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(54) **Title:** AMMONIA-BASED DESULFURIZATION PROCESS AND APPARATUS THROUGH AMMONIA-ADDING IN DIFFERENT CHAMBERS

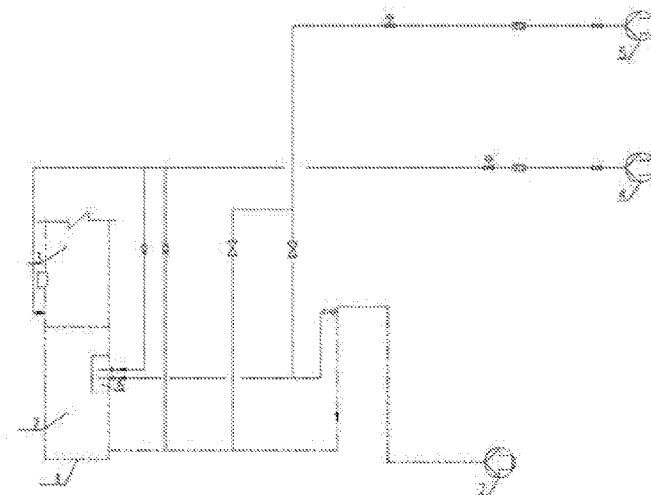


Fig 1

(57) **Abstract:** An ammonia-based desulfurization process through ammonia-adding in different chambers and an apparatus for implementing the process. An oxidation section comprises an oxidation chamber (2) and an ammonia-mixing chamber (6) in fluid communication with each other, and an ammonia absorbent (4) is added to the ammonia-mixing chamber (6).



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# Ammonia-based Desulfurization Process and Apparatus through Ammonia-Adding in Different Chambers

## Technical Field

5 The present invention relates to an ammonia-based desulfurization process through ammonia-adding in different chambers and an apparatus thereof. More particularly, the present invention relates to an ammonia-based desulfurization process through ammonia-adding in different chambers and an apparatus thereof, wherein an oxidation section comprises at least one oxidation chamber and at least  
10 one ammonia-mixing chamber, and an ammonia absorbent is added to the ammonia-mixing chamber.

## Background Art

At present, limestone desulfurization process and ammonia-based  
15 desulfurization process are mainstream processes worldwide for removing sulfur dioxide from gases. In the limestone desulfurization process, large quantities of waste water and gypsum slags are produced during desulfurization, and a lot of investment and operating costs are required to treat these waste water and waste  
20 slags. Also, in the limestone desulfurization process, while 1 ton of sulfur dioxide is removed, about 0.7 ton of carbon dioxide is produced synchronously. With the ammonia-based desulfurization process, basically no waste water or waste slags are produced, and the ammonia desulfurizer that is fed is converted into a useful ammonium sulfate fertilizer, thus it is more environmentally friendly.

Chinese patents CN 1283346C and CN 1321723C disclose a process for  
25 removing SO<sub>2</sub> from coal-fired flue gas by using ammonia as a removal agent, so that the SO<sub>2</sub> concentration in the clean gas is less than 100 mg/Nm<sup>3</sup>. However, the amount of ammonia slip in the clean gas can be up to 12 mg/Nm<sup>3</sup>. In the patents, no attention is paid to the formation of aerosols.

Chinese Patent CN 100428979C discloses an ammonia-based desulfurization  
30 process and an apparatus thereof by crystallization inside a tower, wherein the desulfurization tower is designed to be of a multi-section structure, successively including an oxidation section, a crystallization section, a cooling absorption section, a main absorption section, and a dehydration-demisting section from

bottom to top. In the process, the evaporating ability of flue gas is utilized for crystallization to reduce operation energy consumption, the SO<sub>2</sub> concentration in the clean gas is less than 200 mg/Nm<sup>3</sup>, and the ammonia content in the clean gas can be as low as 3 mg/Nm<sup>3</sup>.

