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An agency of Industry Canada

CA 2622064 C 2014/11/18

(11)(21) **2 622 064**

(12) BREVET CANADIEN / CANADIAN PATENT

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date:** 2006/09/14
(87) **Date publication PCT/PCT Publication Date:** 2007/03/22
(45) **Date de délivrance/Issue Date:** 2014/11/18
(85) **Entrée phase nationale/National Entry:** 2008/03/10
(86) **N° demande PCT/PCT Application No.:** EP 2006/066358
(87) **N° publication PCT/PCT Publication No.:** 2007/031551
(30) **Priorité/Priority:** 2005/09/15 (US11/229,011)

(51) **Cl.Int./Int.Cl.** ***B01D 53/50*** (2006.01)

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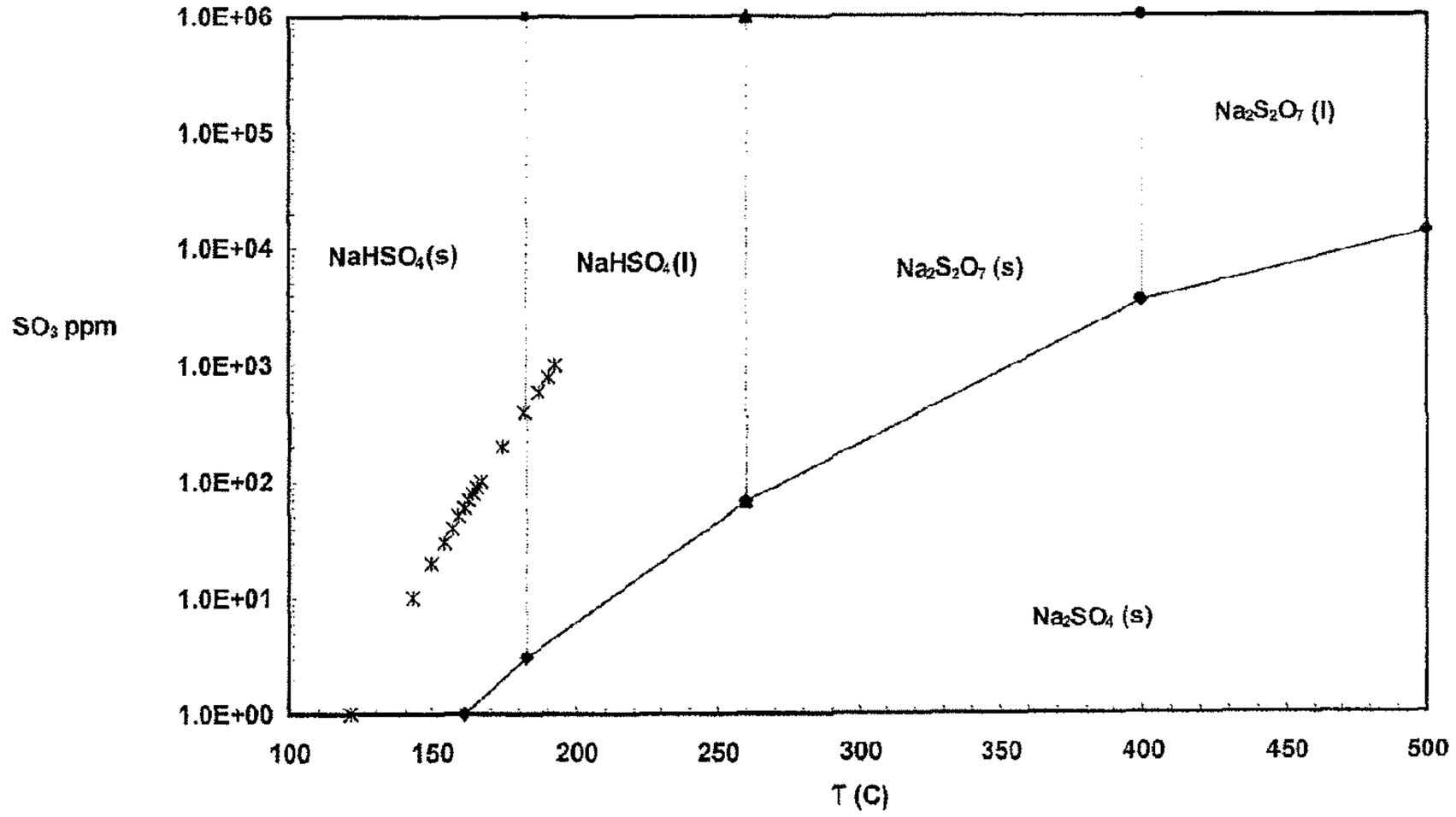
(54) **Titre : PROCEDE D'ELIMINATION DE TRIOXYDE DE SOUFRE DANS UN FLUX DE GAZ DE COMBUSTION**
(54) **Title: METHOD OF REMOVING SULFUR TRIOXIDE FROM A FLUE GAS STREAM**



(57) **Abrégé/Abstract:**
A method of removing SO_3 from a flue gas stream includes providing a reaction compound selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, and mixtures thereof. The reaction compound is injected into the flue gas stream. The temperature of the flue gas is between about 500° F and about 850° F. The reaction compound is maintained in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 March 2007 (22.03.2007)

