca UTILIZATION RATIO

50

0

0   1   2   3   4   5

Ca/S EQUIVALENT RATIO

FIG.4

FURNACE DESULFURIZATION EFFICIENCY

100

50

0

0   10   20   30   40 (%)

RATIO OF CONVERSION TO $CaCl_2$

FIG.5

(a)

(b)

(c)

(d)

NEUTRALIZATION

THERMAL DECOMPOSITION

DESULFURIZATION

α: $CaSO_4$
β: NEUTRALIZATION PRODUCT
γ: CaO (UNREACTED SUBSTANCE)

3,7

FIG.6

DESULFURIZING
AGENT

FUEL

REDUCING AGENT

ASH

FIG.7

DESULFURIZING AGENT

REDUCING AGENT

ASH

FUEL

FIG.8

PROPANE

PULVERIZED COAL

Air

SO₂

CaCO₃

16

19 TR

WASTE-AND REDUCING
AGENT-CONTAINING ASH

21

19 TR

17 AR

Air

TR 19

12

11

12

19 TR

COOLING AIR

19 TR

14

19 TR

COOLING
WATER

15

19 TR

COMPRESSED
AIR

18 AR

20 F1

TREATED
EXHAUST
GAS

13

ASH

614

FIG.9

(%)

DESULFURIZATION EFFICIENCY

100

C   A

B

50

0
0   1   2   3   4

Ca/S EQUIVALENT RATIO

FIG.10

(%)

DENITRATION EFFICIENCY

100

50

0
0   1   2   3   4   5

NH₃/NO EQUIVALENT RATIO

FIG.11

TRANSPORT AIR

DESULFURIZING AGENT

51

52

TRANSPORT AIR

PULVERIZED COAL

43

COMBUSTION AIR

42

41

TRANSPORT AIR

AMMONIA GAS

44

45

46

47

EXHAUST GAS

48

ASH CONTAINING ACTIVATED WASTE AGENT

ASH CONTAINING WASTE DESULFURIZING AGENT

HCL GAS

56

49

50

53

55

54

AIR

DISCHARGED ASH

TRANSPORT AIR

DRY PROCESSES FOR TREATING COMBUSTION EXHAUST GAS

The present invention relates to a dry process

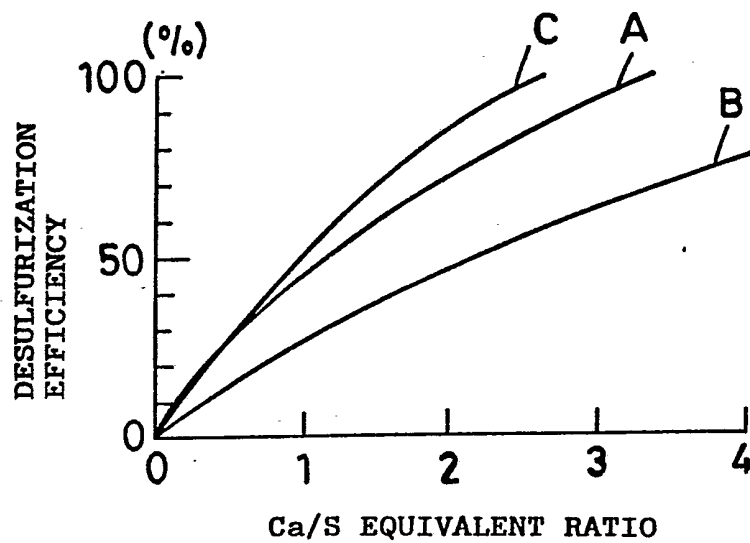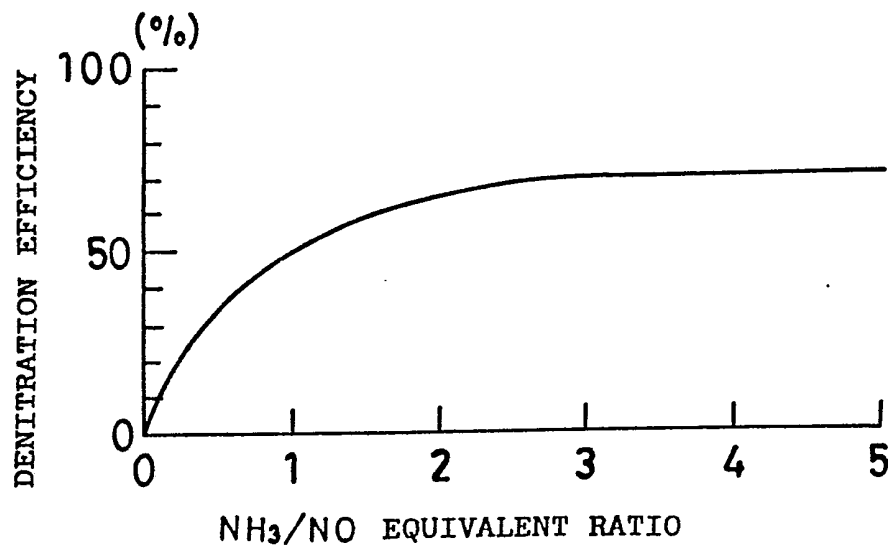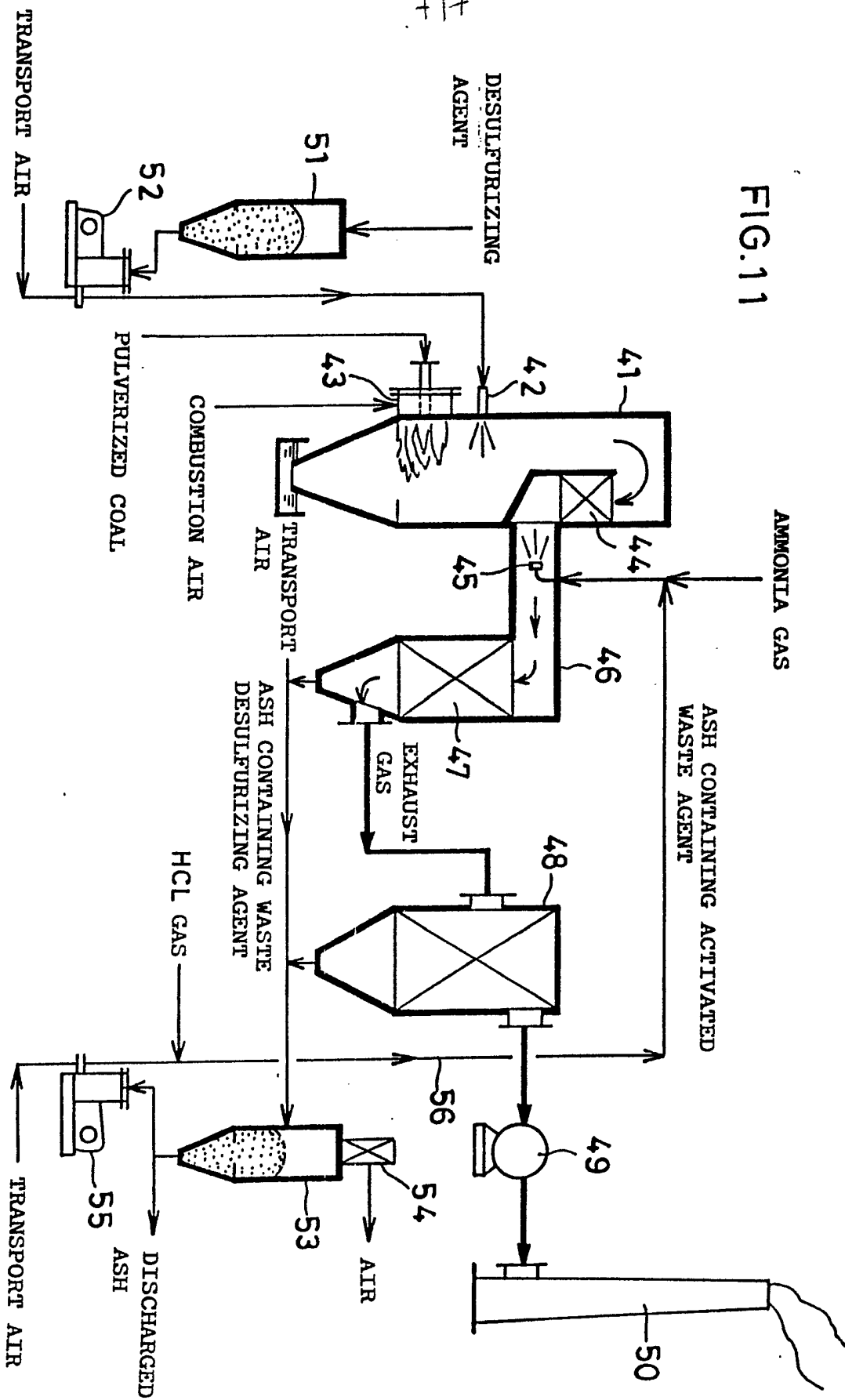5   for treating combustion exhaust gases discharged from