5 Chinese Patent CN 103301705B discloses an apparatus and a process for controlling fine particulate matters in desulfurized flue gas, wherein an absorption liquid demister for removing most of the droplets larger than 10 μm and a flue gas demister for removing fine particulate matters by rewashing and water scrubbing are provided after an absorption section, thereby achieving no less than 60%  
10 removal rate of fine particulate matters.

However, there is still a need for an ammonia-based desulfurization process through ammonia-adding in different chambers and an apparatus thereof capable of further inhibiting ammonia slip and aerosol formation.

## 15 **Summary of the Invention**

In order to address the problems of ammonia slip and aerosol formation suffered by the prior art ammonia-based desulfurization processes, the present inventors have conducted diligently researches. The results show that, by adopting the technical means of controlling solutions in different zones of an  
20 ammonia-based desulfurization apparatus to have different compositions through ammonia-adding in different chambers and ammonia-adding in different sections, efficient desulfurization as well as control of ammonia slip and aerosol formation can be achieved. The present invention is thus completed.

Therefore, in one aspect, the present invention relates to an ammonia-based  
25 desulfurization process through ammonia-adding in different chambers, wherein an oxidation section comprises an oxidation chamber and an ammonia-mixing chamber in fluid communication with each other, and an ammonia absorbent is added to the ammonia-mixing chamber.

In an embodiment, the absorption-oxidation cycle of the ammonia-based  
30 desulfurization process comprises liquid circulation between the oxidation chamber and a secondary spray absorption section and liquid circulation between the ammonia-mixing chamber and a primary spray absorption section, and there is a communication between the two circulations at least through the fluid

communication between the oxidation chamber and the ammonia-mixing chamber.

In another aspect, the present invention relates to an ammonia-based desulfurization apparatus, comprising:

5 a primary spray absorption section, configured to allow countercurrent contact between a first spray liquid sprayed from the upper part thereof and a gas stream entering from the lower part thereof, allow to take out the contacted first spray liquid from the lower part thereof to provide a reflux liquid, and allow the preliminarily absorbed gas stream to enter a secondary spray absorption section, for example, through a partition with a gas cap;

10 the secondary spray absorption section, configured to allow countercurrent contact between a second spray liquid sprayed from the upper part thereof and the gas stream entering from the primary spray absorption section, and allow to take out the contacted spray liquid from the lower part thereof to provide a reflux liquid; and

15 an oxidation section, comprising:

an oxidation chamber, configured to allow contact and reaction between at least part of the reflux liquid from the secondary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections and an oxygen-containing gas, and allow to take out at least part of the liquid phase from the lower part thereof for circulation to the secondary spray absorption section or both the secondary and primary spray absorption sections; and

25 an ammonia-mixing chamber, configured to be in fluid communication with the oxidation chamber on the top and/or side thereof, allow at least part of the reflux liquid from the primary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections to enter from the upper part thereof and mix with an ammonia absorbent, and allow to take out a liquid stream from the lower part thereof for circulation to the primary spray absorption section or both the secondary and primary spray absorption sections.

30 In an embodiment, the apparatus further comprises a cooling-and-concentrating section in the upstream of the primary spray absorption section, wherein the cooling-and-concentrating section is configured to allow a gas stream to be treated, e.g. a flue gas produced in coal-fired boilers, to be washed and

cooled by a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the gas stream, and allow the cooled gas stream to enter the primary spray absorption section, for example, through a partition with a gas cap.

### **Brief Description of the Drawings**

Drawings are provided to assist in understanding of the present invention. However, the drawings are not intended to limit the present invention in a manner inconsistent with the claims. In the drawings,

Figure 1 is a schematic diagram of a process in accordance with an embodiment of the present invention.

Figure 2 is a schematic flow diagram of an absorption cycle in accordance with an embodiment of the present invention.

Figure 3 is a schematic diagram of openings of an ammonia-mixing chamber in accordance with an embodiment of the present invention.