PCT

(10) International Publication Number
WO 2007/031551 A1

(51) International Patent Classification:
B01D 53/50 (2006.01)

(21) International Application Number:
PCT/EP2006/066358

(22) International Filing Date:
14 September 2006 (14.09.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/229,011 15 September 2005 (15.09.2005) US

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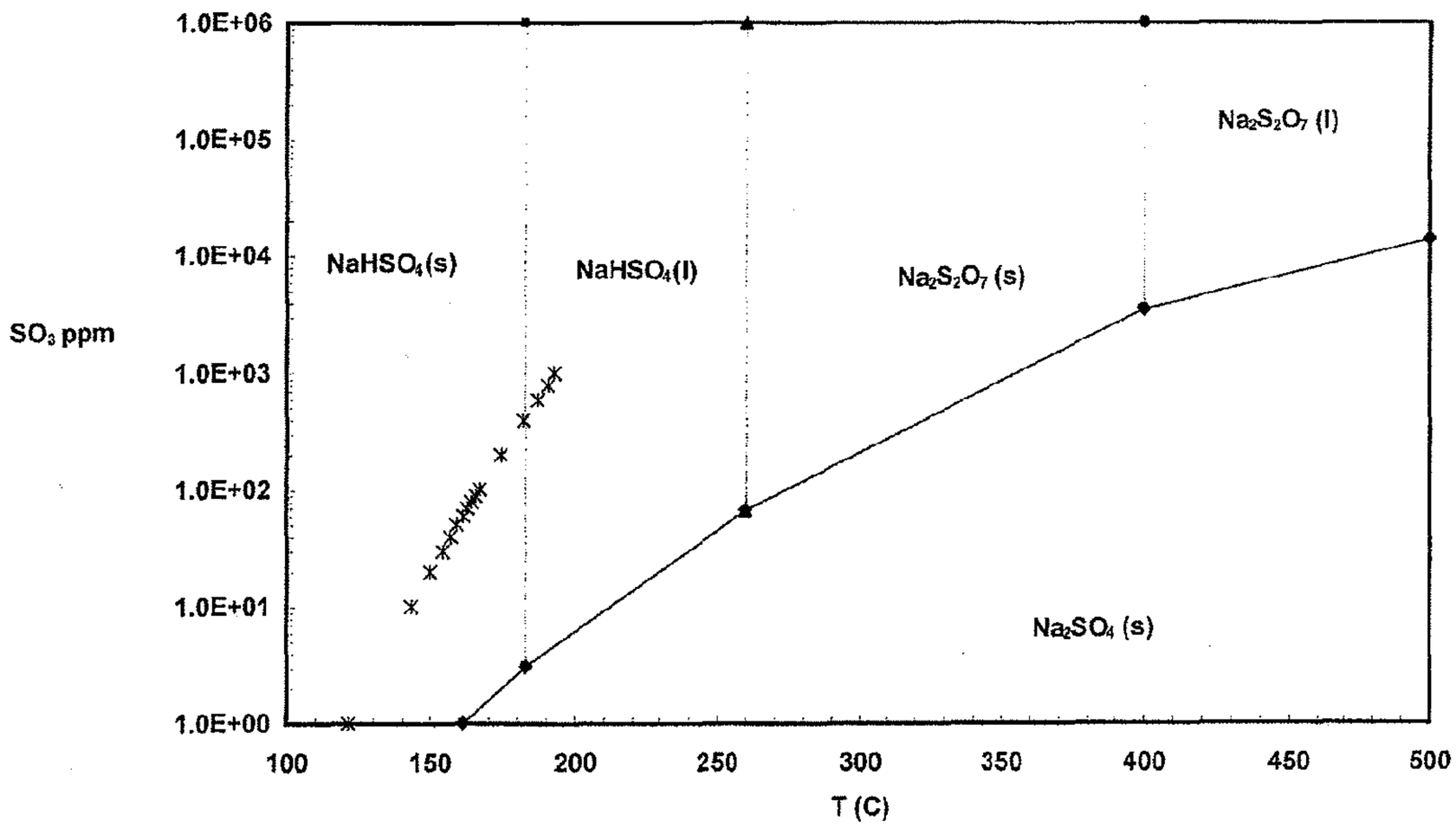
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF REMOVING SULFUR TRIOXIDE FROM A FLUE GAS STREAM



(57) Abstract: A method of removing SO_3 from a flue gas stream includes providing a reaction compound selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, and mixtures thereof. The reaction compound is injected into the flue gas stream. The temperature of the flue gas is between about 500° F and about 850° F. The reaction compound is maintained in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream.

WO 2007/031551 A1

Method of removing sulfur trioxide from a flue gas stream

The present invention relates to the purification of gases, and more particularly to a method of purifying flue gases which contain noxious gases such as SO_3.

SO_3 is a noxious gas that is produced from the combustion of sulfur-containing fuel. When present in flue gas, the SO_3 can form an acid mist that condenses in electrostatic precipitators, ducts or bag houses, causing corrosion. SO_3 at concentrations as low as 5-10 ppm in exhaust gas can also result in white, blue, purple, or black plumes from the cooling of the hot stack gas in the cooler air in the atmosphere.