boilers, furnaces, refuse incinerators and the like for

the control of air pollution, and more particularly to

a process for removing acid gases, such as sulfur oxides

(SOx) and hydrogen chloride (HCl), from combustion

10   exhausts or flue gases, and to a process for removing

such acid gases and nitrogen oxides (NOx) at the same

time.

Processes still remain to be established for

15   simultaneously removing SOx and Nox from combustion gases

or flue gases, so that these oxides are removed by

different processes individually. Typical of desulfur-

ization processes is the lime-gypsum process wherein the

exhaust gas is washed with a lime slurry to absorb SOx.

20   This process has technically matured to completion and

is practiced by many actual apparatus, whereas the

process, which is of the wet type, requires water, and

treatment of the effluent and white smoke. Accordingly,

dry processes are desired which need not meet these

requirements. Typical of the dry processes is the furnace desulfurization process wherein a Ca desulfurizing agent, such as $CaCO_3$ or $Ca(OH)_2$, is placed directly into the furnace of a pulverized coal firing

5 boiler, refuse incinerator or the like to absorb and remove SO_2 and HCl produced in the furnace. This process is completely of the dry type, is therefore free of the above-mentioned problem of the wet process but has the most serious problem of being low in desulfurization

10 efficiency. At present, this process has yet to be practiced.

On the other hand, predominantly employed for denitration is the selective catalytic reduction process which is practiced with use of ammonia as a

15 reducing agent and a titanium-vanadium catalyst and which has proved useful in many cases. Another denitration process is known in which ammonia is introduced into a high-temperature region of at least 900° C to non-catalytically remove NOx. This process employs

20 ammonia, or depending on the conditions concerned, a compound which produces ammonia on thermal decomposition, such as ammonium carbonate, urea, ammonium formate or ammonium oxalate. However, the process requires a larger amount of such a reducing agent than the catalytic

25 process and is as low as about 50% in denitration

efficiency.

Accordingly, in the case where both SOx and NOx need to be removed at the same time, the lime-gypsum wet process and the selective catalytic reduction process with use of ammonia are employed in combination. The combined process has been practiced most widely and is excellent in that the process achieves a high desulfurization efficiency and a high denitration efficiency, whereas the process, which is essentially the combination of two proceeses, is not always satisfactory since the combined process is complex, effects desulfurization by the wet method and is high in both the initial cost and the running cost.

The low efficiency of the furnace desulfurization process is thought attributable to the following causes.

The furnace desulfurization process generally uses Ca desulfurizing agents, typical of which are $CaCO_3$ and $Ca(OH)_2$.

When the desulfurizing agent is charged into the high-temperature region of furnaces, the following reactions take place for the absorption of SO_2.
Decomposition of $CaCO_3$ or $Ca(OH)_2$ in the high-temperature region:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \qquad (1)$$

$$Ca(OH)_2 \rightarrow CaO + H_2O\uparrow \qquad (2)$$
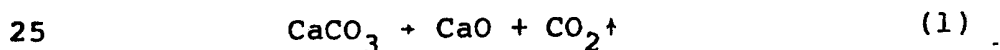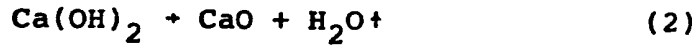
Absorption of SO_2 by desulfurizing agent in the high-temperature region:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (3)$$
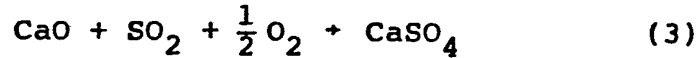
5   With the reaction of the formula (3), however, the SO_2 absorption reaction velocity greatly decreases with time owing to the causes (a) to (e) given below.

(a) With the absorption of SO_2, a $CaSO_4$ layer is formed over the surfaces of CaO particles, and the layer

10   reduces the reaction velocity.

(b) With the absorption of SO_2, the SO_2 concentration around the surfaces of CaO particles lowers, thereby reducing the reaction velocity.

(c) The internal temperature of furnaces usually lowers

15   downstream thereof, so that the reaction velocity lowers with the decrease in the temperature.

(d) Generally in the furnace desulfurization process, the desulfurizing agent in the form of a powder or slurry is uniformly charged into the furnace, dis-

20   persed and brought into contact with the exhaust gas. Since this contact is effected in a large space, the contact efficiency is low.

(e) Since the reaction between the desulfurizing agent and the gas is rate-determined by the surface area

25   of particles of the agent, it is desired that the

particle size of the desulfurizing agent be smaller to
afford an increased surface area for the reaction,
whereas it is technically difficult to uniformly disperse
fine particles within the furnace.

Because of these causes, the conventional furnace
desulfurization process is thought to be inevitably
low in efficiency.

It is now assumed that the ratio of the amount of
Ca (moles/hour) charged into the furnace to the amount of
SO_2 gas (moles/hour) produced in the furnace is a Ca/S
mole equivalent ratio (hereinafter referred to as the
"Ca/S equivalent ratio"). For example, according to the
data presently made public by EPA (Environmental
Protection Agency, U.S.A.), the furnace desulfurization
efficiency is about 60% at Ca/S = 3. Such a low
efficiency appears attributable to the above causes;
highly efficient desulfurization will not be achieved
unless these causes are obviated.

It is an object of the present invention to provide
an improved process for treating combustion exhaust gas.

- 5 -

The present invention provides a furnace
desulfurization process comprising supplying a desulfu-
rizing agent into a furnace or flue to cause the agent
to absorb SO_2 in the exhaust gas, the desulfurizing
agent being a salt obtained by at least partly neutral-
izing a Ca desulfurizing agent with an acid (hereinafter
referred to as a "first process").

The present invention further provides a
furnace desulfurization process comprising supplying a Ca
desulfurizing agent into a furnace or flue to effect a
first-stage desulfurization reaction, collecting ash con-
taining a waste of the agent having an unreacted substance
enclosed therein from the exhaust gas, adding an acid to
the collected ash to at least partly neutralize the
unreacted portion of the desulfurizing agent, and
recycling the ash containing the resulting salt into the
furnace or flue to effect a second-stage desulfurization
reaction (hereinafter referred to as a "second process").

The present invention further provides a dry
simultaneous desulfurization-denitration process compris-
ing supplying a Ca desulfurizing agent into a furnace or
flue to effect a desulfurization reaction, collecting
ash containing a waste of the agent having an unreacted

-6-

substance enclosed therein from the exhaust gas, adding a
denitrating reducing agent to the collected ash, and
recycling the ash containing the waste desulfurizing
agent and the reducing agent into the furnace or flue to
effect desulfurization and denitration reactions
(hereinafter referred to as a "third process").