In the drawings, like reference numerals refer to like streams or units, wherein: 1 means an absorption tower, 2 means an oxidation chamber, 3 means a cooling-and-concentrating section, 4 means an aqueous ammonia, 5 means liquid ammonia, 6 means an ammonia-mixing chamber, 7 means air, 8 means a primary spray absorption section, 9 means a secondary spray absorption section, 10 means a gas cap, 11 means a primary spray absorption circulating pump, and 12 means a secondary spray absorption circulating pump.

### **Description of the Preferred Embodiments**

In one aspect, the present invention provides an ammonia-based desulfurization process through ammonia-adding in different chambers, wherein an oxidation section comprises an oxidation chamber and an ammonia-mixing chamber in fluid communication with each other, and an ammonia absorbent is added to the ammonia-mixing chamber.

In some embodiments, the absorption-oxidation cycle of the ammonia-based desulfurization process comprises liquid circulation between the oxidation chamber and a secondary spray absorption section and liquid circulation between

the ammonia-mixing chamber and a primary spray absorption section, and there is a communication between the two circulations at least through the fluid communication between the oxidation chamber and the ammonia-mixing chamber.

In some embodiments, the ammonia-based desulfurization process comprises:

5 providing a sulfur dioxide-containing gas stream to be treated;

feeding the sulfur dioxide-containing gas stream to be treated into a cooling-and -concentrating section, where the gas stream is washed and cooled using a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating  
10 section using the heat in the gas stream;

allowing the gas stream from the cooling-and-concentrating section to enter the primary spray absorption section, where the gas stream is in countercurrent contact with a first spray absorption liquid;

allowing the gas stream from the primary spray absorption section to enter the  
15 secondary spray absorption section, where the gas stream is in countercurrent contact with a second spray absorption liquid;

feeding the liquid stream from the bottom of the primary spray absorption section and the liquid stream from the bottom of the secondary spray absorption section as a reflux liquid respectively into the ammonia-mixing chamber and the  
20 oxidation chamber, or combining the two streams and then separately feeding the combined liquid stream into the ammonia-mixing chamber and the oxidation chamber, feeding an oxygen-containing gas into the oxidation chamber, and feeding an ammonia absorbent into the ammonia-mixing chamber, which is in fluid communication with the oxidation chamber;

25 feeding at least part of the liquid stream taken out from the lower part of the oxidation chamber as the second spray absorption liquid into the secondary spray absorption section, and optionally, feeding at least part of the liquid stream taken out from the lower part of the oxidation chamber into a subsequent unit to recover ammonium sulfate;

30 feeding the liquid stream taken out from the lower part of the ammonia-mixing chamber as the first spray absorption liquid into the primary spray absorption section; and

venting the gas stream from the upper part of the secondary spray absorption

section after removing the droplets, optionally after further removal of fine particulate matters.

In the process of the present invention, the sulfur dioxide-containing gas to be treated may be any sulfur dioxide-containing gas produced in any industrial production process. Examples of the sulfur dioxide-containing gas to be treated include, but are not limited to, flue gas produced by coal combustion and flue gas produced in a fluidized-bed catalytic cracking process.

In the process of the present invention, ammonia is used as an absorbent to remove sulfur oxides in the gas stream. The ammonia may be in the form of liquid ammonia, gaseous ammonia, aqueous ammonia or a combination thereof.

In the process of the present invention, the oxygen-containing gas may be, for example, oxygen, air, oxygen-enriched air, oxygen-poor air, or the like.

A key feature of the process of the present invention is that, in the oxidation section, the oxidation chamber and the ammonia-mixing chamber in fluid communication with each other are separately provided, and usually the ammonia absorbent is only introduced into the ammonia-mixing chamber. In this way, the oxidation rates and the pH of the materials in the oxidation chamber and the ammonia-mixing chamber can be controlled separately.