The effort to reduce NO_x emissions from coal-fired power plants via selective catalytic reactors (SCRs) has resulted in the unintended consequence of oxidizing SO_2 to SO_3 and thereby increasing total SO_3 emissions. SCRs employ a catalyst (typically vanadium pentoxide) to convert NO_x to N_2 and H_2O with the addition of NH_3, but there is also an unintended oxidation of the SO_2 to SO_3. Although the higher stack SO_3 concentrations are still relatively low, the emissions can sometimes produce a highly visible secondary plume, which, although unregulated, is nonetheless perceived by many to be problematic. Efforts to reduce the SO_3 levels to a point where no secondary SO_3 plume is visible can impede particulate collection for stations that employ electrostatic precipitators (ESPs). SO_3 in the flue gas absorbs onto the fly ash particles and lowers fly ash resistivity, thereby enabling the ESP to capture the particle by electrostatic means. Some plants actually inject SO_3 to lower fly ash resistivity when ash resistivity is too high.

SO_3 reacts with water vapor in the flue gas ducts of the coal power plant and forms vaporous H_2SO_4. A portion of this condenses out in the air heater baskets. Another portion of the sulfuric acid vapor can condense in the duct if the duct temperature is too low, thereby corroding the duct. The remaining acid vapor condenses either when the plume is quenched when it contacts the relatively cold atmosphere or when wet scrubbers are employed for flue gas desulfurization (FGD), in the scrubber's quench zone. The rapid quenching of the acid vapor in the FGD tower results in a fine acid mist. The droplets are often too fine to be absorbed in the FGD tower or to be captured in the mist

eliminator. Thus, there is only limited SO_3 removal by the FGD towers. If the sulfuric acid levels emitted from the stack are high enough, a secondary plume appears.

Dry sorbent injection (DSI) has been used with a variety of sorbents to remove SO_3 and other gases from flue gas. However, DSI has typically been done in the past at temperatures lower than around 370° F because equipment material, such as baghouse media, cannot withstand higher temperatures. Additionally, many sorbent materials sinter or melt at temperatures greater than around 400° F, which makes them less effective at removing gases. The reaction products of many sorbent materials also adhere to equipment and ducts, which requires frequent cleaning of the process equipment.

In one aspect, a method of removing SO_3 from a flue gas stream including SO_3 is provided. The method includes providing a reaction compound selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, and mixtures thereof. The reaction compound is injected into the flue gas stream. The temperature of the flue gas is between about 500° F and about 850° F. The reaction compound is maintained in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream.

In another aspect, a method of removing SO_3 from a flue gas stream including at least about 3 ppm SO_3 includes providing a source of trona having a mean particle size between about 10 micron and about 40 micron. The trona is injected as a dry granular material into the flue gas stream. The temperature of the flue gas is between about 275° F and about 365° F. The trona is maintained in contact with the flue gas for a time sufficient to react a portion of the sodium sorbent with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream. The reaction product comprises Na_2SO_4.

The invention as claimed is however more specifically directed to a method of removing SO_3 from a flue gas stream comprising SO_3 at a concentration between 10 ppm and 200 ppm, comprising:

- providing a reaction compound selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, and mixtures thereof;
- injecting the reaction compound into the flue gas stream, wherein the temperature of the flue gas is between about 500°F and about 850°F; and
- maintaining the reaction compound in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream, wherein the reaction product of the reaction compound and the SO_3 is less than 5% NaHSO4 and is collected on an electrostatic precipitator.

The foregoing paragraphs have been provided by way of general introduction, and are not intended to limit the scope of the following claims. The presently preferred embodiments, together with further advantages, will be best understood by reference to the following detailed description taken in conjunction with the accompanying drawings.

FIG. 1 is a phase diagram showing the reaction products of trona with SO_3 as a function of flue gas temperature and SO_3 concentration.

FIG. 2 is a schematic of one embodiment of a flue gas desulfurization system.

The invention is described with reference to the drawings in which like elements are referred to by like numerals. The relationship and functioning of the various elements of this invention are better understood by the following detailed description. However, the embodiments of this invention as described below are by way of example only, and the invention is not limited to the embodiments illustrated in the drawings.

Dry sorbent injection (DSI) has been used as a low cost alternative to a spray dry or wet scrubbing system for the removal of SO_3. In the DSI process, the sorbent is stored and injected dry into the flue duct where it reacts with the acid gas. Under certain processing conditions, the reaction product of the sorbent and the acid gas is a sticky ash. The sticky ash tends to stick to the process equipment and ducts, thus requiring frequent cleaning. Thus, it would be beneficial to have a process that minimizes the amount of sticky ash reaction product.

The present invention provides a method of removing SO_3 from a flue gas stream comprising SO_3 by injecting a reaction compound such as sodium sesquicarbonate, sodium bicarbonate, or soda ash into a flue gas stream to react with SO_3. Sodium sesquicarbonate is preferably provided from trona. Trona is a mineral that contains about 85-95% sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). A vast deposit of mineral trona is found in southwestern Wyoming near Green River. As used herein, the term "trona" includes other sources of sodium sesquicarbonate. The term "flue gas" includes the exhaust gas from any sort of combustion process (including coal, oil, natural gas, etc.). Flue gas typically includes acid gases such as SO_2, HCl, SO_3, and NO_x.