The present invention further provides a dry
simultaneous desulfurization-denitration process
comprising supplying a Ca desulfurizing agent into a
furnace or flue to effect a desulfurization reaction,
collecting ash containing a waste of the agent having an
unreacted substance enclosed therein from the exhaust
gas, adding an acid to the collected ash to at least
partly neutralize the unreacted substance, adding a
denitrating reducing agent to the ash containing the
resulting salt, and recycling the ash containing the salt
and the reducing agent into the furnace or flue to effect
desulfurization and denitration reactions (hereinafter
referred to as a "fourth process").

Examples of the present invention will now be
described in more detail, by way of example only, and
with reference to the accompanying drawings, in which:

Fig. 1 is a graph showing the relationship between
the Ca/S equivalent ratio and the desulfurization
efficiency;

Fig. 2 is a graph showing the relationship between
the Ca/S equivalent ratio and the furnace

- 7 -

desulfurization efficiency;

FIG. 3 is a graph showing the relationship between the Ca/S equivalent ratio and the effective Ca utilization ratio;

5   FIG. 4 is a graph showing the relationship between the $CaCl_2$ conversion ratio and the furnace desulfurization efficiency;

FIGS. 5 (a), (b), (c) and (d) are each a diagram in section showing a particle of waste desulfurizing

10   agent having an unreacted substance enclosed therein;

FIGS. 6 to 8 are flow charts showing processes of the invention;

FIG. 9 is a graph showing the relationship between the Ca/S equivalent ratio and the desulfuriza-

15   tion efficiency;

FIG. 10 is a graph showing the relationship between the NH_3/NO equivalent ratio and the denitration efficiency; and

FIG. 11 is a flow chart showing an embodiment

20   of the invention.

A)   The furnace desulfurization process as the first process has been accomplished based on the following finding.

25   Generally in the case of the absorption

-8-

reaction of the formula (3) given above

the smaller the particle size of the Ca desulfurizing agent used, the higher is the absorption efficiency. We tested $CaCO_3$ for desulfurization

5   efficiency, with the results shown in FIG. 1. Curve A in the graph represents the result obtained with $CaCO_3$, 12 μ in mean particle size, and Curve B the result when the mean particle size was up to 3 μ. The graph indicates that the smaller the particle size of the desulfurizing

10   agent, the higher is the desulfurization efficiency. Borgwardt (Chemical Engineering Science, Vo.. 44, No. 1, 1988) reported that the specific surface area of CaO obtained by the thermal decomposition of $CaCO_3$ according to the reaction formula (1) was 104 m^2/g when maximum,

15   and that the specific surface area of CaO obtained from $Ca(OH)_2$ according to the reaction formula (2) was 76 m^2/g when maximum. When we tested $CaCO_3$ and $Ca(OH)_2$ of the same particle size for desulfurization efficiency in the same manner as above, the former similarly achieved a

20   higher efficiency. The reason appears to be as follows. The reaction between CaO and SO_2 is a solid-gas reaction, the velocity of which is determined by the specific surface area of CaO. $CaCO_3$ attains a higher desulfurization efficiency because the CaO resulting from

25   the thermal decomposition of $CaCO_3$ has a larger specific

surface area than the CaO resulting from that of Ca(OH)$_2$ as reported by Borgwardt.

We have carried out intesive research on how to give an increased specific surface area to the CaO resulting from the thermal decomposition of Ca desulfurizing agents based on this principle and accomplished the present invention.

Examples of acids for use in the first process of the invention are preferably organic acids, such as acetic acid, oxalic acid and formic acid, which are used singly or in combination.

It is also possible to use an organic acid salt of a desulfurizing metal as the desulfurizing agent in the form of a salt. The organic acid salt of desulfurizing metal to be used is preferably calcium acetate.

Preferably, the desulfurizing agent in the form of a salt is blown, in the form of a powder or slurry, into the furnace or flue in the region thereof having a temperature of 500 to 1200° C.

B) In exploring measures for eliminating the causes (a) to (e) mentioned above in relation to formula (3),

we have found that the desulfurization efficiency can be improved greatly especially by activating the waste desulfurizing agent resulting from use and having an unreacted portion of desulfurizing agent enclosed

-10-

.therein and recycling the agent thus treated. The furnace desulfurization process as the second process has been accomplished based on this finding.

Examples of preferred acids for use in the

5   second process are inorganic acids, such as hydrochloric acid, nitric acid and hydrogen chloride, and organic acids, such as acetic acid, oxalic acid and formic acid. These acids are used singly or in combination. Also usable are halogen gases such as chlorine, bromine,

10 fluorine and iodine.

With the second process, the amount of fresh desulfurizing agent to be supplied can be greatly reduced, whereas the process achieves a high desulfurization efficiency of at least 90% when the equivalent ratio of

15 the Ca supply to S is 2.

C)   With the third process, the Ca desulfurizing agent may be supplied into the furnace or flue singly (see FIG. 6), or along with the ash containing the waste of the agent and the denitrating reducing agent

20 (see FIG. 7).

Examples of desirable denitrating reducing agents are ammonia; ammonium salts such as ammonium carbonate, ammonium formate and ammonium oxalate; urea and urea derivatives, which are used singly or in

25 combination in the form of a powder or solution.

-11-

The ash containing the waste desulfurizing agent and the reducing agent is blown, in the form of a powder or slurry, into the furnace or flue in the region thereof having a temperature preferably of 500 to 1000° C, more preferably 600 to 900° C. At temperatures higher than 1000° C, the process fails to remove NOx due to the formation of NOx. At temperatures lower than 500° C, both the desulfurization efficiency and denitration efficiency lower to levels which are not useful practically.

Preferably, the content of waste desulfurizing agent in the collected ash is increased by removing the ash by a pneumatic classifier or like ash separator.

The desulfurization-denitration process of the present invention achieves a desulfurization efficiency of at least 80% and a denitration efficiency of at least 60%. For example, when ash containing a waste desulfurizing agent and 20% of urea is blown into a region of about 800° C in temperature at a Ca/S ratio of 3, the process achieves a desulfurization efficiency of about 90% and a denitration efficiency of about 70%.

If no reducing agent is added, neither of desulfurization and denitration reactions occurs in the temperature region of 500 to 1000° C. The fact that the addition of the reducing agent to the collected ash

-12-

effects desulfurization and denitration in the low

temperature region is an entirely novel finding. This

fact is thought attributable to the activation of the

surfaces of particles of the Ca desulfurizing agent by

5   the reducing agent.

FIG. 6 is a flow chart showing a mode of

practicing the third process of the invention. The

illustrated system consists essentially of a boiler 1,

an air heater 2 for cooling the exhaust gas produced in

10 the boiler, a dust collector 3, such as an electric

dust collector or bag filter, for removing dust from the

exhaust gas, an injector 4 for injecting a Ca desulfu-

rizing agent into the furnace of the boiler 1, an ash

separator 7, such as a pneumatic classifier, for

15 increasing the content of waste desulfurizing agent in

the ash collected by the dust collector 3, a mixer 5

for mixing the collected ash with a denitrating reducing

agent, and an injector 6 for injecting the ash contain-

ing the waste desulfurizing agent and the reducing

20 agent into the flue. The Ca desulfurizing agent is

supplied into the furnace of the boiler 1 by the injector

4 to effect a desulfurization reaction. The exhaust gas

produced by the boiler 1 is cooled by the air heater 2,

and the ash containing the waste desulfurizing agent

25 having an unreacted substance enclosed therein is

-13-

subsequently collected from the exhaust gas by the dust

collector 3. The waste desulfurizing agent present in

the collected ash is concentrated to a content of at

least 30% by the ash separator 7, whereupon the reducing

5   agent is admixed with the ash by the mixer 5. The

resulting ash containing the waste desulfurizing agent

and the reducing agent is recycled into the flue of the

boiler 1 by the injector 6 to effect desulfurization

and denitration reactions.