In the process of the present invention, the addition method of the ammonia absorbent is not particularly limited. In an embodiment, the ammonia absorbent is added directly to a liquid stream using a tubular distributor, a microporous distributor, a static mixer, or the like. In another embodiment, the ammonia absorbent is first mixed with a gas stream, e.g. air, and then the mixed gas stream is added directly to, for example, the ammonia-mixing chamber, or added to a liquid stream, for example, the liquid stream to the ammonia-mixing chamber, using a tubular distributor, a microporous distributor, a static mixer, or the like. In the case where the ammonia absorbent such as liquid ammonia is mixed with the gas stream, the amount of the gas stream is not particularly limited, but the amount can be preferably such that the volume ratio of the gaseous ammonia after liquid ammonia gasification to the gas stream is 1: 0.03-1: 0.2, preferably 1: 0: 0.3-1: 0.1.

In the process of the present invention, there are two absorption-oxidation cycles, one is the liquid stream circulation between the secondary spray absorption section and the oxidation chamber, and the other is the liquid stream circulation

between the primary spray absorption section and the ammonia-mixing chamber, and there is a communication between the two circulations at least through fluid communication between the oxidation chamber and the ammonia-mixing chamber. In addition, the pipelines transporting circulating spray absorption liquids from the oxidation chamber and the ammonia-mixing chamber can be independent of each other, but a communication pipeline controlled by a valve between the two is preferably arranged to allow adjustment of the amounts and/or pH of the liquids entering the primary spray absorption section and the secondary spray absorption section. In addition, the reflux liquid from the primary spray absorption section and the reflux liquid from the secondary spray absorption section can be fed to the ammonia-mixing chamber and the oxidation chamber respectively, or can be combined, then part of the combined reflux liquid is fed to the ammonia-mixing chamber, and the other part is fed to the oxidation chamber. Based on the total amount of the reflux liquids from the primary spray absorption section and the secondary spray absorption section, 30 vol%-85 vol%, e.g. about 60 vol%-about 70 vol%, for example about 60 vol%, of the reflux liquid enters the ammonia-mixing chamber, and the remaining reflux liquid enters the oxidation chamber.

In a specific embodiment, the spray liquid from the bottom of the primary spray absorption section and the spray liquid from the bottom of the secondary spray absorption section are combined and refluxed, wherein about 60 vol%-about 70 vol%, e.g. 65 vol%, of the combined reflux liquid enters the ammonia-mixing chamber, where the reflux liquid is combined with the ammonia absorbent to adjust the pH value, and the remaining part of the combined reflux liquid enters the oxidation chamber.

In some specific embodiments, liquid ammonia is used as the ammonia absorbent, wherein part of the liquid ammonia (e.g. about 55 mol% based on the total ammonia added to the ammonia-mixing chamber) uniformly enters the reflux liquid part in the ammonia-mixing chamber through a microporous distributor or other types of distributors, while the other part (e.g. about 45 mol% based on the total ammonia added to the ammonia-mixing chamber) is mixed with an oxygen-containing gas, e.g. air, and then added to the ammonia-mixing chamber. The volume of the oxygen-containing gas, e.g. air, is about 3%-about 10%, e.g.

about 5%, of the volume of gaseous ammonia after liquid ammonia gasification.

Mainly by regulating the amount of the ammonia absorbent introduced into the ammonia-mixing chamber and regulating the relative amount of the two adsorption-oxidation cycles, it is possible to control the pH of the circulating liquids at the outlet of the ammonia-mixing chamber and at the outlet of the oxidation chamber and respective oxidation rates in the oxidation chamber and the ammonia-mixing chamber. In some embodiments, the pH of the circulating liquid at the outlet of the ammonia-mixing chamber is in a range of 4.6-8.0, preferably 5.6-6.4, the oxidation rate in the ammonia-mixing chamber is in a range of 93%-99.5%, preferably 97.5%-99%, the pH of the circulating liquid at the outlet of the oxidation chamber is in a range of 4.0-6.8, preferably 4.5-5.9, and the oxidation rate in the oxidation chamber is not less than 98.5%, preferably 98.5%-99.5%. The term "oxidation rate", as used herein, refers to the conversion rate of ammonium sulfite (ammonium bisulfite) in the reflux liquid entering the oxidation chamber and the ammonia-mixing chamber being oxidized to ammonium sulfate.