When heated at or above 275° F, sodium sesquicarbonate undergoes rapid calcination of contained sodium bicarbonate to sodium carbonate, as shown in the following reaction:

$$2\ [\ Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O] \rightarrow 3Na_2CO_3 + 5H_2O + CO_2$$

Sodium bicarbonate undergoes a similar reaction at elevated temperatures:

$$2\ NaHCO_3 \rightarrow 3Na_2CO_3 + H_2O + CO_2$$

A preferred chemical reaction of the reaction compound with the SO_3 is represented below:

$$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2$$

However, under certain conditions, undesirable reactions may occur which produce sodium bisulfate. If the sodium sesquicarbonate or sodium bicarbonate

is not completely calcined before reaction with SO_3, the following reaction occurs:

$$NaHCO_3 + SO_3 \rightarrow NaHSO_4 + SO_3$$

Under certain conditions, another undesirable reaction produces sodium bisulfate as represented below:

$$Na_2CO_3 + 2SO_3 + H_2O \rightarrow 2NaHSO_4 + CO_2$$

Sodium bisulfate is an acid salt with a low melt temperature and is unstable at high temperatures, decomposing as indicated in the following reaction:

$$2NaHSO_4 \rightarrow Na_2S_2O_7$$

The type of reaction product of the Na_2CO_3 and the SO_3 depends on the SO_3 concentration and the temperature of the flue gas. FIG. 1 is a phase diagram showing the typical reaction products of trona with SO_3 as a function of flue gas temperature and SO_3 concentration. In particular, above a certain SO_3 concentration, the reaction product can be solid $NaHSO_4$, liquid $NaHSO_4$, Na_2SO_4, or $Na_2S_2O_7$, depending on the flue gas temperature. The boundary between the liquid $NaHSO_4$ and the solid Na_2SO_4 at a temperature above 370° F may be represented by the equation $\log[SO_3]=0.009135T-2.456$, where $[SO_3]$ is the log base 10 of the SO_3 concentration in ppm and T is the flue gas temperature in °F. Liquid $NaHSO_4$ is particularly undesirable because it is "sticky" and tends to adhere to the process equipment, and cause other particulates, such as fly ash, to also stick to the equipment. Thus, it is desirable to operate the process under conditions where the amount of liquid $NaHSO_4$ reaction product is minimized. Thus, the process may be operated at a temperature below about 370° F, above about 525° F, or at a temperature and SO_3 concentration where $\log[SO_3]<0.009135T-2.456$.

The temperature of the flue gas varies with the location in the injection system and may also vary somewhat with time during operation. As the temperature of the flue gas increases, the reaction product of the sodium compound and the SO_3 ranges from solid $NaHSO_4$, to liquid $NaHSO_4$, to solid Na_2SO_4 or $Na_2S_2O_7$. Therefore, to avoid the formation of sticky ash, the process is preferably operated in a suitable temperature range. In one embodiment, the temperature of the flue gas where the trona is injected is between about 500° F and about 850° F. The trona is maintained in contact with the flue gas for a time sufficient to react a portion of the trona with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream. The temperature of the flue gas is preferably greater than about 500° F. The temperature of the flue gas is

preferably less than about 800° F, and most preferably less than about 750° F. The temperature of the flue gas is most preferably between about 525° F and about 750° F. In another embodiment, the temperature of the flue gas is between about 275° F and about 365° F. This temperature range is below the temperature for formation of the sticky $NaHSO_4$.

The SO_3 concentration of the flue gas stream to be treated is generally at least about 3 ppm, and commonly between about 10 ppm and about 200 ppm. In order to avoid the adhesion of waste material on the process equipment, when operated at flue gas temperatures greater than about 500° F the non-gaseous reaction product is preferably less than about 5% $NaHSO_4$, and most preferably less than about 1% $NaHSO_4$. The desired outlet SO_3 concentration of the gas stack is preferably less than about 50 ppm, more preferably less than about 20 ppm, even more preferably less than about 10 ppm, and most preferably less than about 5 ppm. The byproduct of the reaction is collected with fly ash.

Trona, like most alkali reagents, will tend to react more rapidly with the stronger acids in the gas stream first, and then after some residence time it will react with the weaker acids. Such gas constituents as HCl and SO_3 are strong acids and trona will react much more rapidly with these acids than it will with a weak acid such as SO_2. Thus, the injected reaction compound can be used to selectively remove SO_3 without substantially decreasing the amount of SO_2 in the flue gas stream.

A schematic of one embodiment of the process is shown in FIG. 2. The furnace or combustor 10 is fed with a fuel source 12, such as coal, and with air 14 to burn the fuel source 12. From the combustor 10, the combustion gases are conducted to a heat exchanger or air heater 30. Ambient air 32 may be injected to lower the flue gas temperature. A selective catalytic reduction (SCR) device 20 may be used to remove NO_x gases. A bypass damper 22 can be opened to bypass the flue gas from the SCR. The outlet of the heat exchanger or air heater 30 is connected to a particulate collection device 50. The particulate collection device 50 removes particles made during the combustion process, such as fly ash, from the flue gas before it is conducted to an optional wet scrubber vessel 54 and then to the gas stack 60 for venting. The particulate collection device 50 may be an electrostatic precipitator (ESP). Other types of particulate collection devices, such as a baghouse, may also be used for solids removal. The baghouse contains filters for separating particles made during the combustion process from the flue gas.