10   The content of the waste desulfurizing agent

in the ash, the amount of reducing agent to be added to

the ash and the ratio between the ash and the reducing

agent are determined according to the contemplated

desulfurization efficiency and denitration efficiency.

15   When higher desulfurization and denitration efficiencies

are required, the ash containing the waste and the

reducing agent is introduced into the flue invariably

in an increased amount.

FIG. 7 is a flow chart showing another mode

20   of practicing the third process of the invention. The

illustrated system differs from the one shown in FIG. 6

in the position where fresh Ca desulfurizing agent is

added. In the present mode, the desulfurizing agent is

not injected singly into the furnace of the boiler 1

25   but is admixed with the ash containing the waste.

-14-

desulfurizing agent and the reducing agent within the

mixer 5 and supplied to the flue along with the ash.

Although the present process is basically the same as

the foregoing process of FIG. 6, the system is simplified

5   in corresponding relation to the absence of the injector

for supplying the Ca desulfurizing agent into the

furnace. However, since no desulfurization occurs within

the furnace, the ash containing the waste desulfurizing

agent and the reducing agent is added in an increased

10   amount. For the discharged exhaust gas to have the same

SO_2 concentration as in the case of the flow chart of

FIG. 6 although no desulfurization occurs in the furnace,

the ash containing the waste and the reducing agent needs

to achieve a higher desulfurization efficiency and is

15   therefore supplied in a larger amount. The two systems

are exactly the same in respect of the removal of NOx,

and there is no difference therebetween in the amount of

waste- and reducing agent-containing ash in this respect.

The third process of the invention, which is

20   completely of the dry type, effects desulfurization and

denitration at the same time with an exceedingly greater

ease than the conventional combination of the wet lime-

gypsum process and the catalytic reduction process with

use of ammonia. The desulfurization and denitration

25   effected at the same time in a low-temperature region

by using the collected ash containing the denitrating reducing agent are not only advantageous to the purification of exhaust gas but also of great economical advantage since the waste desulfurizing agent having an

5 unreacted substance enclosed therein is effectively utilized. The waste desulfurizing agent in the ash contains a high proportion of $CaSO_4$, so that the present process is also advantageous from the viewpoint of ease of aftertreatment.

10 D) In the fourth process of the invention, the salt- and reducing agent-containing ash is blown, preferably in the form of a powder or slurry, into the furnace or flue in the region thereof having a temperature preferably of 500 to 1000° C, more preferably 600 to

15 900° C. At temperatures higher than 1000° C, the process fails to remove NOx since NOx is formed. At temperatures lower than 500° C, both the desulfurization efficiency and the denitration efficiency lower to levels which are not useful practically.

20 Examples of preferred denitrating reducing agents are ammonia; ammonium carbonate, ammonium formate, ammonium oxalate and like ammonium salts; urea and urea derivatives, which are used singly or in combination in the form of a powder or solution.

25 Examples of preferred acids are hydrochloric acid,

-16-

nitric acid, hydrogen chloride and like inorganic acids, and acetic acid, oxalic acid, formic acid and like organic acids, which are used singly or in combination. Also usable are halogen gases such as chlorine, bromine,

5   fluorine and iodine.

Preferably, the content of waste desulfurizing agent in the collected ash. is increased by removing the ash by a pneumatic classifier or like ash separator.

The circumstances will be described below which

10   have led us to complete the fourth process of the invention, i.e., simultaneous desulfurization-denitration process.

The desulfurization efficiency of the furnace direct desulfurization process can be improved by:

15   i) charging the desulfurizing agent into the furnace

in the region thereof having an optimum temperature,

ii) ingeniously charging a powder of desulfurizing

agent into the furnace to uniformly disperse the agent

and thereby effectively contact the agent with the

20   exhaust gas, and

iii) using particles of absorbing agent which are large

in surface area, i.e., small in size since the SO_2

absorbing reaction by the desulfurizing agent is a

solid-gas reaction which is governed by the surface

25   area of particles thereof.

-17-

As already mentioned, EPA of U.S.A. recently
reported that the desulfurization efficiency achieved
at a Ca/S equivalent ratio of 3 is about 60%. According
to the report, the ratio of effective utilization of
the Ca desulfurizing agent is 20%, and the remaining 80%
of Ca component is discharged and disposed of along with
ash in the form of CaO or $CaCO_3$. Thus, the effective
Ca utilization of the conventional furnace desulfurization
process is generally much lower than the Ca utilization
ratio of the wet process which is at least 95%, and must
therefore be improved.

The effective utilization ratio can be improved
by recycling into the furnace the waste of desulfurizing
agent having enclosed therein an unreacted substance
present in the ash to utilize the agent again for absorb-
ing SO_2.

The most typical of such recycling systems is
the recycling fluidized bed system. Literature says that
this system achieves a desulfurization efficiency of 90%
at Ca/S = 1.5. The Ca utilization ratio then achieved is
about 60%, which is a remarkable improvement over the
corresponding ratio of the conventional furnace desulfu-
rization process. With the fluidized bed system, the
recycling rate is said to be about 100 times the rate of
discharge of ash to result in a considerably great power

loss due to recycling.

Thus, the conventional furnace desulfurization process (a) fails to achieve a high desulfurization efficiency of at least 90% and therefore to meet the

5   standard for discharging SO_2 in countries where stringent pollution control regulations are set, and (b) is extremely low in effective Ca utilization ratio, consequently discharging an increased amount of ash and entailing a higher cost for the chemical agent, and is

10   therefore practiced on a smaller scale in this country than in the U.S. and European countries recently.

In order to overcome the foregoing problems of the furnace desulfurization process, we have made basic improvements in the methods i) to iii), practiced

15   the recycling of the waste desulfurizing agent having an unreacted substance enclosed therein, and investigated how to activate the waste desulfurizing agent to improve the SO_2 absorbing ability of the waste, further conducting tests on simultaneous desulfurization-

20   denitration processes along with these attempts.

Our efforts have revealed the following.

(1) The absorbing agent, when reduced in particle size, results in an improved desulfurization efficiency.

For example, $CaCO_3$, when up to 3 μ in particle size,

25   achieves a desulfurization efficiency of 90% at

-19-

Ca/S = 3.

(2) The waste desulfurizing agent enclosing the
unreacted substance, when recycled for reuse, causes
desulfurization again. Based on the effective Ca
of the unreacted substance present in the waste,
the desulfurization efficiency achieved at Ca/S = 3
is about 67%. When the waste desulfurizing agent is
recycled at an increased rate, a still higher
desulfurization efficiency can be achieved, which
nevertheless is lower than the efficiency attained
in the above case (1).

(3) The waste desulfurizing agent enclosing the
unreacted substance can be activated by at least
partly neutralizing the unreacted substance in the
waste with an acid. When the waste agent thus
treated is placed into the high-temperature region
of the furnace, the decomposition reaction of the
Ca salt in this region permits the waste enclosing
the unreacted substance to achieve a desulfurization
efficiency of above 90% at Ca/S = 3 by the absorp-
tion of SO_2.

(4) When ammonia is supplied to the furnace after the
neutralization treatment (3), denitration occurs
simultaneously with desulfurization within the
furnace. For example, when ammonia is used at a

-20-

at a rate of 3 in NH_3 (mole)/NO (mole), the denitration
efficiency attained is 70%. In this case, if the
furnace is adapted for combustion with inhibited
NOx to produce an exhaust gas which has a decreased

5   NOx concentration of about 200 ppm and to which the
present process of the invention is applied, the NOx
concentration can be reduced to 60 ppm.