Optionally, in the process of the present invention, an ammonia absorbent is also added in at least one of the oxidation chamber, the cooling-and-concentrating section (the pH is controlled in a range of 2.5-5.5, preferably in a range of 3-3.5), the primary spray absorption section and the secondary spray absorption section to control the pH of the material in each section.

Referring to Figures 1 and 2, one embodiment of the process of the present invention is described. The gas stream to be treated, e.g. flue gas produced in coal-fired boilers, enters a cooling-and-concentrating section 3, where the gas stream is washed and cooled using a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the flue gas. As shown in Figure 1, an ammonia absorbent 4 (e.g. aqueous ammonia) is also introduced into the gas stream in the cooling-and-concentrating section 3, although this is not necessary. The cooled gas stream enters (e.g. through a gas cap) a primary spray absorption section 8 upward, where the gas stream is in countercurrent contact with a first spray liquid entering through a sprayer from the upper part of the primary spray absorption section 8 so that at least part of the sulfur oxides in the gas stream is absorbed into the spray liquid and the sulfur

oxides content in the gas stream is reduced accordingly. The contacted first spray liquid is collected at the bottom of the primary spray absorption section 8, and is taken out as the reflux liquid entering an oxidation chamber 2 and an ammonia-mixing chamber 6. The gas stream primarily absorbed in the primary spray absorption section 8 enters (e.g. through a gas cap) a secondary spray absorption section 9 upward, where the gas stream is in countercurrent contact with a second spray liquid entering through a sprayer from the upper part of the secondary spray absorption section 9 so that the sulfur oxides content in the gas stream is further reduced and possibly the amount of entrained ammonia is reduced.

The contacted second spray liquid is collected at the bottom of the secondary spray absorption section 9, and is taken out as the reflux liquid entering the oxidation chamber 2 and the ammonia-mixing chamber 6. The gas stream further treated in the secondary spray absorption section 9 may be vented after removing droplets, or vented after further treatment through a subsequent optional section of removing fine particulate matters. The reflux liquid from the secondary spray absorption section 9 or part of the combined reflux liquid from the primary spray absorption section 8 and the secondary spray absorption section 9 (as shown in Figure 1) enters the oxidation chamber 2, and is mixed with an oxygen-containing gas 7, e.g. air, therein so that at least part of ammonium sulfite (ammonium bisulfite) in the reflux liquid is oxidized to ammonium sulfate. Part of the liquid phase in the lower part of the oxidation chamber 2 is taken out through a pipeline 13, at least part of the liquid stream taken out is fed to the upper part of the secondary spray absorption section 9 via a circulating pump 12 as the spray absorption liquid, and optionally, at least part of the liquid stream taken out is fed to a downstream unit for treatment to recover ammonium sulfate. An ammonia-mixing chamber 6 is further provided, and is in fluid communication with the oxidation chamber 2 through openings on the top and side thereof, allowing material exchange between the two chambers. At least part of the reflux liquid from the bottom of the primary spray absorption section 8 or at least part of the combined reflux liquid from the bottom of the primary spray absorption section 8 and the bottom of the secondary spray absorption section 9 enters the ammonia-mixing chamber 6 at its upper part, and is combined with an ammonia absorbent 5 (e.g. liquid ammonia) (e.g. via a microporous distributor). Additional ammonia absorbent 5 (e.g. liquid ammonia)

is mixed with air 7 and is then added to the ammonia-mixing chamber 6. Part of the liquid is taken out from the lower part of the ammonia-mixing chamber 6 through a pipeline 14, and is fed to the upper part of the primary spray absorption section 8 through a circulating pump 11 as the spray absorption liquid. A communication channel may be provided between the pipelines 13 and 14, thereby allowing adjustment of the amounts and pH values of the spray liquids entering the primary spray absorption section 8 and the secondary spray absorption section 9. In the process, an ammonia absorbent is introduced into not only the ammonia-mixing chamber 6 and the cooling-and-concentrating section 3, but also optionally one or more of the primary spray absorption section 8, the secondary spray absorption section 9, and optionally the section of removing fine particulate matters, to regulate and control the composition and pH of the stream in each section (not shown).