The SO_3 removal system includes a source of reaction compound 40. The reaction compound is selected from sodium sesquicarbonate, sodium bicarbonate, and soda ash. The reaction compound is preferably provided as particles with a mean particle size between about 10 micron and about 40 micron, most preferably between about 24 micron and about 28 micron. The reaction compound is preferably in a dry granular form.

The reaction compound is preferably sodium sesquicarbonate in the form of trona. A suitable trona source is T-200® trona, which is a mechanically refined trona ore product available from Solvay Chemicals. T-200® trona contains about 97.5% sodium sesquicarbonate and has a mean particle size of about 24-28 micron. The SO_3 removal system may also include a ball mill pulverizer, or other type of mill, for decreasing and/or otherwise controlling the particle size of the trona or other reaction compound.

The reaction compound is conveyed from the reaction compound source 40 to the injector 42. The reaction compound may be conveyed pneumatically or by any other suitable method. Apparatus for injecting the reaction compound is schematically illustrated in FIG. 2. The injection apparatus 42 introduces the reaction compound into flue gas duct section 44, which is preferably disposed at a position upstream of the air heater 30. The injection system is preferably designed to maximize contact of the reaction compound with the SO_3 in the flue gas stream. Any type of injection apparatus known in the art may be used to introduce the reaction compound into the gas duct. For example, injection can be accomplished directly by a compressed air-driven eductor. Ambient air 32 may be injected to lower the flue gas temperature before the injection point 42.

The process requires no slurry equipment or reactor vessel if the reaction compound is stored and injected dry into the flue duct 44 where it reacts with the acid gas. However, the process may also be used with humidification of the flue gas or wet injection of the reaction compound. Additionally, the particulates can be collected wet through an existing wet scrubber vessel 54 should the process be used for trim scrubbing of acid mist. In particular, the flue gas desulfurization system may be operated so that the SO_3 removal is accomplished by injecting the reaction compound with the SO_3, while the majority of the SO_2 is removed by the wet scrubber 54.

The process may also be varied to control the flue gas temperature. For example, the flue gas temperature upstream of the trona may be adjusted to obtain the desired flue gas temperature where the reaction compound is injected.

Additionally, ambient air 32 may be introduced into the flue gas stream to lower the flue gas temperature and the flue gas temperature monitored where the reaction compound is injected. Other possible methods of controlling the flue gas temperature include using heat exchanges and/or air coolers. The process may also vary the trona injection location or include multiple locations for reaction compound injection.

For the achievement of desulfurization, the reaction compound is preferably injected at a rate with respect to the flow rate of the SO_3 to provide a normalized stoichiometric ratio (NSR) of sodium to sulfur of about 1.0 or greater. The NSR is a measure of the amount of reagent injected relative to the amount theoretically required. The NSR expresses the stoichiometric amount of sorbent required to react with all of the acid gas. For example, an NSR of 1.0 would mean that enough material was injected to theoretically yield 100 percent removal of the SO_3 in the inlet flue gas; an NSR of 0.5 would theoretically yield 50 percent SO_3 removal. The reaction of SO_3 with the sodium carbonate is very fast and efficient, so that a NSR of only one is generally required for SO_3 removal. The reaction compound preferentially reacts with SO_3 over SO_2, so SO_3 will be removed even if large amounts of SO_2 are present. Preferably, an NSR of less than 2.0 or more preferably less than 1.5 is used such that there is no substantial reduction of the SO_2 concentration in the flue gas caused by reaction with excess sorbent.

In one embodiment, the flue gas stream further comprises SO_2, and sufficient reaction compound is added to also remove some of the SO_2. The reaction compound is maintained in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_2 to reduce the concentration of the SO_2 in the flue gas stream. This may be particularly useful in small plants, where it is more economical to have a single system for removing both SO_2 and SO_3 rather than adding a wet scrubber to remove the SO_2.

Because NO_x removal systems tend to oxidize existing SO_2 into SO_3, the injection system may also be combined with an NO_x removal system. The trona injection system may also be combined with other SO_x removal systems, such as sodium bicarbonate, lime, limestone, etc. in order to enhance performance or remove additional hazardous gases such as HCl, NO_x, and the like.

Surprisingly, it has been observed that when the temperature of the flue gaz is between about 500°F and about 850°F (preferably between about 550°F and

about 750°F), or between about 275°F and about 365°F, the reaction product is not sticky. Solid build ups in the filter are avoided, in particular when it is a ESP. This effect is particularly pronounced in the upper temperature range.

Consequently, he invention concerns also the use of the method of removing SO_3 from a flue gaz according to the invention and its preferred embodiments to avoid the formation of sticky reaction products.