    The dry simultaneous desulfurization-denitration
process, i.e., the fourth process, achieves a high

10   desulfurization efficiency of at least 90% at a low Ca/S
equivalent ratio, i.e., with consumption of a reduced
amount of fresh desulfurizing agent, and further attains
a high denitration efficiency of at least 70% within
the furnace at the same time.

15   EXAMPLES

Example 1

    This example corresponds to the first process
of the invention.

    $CaCO_3$ serving as a desulfurizing agent and

20   up 3 μ in particle size was neutralized with acetic acid
in an amount of 10% based on weight. The treated agent
was checked for SO_2 absorption efficiency. The result
is represented by Curve C in FIG. 1.

    A comparison of the three curves in the graph

25   shows that the $CaCO_3$ was considerably improved in

desulfurization efficiency by the treatment. For example, the pretreatment with acetic acid apparently produces the following effect at Ca/S = 2.
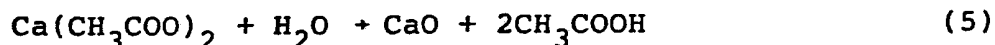
Curve	Desulfurizing agent	Efficiency
(A)	Particles of 12 μ	55%
(B)	Particles of up to 3 μ	70%
(C)	Particles of up to 3 μ as treated	80%

We consider the effect to be attributable to the following.

Reaction between $CaCO_3$ and acetic acid:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O \qquad (4)$$

Thermal decomposition of product:

$$Ca(CH_3COO)_2 + H_2O \rightarrow CaO + 2CH_3COOH \qquad (5)$$

The thermal decomposition of calcium acetate according to the reaction formula (5) produces CaO, which is greater in specific surface area than the CaO resulting from the thermal decomposition of $CaCO_3$, hence a higher desulfurization efficiency.

Such an effect is available also when an inorganic acid is used in place of the organic acid. For example, hydrogen chloride, when used, achieves a remarkable improvement in denitration efficiency like acetic acid.

However, when hydrogen chloride is used as the inorganic acid, decomposition of the neutralization

-22-

product releases HCl, which gives rise to corrosion of devices.

$$CaCl_2 + H_2O \rightarrow CaO + 2HCl \uparrow \qquad (6)$$
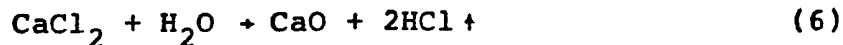
On the other hand, when an organic acid, e.g., acetic acid, is used, decomposition of the neutralization product produces CH_3COOH, which undergoes a combustion reaction in a high-temperature atmosphere in the presence of oxygen and becomes decomposed into harmless water and carbon dioxide. Accordingly, the organic acid is desirable to use.

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad (7)$$
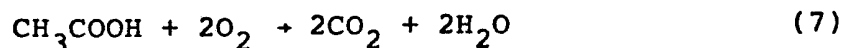
Example 2

This example corresponds to the second process.

(1) Efficient dispersion of desulfurizing agent of
     reduced particle size

$CaCO_3$ serving as a desulfurizing agent and up to 3 μ in particle size was uniformly dispersed into a furnace to conduct a desulfurization reaction at an optimum temperature selected. The desulfurization efficiency achieved was exceedingly higher than is attained by the conventional process wherein larger particles are used. We conducted furnace desulfurization tests by firing pulverized coal at a rate of 10 kg/hour in a test furnace having a capacity of 0.38 m^3 (hereinafter referred to as a "small test furnace"),

-23-

with the results given below.

Finely divided $CaCO_3$ was charged into the
test apparatus as uniformly dispersed and tested for
desulfurization. FIG. 2, Curve C represents the result

5 for illustrative purposes. Curve C indicates that a
desulfurization efficiency of 70% can be achieved at
Ca/S = 2, and a desulfurization efficiency of 90% at
Ca/S = 3. The desulfurization efficiency is much higher
than the aforementioned FPA data, presumably because the

10 causes (d) and (e) mentioned above in relation to formula (3)
have been obviated.

(2) Recycling of waste desulfurizing agent enclosing
unreacted substance

FIG. 3 shows calculated ratios of effective

15 utilization of the Ca in the chemical agent used for
the desulfurization test represented by Curve C of FIG.
2. (The inflection point between 3 and 4 in Ca/S means
that the desulfurization efficiency will not exceed 100%
even if the Ca/S ratio is made higher than the ratios

20 in this region.) FIG. 3 reveals that for example, the
desulfurization efficiency of 70% at Ca/S = 2 effectively
utilizes 35% of the Ca and that the first-stage desulfu-
rization, when effected alone, permits 65% of the
effective Ca component of the waste desulurizing agent

25 enclosing the unreacted substance to be discharged and

-24-

discarded along with the ash.

According to the present invention, the waste desulfurizing agent is recycled for reuse.

The waste desulfurizing agent having the unreacted substance enclosed therein was charged into the small test furnace and tested for desulfurization efficiency. In this test, the waste was placed into the region with a temperature of 1200° C within the furnace. FIG. 2, Curve A represents the test result. Table 1 given later shows the composition of the waste agent tested. The ash containing the waste was prepared from the ash resulting from the above test conducted at Ca/S = 3 for continuous desulfurization, by removing a portion of ash with a pneumatic classifier. Accordingly, the ash content is lower than the ash content of usual waste desulfurizing agent.

The effective CaO content given in Table 1 is 34.5 wt. %. The desulfurization efficiency represented by FIG. 2, Curve A was as low as 40% at Ca/S = 4. When the same ash containing the waste was charged into the test furnace in the region thereof having a temperature of up to 1000° C, the desulfurization efficiency represented by FIG. 2, Curve B was achieved. The ash thus charged in improved the efficiency to 75% at Ca/S = 4. The difference between Curves A and B is due to

the difference in the temperature of atmosphere between

the different positions where the ash was supplied.

Differential thermal analysis revealed that under the

conditions of Curve A, $CaSO_4$ was decomposed to release

5   SO_2. The result indicates that it is possible to obtain

a high desulfurization efficiency even with use of the

waste desulfurizing agent having the unreacted substance

enclosed therein, if the waste is charged into the

region of optimum temperature in a large quantity.

10   Nevertheless, the waste is apparently inferior

to the fresh desulfurizing agent in properties, and the

impaired properties are attributable to the cause (a)

already mentioned.

(3) Activation of waste desulfurizing agent

15   If the waste desulfurizing agent enclosing the

unreacted substance is recycled in a large quantity for

the second-stage desulfurization, a large amount of ash

is recycled through the system, giving rise to problems

such as clogging or wear of the piping or ducts with

20   particles, necessity to use a dust collector of increased

capacity, and an increased running cost for transport.

The amount to be recycled is therefore preferably a

minimum required. In an attempt to decrease the amount

of recycle, addition of an acid gas was tested for

25   the activation of the waste desulfurizing agent using

the small test furnace. More specifically, an ash

containing the waste agent enclosing the unreacted

substance was treated with a predetermined proportion

of HCl gas, then charged into the region having a

5 temperature of up to 1000° C at Ca/S = 1.3 and checked

for desulfurization efficiency. FIG. 4 shows the result,

which reveals a remarkable improvement over the

efficiency represented by FIG. 2, Curve B. The reason

will be as follows. The unreacted substance, CaO, in

10 the waste agent is neutralized with the HCl added. In this

case, it is seen that the greater the ratio of conversion

to $CaCl_2$, the higher is the desulfurization efficiency.