In another aspect, the present invention provides an ammonia-based desulfurization apparatus suitable for carrying out the above process of the present invention, comprising:

a primary spray absorption section, configured to allow countercurrent contact between a first spray liquid sprayed from the upper part thereof and a gas stream entering from the lower part thereof, allow to take out the contacted first spray liquid from the lower part thereof to provide a reflux liquid, and allow the preliminarily absorbed gas stream to enter a secondary spray absorption section, for example, through a partition with a gas cap;

a secondary spray absorption section, configured to allow countercurrent contact between a second spray liquid sprayed from the upper part thereof and the gas stream entering from the primary spray absorption section, and allow to take out the contacted second spray liquid from the lower part thereof to provide a reflux liquid; and

an oxidation section, comprising:

an oxidation chamber, configured to allow contact and reaction between at least part of the reflux liquid from the secondary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections and an oxygen-containing gas, and allow to take out at least part of the liquid phase from the lower part thereof for circulation to the secondary spray

absorption section or both the secondary and primary spray absorption sections;  
and

an ammonia-mixing chamber, configured to be in fluid communication with the oxidation chamber on the top and/or side thereof, allow at least part of the reflux liquid from the primary spray absorption section or part of the combined  
5 reflux liquid from the primary and secondary spray absorption sections to enter from the upper part thereof and mix with an ammonia absorbent, and allow to take out a liquid stream from the lower part thereof for circulation to the primary spray absorption section or both the secondary and primary spray absorption sections.

10 In an embodiment, the apparatus further comprises a cooling-and-concentrating section in the upstream of the primary spray absorption section, wherein the cooling-and-concentrating section is configured to allow a gas stream to be treated, e.g. flue gas produced in coal-fired boilers, to be washed and cooled by a circulating washing liquid in the cooling-and-concentrating section  
15 whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the gas stream, and allow the cooled gas stream to enter the primary spray absorption section, for example, through a partition with a gas cap.

In a preferred embodiment, the individual sections of the apparatus are  
20 accommodated in an absorption tower.

In the apparatus of the present invention, the volume of the oxidation chamber can be determined based on the residence time required for oxidation, and the volume of the ammonia-mixing chamber is generally not less than the flow of a circulating pump over 2 minutes.

25 In some embodiments, the oxidation chamber and the ammonia-mixing chamber in the oxidation section may be provided separately. For example, the oxidation chamber and the ammonia-mixing chamber may be provided by two tanks in fluid communication with each other. For another example, the oxidation chamber may be provided in an absorption tower accommodating the individual  
30 sections of the apparatus, and the ammonia-mixing chamber may be provided in the absorption tower or outside the absorption tower.

In some additional embodiments, the oxidation chamber and the ammonia-mixing chamber in the oxidation section are formed by partition of a

tank. In some further additional embodiments, both the oxidation chamber and the ammonia-mixing chamber in the oxidation section are provided in an absorption tower accommodating the individual sections of the apparatus, and are formed by partition of the lower part of the absorption tower. In such embodiments, the cross sectional area of the ammonia-mixing chamber accounts for up to 85%, e.g. no more than 60%, or no more than 50%, or no more than 40%, or from 8% to 50%, or from 10% to 40%, or from 12% to 35% of the cross sectional area of the tank/absorption tower.