EXAMPLES

Studies were conducted in an electric generation plant in Ohio using a hot side electrostatic precipitator (ESP) and no baghouse. The plant used a catalyst for NO_x removal, which caused elevated SO_3 levels in the flue gas. The SO_3 concentration in the flue gas was between about 100 ppm and about 125 ppm. The trona used was T-200® from Solvay Chemicals.

EXAMPLE 1

T-200® trona was injected into the flue gas at a flue gas temperature of 367° F. A perforated plate of an ESP in the plant had significant solids buildup after operation of the SO_3 removal system for about two weeks.

EXAMPLE 2

The operation of Example 1 was repeated with the change that the trona was injected at a flue gas temperature below 365° F. In comparison to the perforated plate of Example 1, a perforated plate of an ESP in the plant had significantly less solids buildup after operation of the SO_3 removal system for two weeks than.

EXAMPLE 3

The operation of Example 1 is repeated with the change that the trona is injected into flue gas at a temperature of about 500° F. A perforated plate of an ESP in the plant is relatively free of solids buildup after operation of the SO_3 removal system for two weeks using T-200® trona.

Of course, the scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

CLAIMS

1. A method of removing SO_3 from a flue gas stream comprising SO_3 at a concentration between 10 ppm and 200 ppm, comprising:

   - providing a reaction compound selected from the group consisting of sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, and mixtures thereof;

   - injecting the reaction compound into the flue gas stream, wherein the temperature of the flue gas is between about 500°F and about 850°F; and

   - maintaining the reaction compound in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_3 to reduce the concentration of the SO_3 in the flue gas stream, wherein the reaction product of the reaction compound and the SO_3 is less than 5% NaHSO4 and is collected on an electrostatic precipitator.

2. The method of claim 1 further comprising providing an NOx removal system upstream of the location where the reaction compound is injected.

3. The method of claim 1 or 2 wherein the reaction compound is sodium sesquicarbonate.

4. The method of any one of claims 1 to 3 wherein the reaction compound is provided in the form of particles with a mean particle size of less than about 40 micron.

5. The method of claim 4 wherein the mean particle size of the reaction compound is between about 10 micron and about 40 micron.

6. The method of claim 5 wherein the mean particle size of the reaction compound is between about 24 micron and about 28 micron.

7. The method of any one of claims 1 to 6 wherein the temperature of the flue gas is greater than about 550°F.

8. The method of any one of claims 1 to 6 wherein the temperature of the flue gas is less than about 750°F.

9. The method of any one of claims 1 to 6 wherein the temperature of the flue gas is between about 550°F and about 750°F.

10. The method of any one of claims 1 to 9 wherein the reaction compound is injected at a rate with respect to the flow rate of the SO_3 to provide a normalized stoichiometric ratio of sodium to sulfur of between about 1.0 and 1.5.

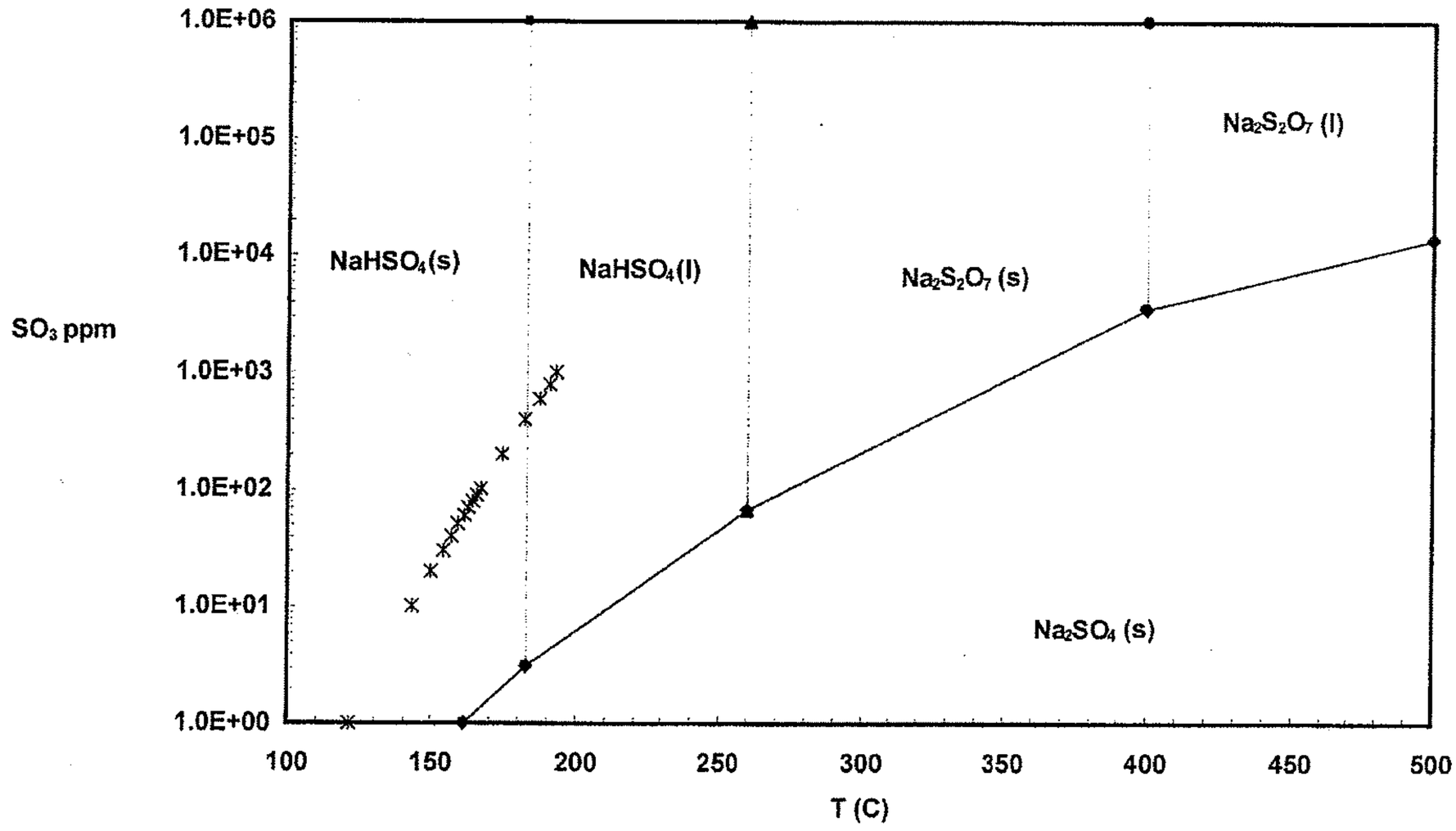
11. The method of any one of claims 1 to 10 wherein the reaction compound is injected as a dry material.