The efficiency shown in FIG. 4 was achieved at a fixed

Ca/S equivalent ratio of 1.3. The waste-containing ash

15 tested had the composition shown in Table 1.

FIG. 1 indicates that when the ratio of

conversion to $CaCl_2$ is, for example, 30%, a desulfuriza-

tion efficiency of about 90% can be achieved even at the

low Ca/S equivalent ratio of 1.3. Presumably, this is

20 because the neutralization reaction breaks down the

$CaSO_4$ layer mentioned in the foregoing cause (a) to

form an activated surface of CaO and result in an
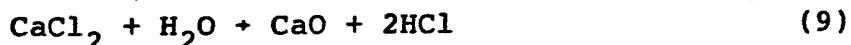
accelerated desulfurization reaction.

It is thought that this process involves the

25 following sequence of reactions. (However, it is likely
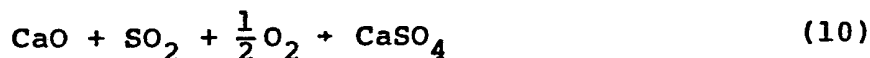
-27-

that the reactions (IV) and (V) occur concurrently.)

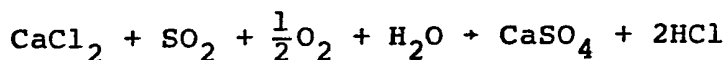(III) Reaction of $CaSO_4$-covered CaO with HCl (at room

temperature):

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \qquad (8)$$
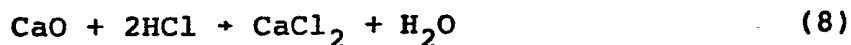
5 (IV) Decomposition of $CaCl_2$ in high-temperature region:

$$CaCl_2 + H_2O \rightarrow CaO + 2HCl \qquad (9)$$

(V) Absorption of SO_2 by CaO having active surface in

high-temperature region:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (10)$$

10 Alternatively, the reactions (IV) and (V) may proceed

as follows:

$$CaCl_2 + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow CaSO_4 + 2HCl$$

(VI) Second reaction between CaO and HCl in low-

temperature region:

15 $$CaO + 2HCl \rightarrow CaCl_2 \qquad (11)$$

For a better understanding of the sequence of

reactions, FIG. 5 schematically shows the particle of

desulfurizing agent. (The secondary reaction product

in this case is $CaCl_2$.)

20 When thermal decomposition occurs in the

above process according to the formula (9) in the high-

temperature region as seen in FIG. 5, (c), the release

of HCl will form pores in the surface of the CaO

particle, consequently giving an increased surface area

25 to activate the particle. (Alternatively, the thermal

-28-

decomposition is considered to break down the CaO

particle into smaller particles to result in an increased
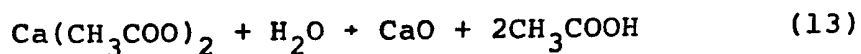
surface area.)

Desulfurization was effected at varying Ca/S

5 equivalent ratios for waste desulfurizing agent, in

which the ratio of conversion of the unreacted substance

CaO to $CaCl_2$ was set to a predetermined value of 10%.

FIG. 2, Curve D represents the desulfurization efficiency

then achieved.

10 This curve indicates that the addition of HCl

fully activated the waste to attain a higher efficiency

than Curve A representing fresh desulfurizing agent.

Next, the use of acetic acid as the neutraliza-

tion activating agent will be described. In the case of

15 acetic acid, the following reaction takes place.

$$CaO + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O \qquad (12)$$
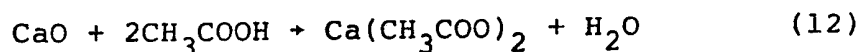
The resulting calcium acetate thermally decomposes as

follows.

$$Ca(CH_3COO)_2 + H_2O \rightarrow CaO + 2CH_3COOH \qquad (13)$$

20 The activation and SO_2 absorption steps are exactly the

same as in the case of HCl. However, acetic acid, which

is an organic substance, burns on contact with oxygen in

the high-temperature region.

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad (14)$$
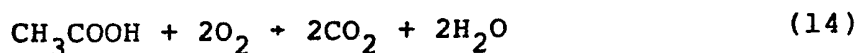
25 Thus, unlike the inorganic neutralizing agent,

-29-

the organic neutralizing agent is converted to CO_2 and H_2O on burning and has the advantage of being in no way likely to cause corrosion to devices like HCl or to release waste HCl with an unreacted substance enclosed

5 therein.

Further in the case of acetic acid, the relationship between the ratio of conversion to $Ca(CH_3COO)_2$ and the desulfurization efficiency is approximate to that shown in FIG. 4; it has been found that acetic acid

10 acts effectively as an activating agent to achieve a desulfurization efficiency which increases with an increase in the conversion ratio.

Cl_2 gas, Br_2 gas or like gas, when used in place of HCl gas, achieves exactly the same result.

15 Especially, Br_2 gas also produces a denitration effect within the furnace and is therefore a favorable substance.

As described above, inorganic acids, inorganic acid gases, organic acids and organic acid gases have

20 proved effective for activating the waste desulfurizing agent. It has also been found that the combination of the activating method with the usual desulfurization process greatly reduces the amount of fresh desulfurizing agent to be supplied and achieves a high desulfurization

25 efficiency of at least 90% at the supply Ca to S equi-

-30-

valent ratio of 2.

Table 1   Composition of Ash Containing
Waste Desulfurizing agent

Component	Proportion (wt. %)
$CaSO_4$	28.56
CaO	32.56
$CaCO_3$	3.60
Ash	35.28

Comparative Examples 1 and 2, and Example 3 given below are concerned with the third process of the invention

Comparative Example 1

In this comparative example, the lime blowing method of the prior art was checked for desulfurization efficiency and denitration efficiency to clarify the feature of Example 3 given below. FIG. 8 is a flow chart showing the test method used in the present comparative example and Example 3.   The system used for testing consists primarily of a combustion chamber 16 for firing pulverized coal, and a reaction chamber 11 disposed downstream from the chamber 16 for desulfurization and denitration. The combustion capacity is 10 kg/hour. With this system, the combustion temperature and the amount of NOx to be produced are controllable by burning

propane as an auxiliary fuel, and the SO_2 concentration
of the exhaust gas is adjustable by injecting SO_2 gas.
The reaction chamber 11 is provided by a stainless steel
tube, 330 mm in inside diameter and 4 m in height, and

5   is controllable to a specified temperature by electric
heaters 12 disposed around the tube. $CaCO_3$ serving as a
desulfurizing agent is injected into the combustion
chamber 16. The ash containing waste desulfurizing agent
and reducing agent and to be used in Example 3 is

10   injected, as entrained in an air stream, into the reaction
chamber 11 through an inlet 21 at the top thereof. The
O_2, SO_2 and NOx concentrations of the exhaust gas are
measured by analyzers 17 and 18 disposed at the outlet of
the reaction chamber 11 and the outlet of a bag filter 13,

15   respectively. The exhaust gas is cooled by an air heater
14 and a gas cooler 15, separated from dust by the bag
filter 13 and released to the atmosphere. The diagram
further shows thermometers 19 and a flowmeter 20.

     Finely divided $CaCO_3$ (3 μ in mean particle

20   size) serving as a desulfurizing agent was charged into
the combustion chamber of the system. The main conditions
involved were given below. The system achieved a
desulfurization efficiency of 62% with a denitration
efficiency of 0%.

25   Fuel: propane-pulverized coal mixture

-32-

(propane: 0.64 Nm^3/hour, coal: 3.24 kg/hour)

Air ratio: 1.81 (oxygen concentration of exhaust gas: 9.4%)

Rate of discharge of exhaust gas: 70 Nm^3/hour

5   NOx concentration: 260 ppm

SO_2 concentration: 900 ppm (as adjusted by addition of pure SO_2)

Reaction time: 4 seconds

Temperature: 1200 to 1300° C in combustion chamber,

10   1100° C in reaction chamber

Ca/S: 2.1

The above-mentioned desulfurization efficiency of 62% was achieved using finely divided $CaCO_3$ at a high reaction temperature. When the system was operated

15   under exactly the same reaction conditions as above with the exception of reducing the reaction temperature from 1100° C to 780° C, the desulfurization efficiency attained was 15%.

Comparative Example 2

20   The system of FIG. 8 was operated under the same conditions as in Comparative Example 1 with the exception of charging no desulfurizing agent into the combustion chamber 16 and placing ash of the composition given in Example 2, Table 1 into the reaction chamber 11.

25   The ash was prepared from the ash collected by

-33-

the bag filter 13, by concentrating the waste desulfu-
rising agent in the ash with use of a pneumatic classi-
fier. The ash was used in such an amount that the ratio
of Ca from CaO and $CaCO_3$ to S, i.e., Ca/S, was 2.1.

5   At a reaction temperature of 780° C, the desulfurization
efficiency achieved was 10 to 15%, and the denitration
efficiency 0%.

Example 3

With the same ash containing the waste desulfu-
10   rizing agent as used in Comparative Example 2 was admixed
urea in the ratio by weight of 4:1 or 9:1 to prepare
mixtures (a) and (b) which were each an ash containing
the waste and the urea serving as a reducing agent. The
system of FIG. 8 was operated under the same conditions
15   as in Comparative Example 1 with the exception of varying
the amount of the mixture to be charged into the reaction
chamber 11. Table below shows the desulfurization
efficiencies and the denitration efficiencies attained.

Ca/S ratio	4:1 Mixture (a)		9:1 Mixture (b)	
	Desulfu-rization (%)	Denitration (%)	Desulfu-rization (%)	Denitration (%)
0.9	39	50	30	47
1.1	53	71	33	61
1.3	60	79	36	78
2.0	90	97	60	98

-34-

In the present example, the ash discharged from the bag filter was checked for ammonium ion, but no ammonium ion was detected.

Example 4

5   This example corresponds to the fourth process of the invention.

In the tests and application example described below, the test apparatus used was a furnace having a capacity of about 0.38 m^3 and adapted to burn pulverized
10   coal at a rate of up to 10 kg/hour. The pulverized coal used was Tatung coal not larger than 200 mesh in particle size. The SO_2 concentration of the exhaust gas was adjusted to 800 ppm by addition of liquefied SO_2. The internal temperature of the furnace was maintained at
15   an optimum level by controlling the amount of heat to be dissipated. For the denitration test, the supply of the pulverized coal was regulated, and the temperature was adjusted to an optimum temperature for denitration. The NOx then produced was 190 to 210 ppm.

20   The desulfurizing agent tested was finely divided $CaCO_3$ up to 3 μ in particle size. The waste desulfurizing agent having an unreacted substance enclosed therein was activated with hydrogen chloride gas, acetic acid, chlorine gas, bromine gas or the like. The
25   denitrating agent used was liquefied ammonia or urea

powder. During testing, the exhaust gas was produced at a total rate of 100 to 120 Nm^3/hour. The desulfurizing agent and the waste thereof enclosing the unreacted substance were dispersed into the furnace by an air spray

5 method.

Test 1

The amount of $CaCO_3$ was increased stepwise from 1 to 3 in terms of Ca/S ratio and checked for SO_2 absorbing ability. In this test, the improving

10 methods i) to iii) described above

were investigated. FIG. 9, Curve A represents an example of test result. The desulfuriza- tion efficiency attained was 90% at Ca/S = 3 and exceedingly higher than that in the EPA report, thus

15 substantiating the great feasibility of the furnace desulfurization process.

Test 2

The waste desulfurizing agent was checked for desulfurization efficiency. $CaSO_4$ was removed from the

20 waste agent having the unreacted substance enclosed therein. The amount of the resulting waste agent was increased stepwise from 1 to 4 in Ca/S ratio based on effective Ca and checked for SO_2 absorbing ability. FIG. 9, Curve B represents the result. The desulfuriza-

25 tion efficiency achieved was 68% at Ca/S = 3. The

result reveals that although the waste desulfurizing
agent enclosing the unreacted substance is less efficient
than the fresh one, the waste attains a higher desulfu-
rization efficiency when used in an increased amount.

5 Test 3

Each of hydrogen chloride gas, acetic acid
vapor, chlorine gas, bromine gas, etc. was singly used
for treating the same waste desulfurizing agent enclosing
the unreacted substance as used in Test 3, and the result-
10 ing wastes were checked for desulfurization efficiency.
Consequently, it was found that the efficiency varied
greatly according to the degree of neutralization of
the unreacted substance CaO (inclusive of $CaCO_3$) in the
waste with the acid. As an example, FIG. 9, Curve C
15 shows the relationship between Ca/S and the desulfuriza-
tion efficiency achieved by the waste containing 10%
neutralization product based on the amount of effective
Ca and treated with hydrogen chloride gas. Curve C
reveals a desulfurization efficiency of at least 90% at
20 Ca/S = 3, indicating that the waste agent containing the
unreacted substance and treated with the acid was
activated by the neutralization to effect desulfurization
more efficiently than the fresh agent.

Test 4

25 The waste desulfurizing agent activated with

-37-

hydrogen chloride gas in Test 3 was further treated with ammonia gas.

In this test, the supply of pulverized coal was limited, and the temperature at the position where the unreacted substance enclosing waste agent was injected was adjusted to 900° C. The quantity of NOx produced at this time was 200 ppm. The amount of ammonia used was increased stepwise from 1 to 5 in terms of NH_3/NO ratio, and the waste was checked for denitration efficiency. The result is shown in FIG. 10, which indicates that a constant NOx removal efficiency of 70% was attained at the NH_3/NO ratio of 3 or higher.

A powder of urea, when to be used, was supplied in such an amount that the NH_3/NO ratio was about twice the corresponding value for ammonia. The denitration efficiency then achieved was comparable to that attained by ammonia. Thus, urea was somewhat less effective than ammonia. However, use of urea resulted in a higher SO_2 removable efficiency and was therefore effective also for desulfurization.

Application Example

In view of the foregoing test results, the present process was practiced in a boiler test plant wherein pulverized coal was supplied at a rate of 1800 kg/hour (dry base).

-38-

FIG. 11 shows the process flow according to the invention. With reference to the flow chart, pulverized coal is burned by a low-NOx combustion device 43 for a test boiler 41. The furnace of the boiler 41

5   has a temperature of 900 to 1200° C. A desulfurizing agent in a tank 51 is sent out to a supply line by a feeder 52 and pneumatically transported to a nozzle 42, from which the agent is sprayed into the furnace. A desulfurization reaction takes place in the furnace,

10   reducing the SO_2 concentration of the exhaust gas in corresponding relation to the amount of supply of Ca. However, the effective Ca utilization ratio inside the furnace is lower than 35%. The waste desulfurizing agent enclosing the unreacted substance and the ash of

15   the pulverized coal become mixed together, pass through a heater 44 and then through an air heater 47, and reach a dust collector 48, in which the ash containing the unreacted substance-enclosing waste is trapped. The exhaust gas flows through a suction fan 49 and then

20   through a stack 50 and is discharged from the system. The collected ash is pneumatically transported from the dust collector 48 to an ash tank 53, in which it is accumulated. The air used for the transport is discharged from the system via a bag filter 54. The ash

25   containing the unreacted substance-enclosing waste

-39-

is partly discharged from the tank 53, pneumatically
transported by a feeder 55 through a recycle line 56 to
a nozzle 55, by which the ash is sprayed into a flue 46.
Hydrogen chloride gas is supplied to the recycle line 56