12. The method of any one of claims 1 to 11 further comprising milling the reaction compound to a desired mean particle size at a location proximate the flue gas stream.

13. The method of any one of claims 1 to 12 wherein the flue gas stream further comprises SO_2, the method further comprising maintaining the reaction compound in contact with the flue gas for a time sufficient to react a portion of the reaction compound with a portion of the SO_2 to reduce the concentration of the SO_2 in the flue gas stream.

14. The method of any one of claims 1 to 13 wherein the concentration of SO_3 after reaction with the reaction compound is less than 5 ppm.

FIG. 1


1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
SO3 ppm
NaHSO4(s)
NaHSO4(l)
Na2S2O7 (s)
Na2S2O7 (l)
Na2SO4 (s)
100
150
200
250
300
350
400
450
500
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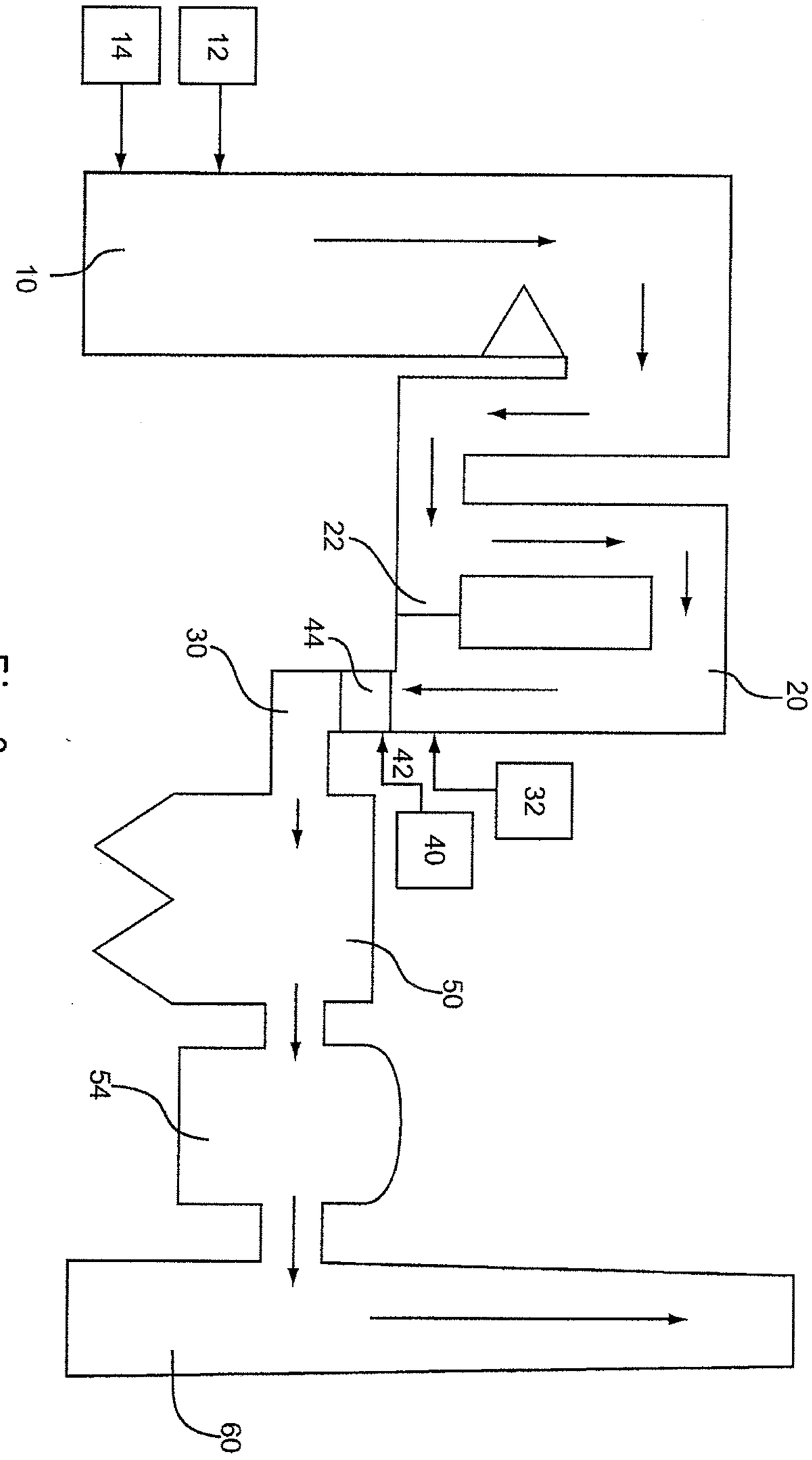
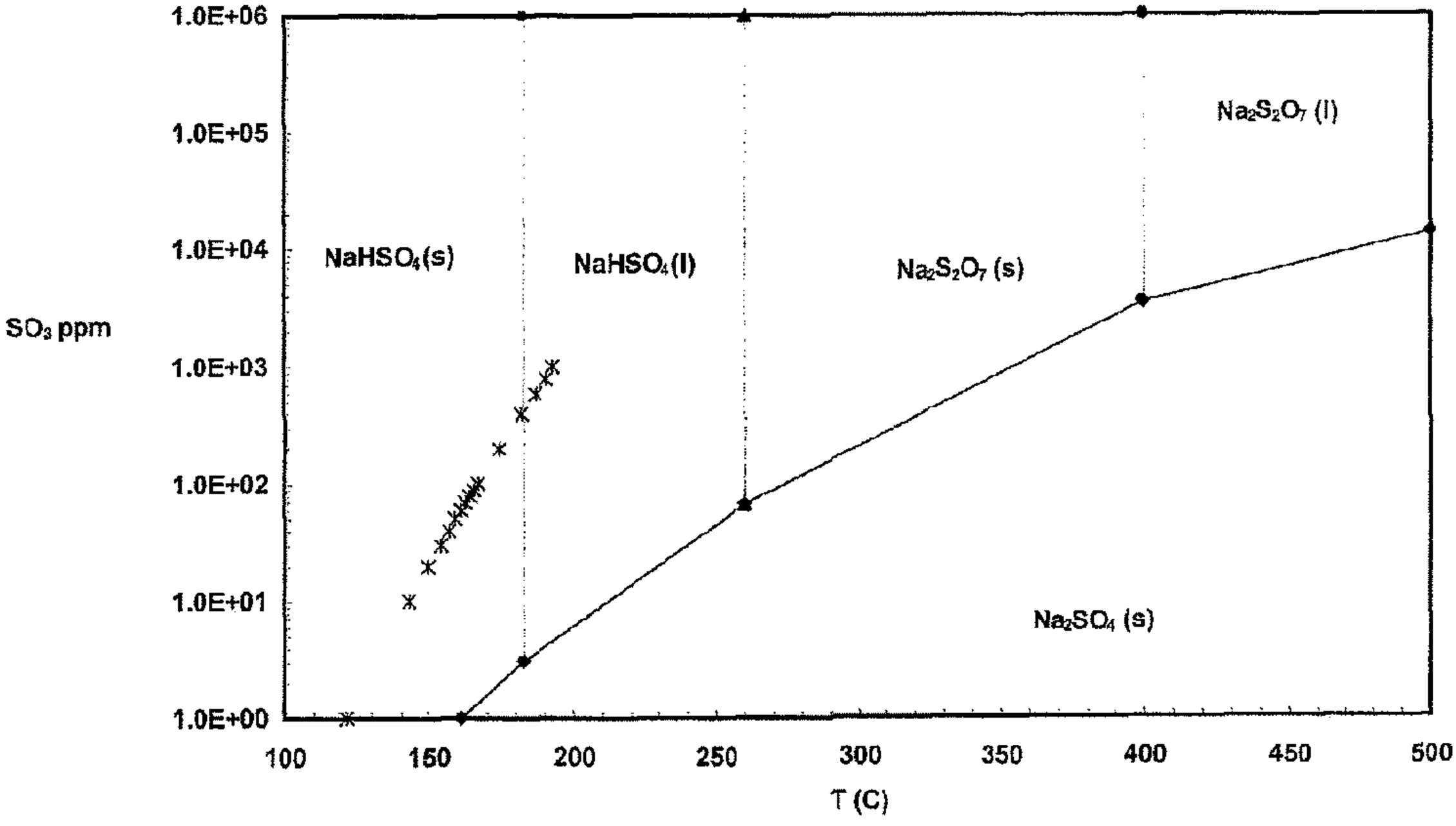


Fig.2


1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
SO3 ppm
NaHSO4(s)
NaHSO4(l)
Na2S2O7 (s)
Na2S2O7 (l)
Na2SO4 (s)
100
150
200
250
300
350
400
450
500
T (C)