5   to partly neutralize the waste desulfurizing agent having
the unreacted substance enclosed therein. The neutralized
waste agent undergoes a complete activation reaction
within the recycle line 56. Ammonia is introduced into
the recycle line 56 in the vicinity of the ash spray

10   nozzle 45. The ash thus obtained and containing the
neutralized salt and the reducing agent undergoes a
desulfurization reaction again at a temperature of 500 to
1000° C in the flue 46 to the upper portion of the air
heater 47 and also undergoes a denitration reaction at

15   the same time. In this way, desulfurization and
denitration are effected simultaneously. Typical condi-
tions for the present process are given below.

a) Combustion of Coal

Item	Value	Unit	Remarks
Kind	Tatung coal	-	
Rate of combustion of pulverized coal	1800	kg/h	dry base (9.3% ash)
SO_2 concn.	800	ppm	adjusted with liquefied SO_2
NOx concn.	200	ppm	after NOx-inhibited combustion
Rate of discharge of exhaust gas	about 17000	Nm^3/h	dry base

-40-

b) Desulfurizing Agent

Item	Value	Unit	Remarks
Kind	$CaCO_3$	-	Up to 3 μ in mean particle size
Supply rate	122	kg/h	
Ca/S equivalent ratio	2.0	-	

c) Ash Containing Waste Desulfurizing Agent

Item	Value
Rate of recycle	1 to 1.5 times the ash discharge rate

d) Hydrogen Chloride Gas

Item	Value	Unit	Remarks
Kind	HCl	-	for industrial use
Rate of supply	4.8	kg/h	
Ratio of conversion to $CaCl_2$	10	%	

e) Ammonia

Item	Value	Unit	Remarks
Kind	Ammonia gas	-	for industrial use
Rate of supply	7.7	kg/h	

f) Composition of Exhaust Gas

Item	Value	Unit
SO_2	50 - 80	ppm
NOx	50 - 60	ppm
HCl	up to 18	ppm

g) Discharged Ash

Item	Value	Unit	Remarks
Rate of discharge	283	kg/h	dry base
Composition			
$CaSO_4$	26.3		
CaO	11.9	wt. %	effective Ca
			utilization ratio 45%
$CaCl_2$	2.5		
Ash	59.3		

The above description thus describes a dry desulfurization process wherein a specific desulfurizing agent is used to thereby achieve a high desulfurization efficiency comparable to that of the wet process. The description also describes a process for removing SOx and NOx at the same time at a low cost, each at a high efficiency.

Whilst endeavouring in the foregoing specification to draw attention to those features of the invention believed to be of particular importance it should be understood that the Applicant claims protection in respect of any patentable feature or combination of features hereinbefore referred to and/or shown in the drawings whether or not particular emphasis has been placed thereon.

CLAIMS

1.   A furnace desulfurization process comprising
supplying a desulfurizing agent into a furnace or flue to
cause the agent to absorb SO_2 from the exhaust gas, the
desulfurizing agent being a salt obtained by at least
partly neutralizing a calcium-based desulfurizing agent
with an acid.

2.   A process as defined in claim 1, wherein the acid
is an organic acid or a combination of organic acids.

3.   A process as defined in claim 2, wherein the
organic acid or one of the organic acids is acetic acid,
oxalic acid or formic acid.

4.   A process as defined in claim 1, 2 or 3 wherein an
organic acid salt of a desulfurizing metal is used as the
desulfurizing agent in the form of a salt.

5.   A process as defined in claim 4 and claim 2 or 3,
wherein calcium acetate is used as the organic acid salt
of desulfurizing metal.

6.   A process as defined in any one of claims 1 to 5,
wherein the desulfurizing agent in the form of a salt is
blown in the form of a powder or slurry into the furnace

43

or flue in a region thereof having a temperature of 500°C to 1200°C.

7.   A furnace desulfurization process comprising supplying a calcium-based desulfurizing agent into a furnace or flue to effect a first-stage desulfurization reaction, collecting ash containing a waste of the agent having an unreacted substance enclosed therein from the exhaust gas, reacting an acid or acids with the collected ash to form a salt by at least partly neutralizing the unreacted portion of the desulfurizing agent, and recycling the ash containing the salt into the furnace or flue to effect a second-stage desulfurization reaction.

8.   A process as defined in claim 7, wherein the or at least one of the acids is inorganic.

9.   A process as defined in claim 8, wherein the or one of the acids is hydrochloric acid, nitric acid or hydrogen chloride or an inorganic acid of chlorine, bromine, fluorine or iodine.

10.   A process as defined in any of claims 7 to 9, wherein the or at least one of the acids is organic.

11.   A process as defined in claim 10, wherein the or one of the acids is acetic acid, oxalic acid or formic acid.

44

12. A dry simultaneous desulfurization-denitration process comprising supplying a calcium-based desulfurizing agent into a furnace or flue to effect a desulfurization reaction, collecting ash containing a waste of the agent having an unreacted substance enclosed therein from the exhaust gas, adding a denitrating reducing agent to the collected ash, and recycling the ash containing the waste desulfurizing agent and the reducing agent into the furnace or flue to effect desulfurization and denitration reactions.

13. A process as defined in claim 12, wherein the calcium-based desulfurizing agent is supplied into the furnace or flue along with the ash containing the waste desulfurizing agent and the reducing agent.

14. A process as defined in claim 12 or 13, wherein the denitrating reducing agent is in the form of a powder or solution and comprises ammonia, an ammonium salt, urea or a urea derivative.

15. A process as defined in claim 14, wherein the denitrating reducing agent comprises ammonium carbonate, ammonium formate or ammonium oxalate.

16. A process as defined in any one of claims 12 to 15 wherein the ash containing the waste desulfurizing agent

45

and the reducing agent is blown in the form of a powder
or slurry into the furnace or flue in a region thereof
having a temperature of 500°C to 1000°C.

17.   A dry simultaneous desulfurization-denitration
process comprising supplying a Ca desulfurizing agent
into a furnace or flue to effect a desulfurization
reaction, collecting ash containing a waste of the agent
having an unreacted substance enclosed therein from the
exhaust gas, adding an acid to the collected ash to at
least partly neutralize the unreacted substance, adding a
denitrating reducing agent to the ash containing the
resulting salt, and recycling the ash containing the salt
and the reducing agent into the furnace or flue to effect
desulfurization and denitration reactions.

18.   A process as defined in claim 17, wherein the ash
containing the salt and the reducing agent is blown in
the form of a powder or slurry into the furnace or flue
in a region thereof having a temperature of 500°C to
1000°C.

19.   A process as defined in claim 17 or 18, wherein the
denitrating reducing agent is in the form of a powder or
solution and comprises ammonia, an ammonium salt, urea or
a urea derivative.

20.   A process as defined in claim 19, wherein the

denitrating reducing agent comprises ammonium carbonate, ammonium formate or ammonium oxalate.

21. A process as defined in any of claims 17 to 20, wherein the or at least one of acids is inorganic.

22. A process as defined in claim 21, wherein the or one of the acids is hydrochloric acid, nitric acid or hydrogen chloride or an inorganic acid of chlorine, bromine, fluorine or iodine.

23. A process as defined in any of claims 17 to 22, wherein the or at least one of the acids is organic.

24. A process as defined in claim 23, wherein the or one of the acids is acetic acid, oxalic acid or formic acid.

25. A process for treating combustion exhaust gas, substantially as described in any of the examples set out above, with reference to the accompanying drawings.

26. Any novel subject matter or combination including novel subject matter disclosed, whether or not within the scope of or relating to the same invention as any of the preceding claims.

47