In general, the ammonia-mixing chamber is provided below the controlled level of the oxidation chamber. For example, the top of the ammonia-mixing chamber may be at least 20 cm below the controlled level of the oxidation chamber, preferably 100-200 cm below the controlled level of the oxidation chamber. In the apparatus of the present invention, there are no openings on the bottom surface of the ammonia-mixing chamber. One or more balancing holes in fluid communication with the oxidation chamber are opened on the side, preferably in the lower part of the side, e.g. in the 1/8 lower part, or in the 1/6 lower part, or in the 1/5 lower part, or in the 1/4 lower part, or in the 1/3 lower part of the side. The area of each opening is generally not more than 0.25 m<sup>2</sup>, preferably not more than 0.1 m<sup>2</sup>, more preferably not more than 0.05 m<sup>2</sup>, and still more preferably not more than 0.01 m<sup>2</sup>. The shape of the opening(s) is not particularly limited. For example, the opening(s) may be a round, a rectangle, a square, an oval, a hexagon, or the like. In a specific embodiment, the opening(s) is/are a square of 80 x 80 mm or 90 x 90 mm or 100 x 100 mm. In another specific embodiment, the opening(s) is/are a round with a diameter of 80, or 85, or 90, or 95, or 100, or 110 mm. The number of the openings on the side can be calculated according to the cross sectional area required to at least reach the flow of a single circulating pump at a flow velocity of 4 m/s and the area of a single opening. In general, the number of the openings on the side enables the total area of the openings to be equal to or larger than the cross sectional area required to reach the flow of a single circulating pump at a flow velocity of 4 m/s. There are also one or more openings on the top of the ammonia-mixing chamber. In general, the number of the openings on the top is 1-3 times as much as the number of the openings on the side, and the size of the openings on the top may be the same as or different from the size of the openings

on the side, and preferably approximately the same. The shape of the openings on the top may be the same as or different from the shape of the openings on the side, and preferably approximately the same. The balancing holes on the side and top of the ammonia-mixing chamber should be generally provided away from the inlets and outlets of the individual streams. Figure 3 schematically describes arrangement of openings of an ammonia-mixing chamber in accordance with an embodiment of the present invention. The arrangement of the openings on the side and/or top of the ammonia-mixing chamber allows the communication between the two circulations.

The shape of the ammonia-mixing chamber is not critical. The shape can generally be determined according to its location and the ease of processing the equipment. For example, in the case where the ammonia-mixing chamber is connected to the tower or tank wall, it can be semi-cylindrical; in the case where the ammonia-mixing chamber is placed in the middle of the tower, it can be processed into a horizontal tank; and in the case where the ammonia-mixing chamber is placed outside the tower, it can be processed into a cylindrical vertical tank.

In a specific embodiment, the apparatus of the present invention is as shown in Figures 1-3, wherein the cross sectional area of the ammonia-mixing chamber 6 is about 15% to about 30%, e.g. 18%, 20%, 22% or 25%, of the cross sectional area of the absorption tower 1; the height of the ammonia-mixing chamber 6 is about 30 to about 42%, e.g. 35%, 38% or 40%, of the height of the oxidation section, and the overall ammonia-mixing chamber 6 is below the controlled level within the oxidation chamber 2, e.g. at least about 50 cm below the controlled level, e.g. 60 cm, 80 cm, 100 cm or 150 cm below the controlled level; the volume of the ammonia-mixing chamber 6 is about 15-40 m<sup>3</sup>, e.g. 18, 22 or 26 m<sup>3</sup>, the volume of the oxidation chamber 2 is about 150-400 m<sup>3</sup>, e.g. 180, 220 or 260 m<sup>3</sup>, and the volume ratio of the ammonia-mixing chamber 6 to the oxidation chamber 2 is about 1 : 10; the ammonia-mixing chamber 6 may have about 5 to about 15, e.g. 10, balancing holes in the lower part of its side (e.g. in the 1/4 or 1/5 or 1/6 of the lower part), and 10 to 30, e.g. 20, balancing holes on its roof, wherein the size of each hole may be 80 x 80 mm, and the balancing holes are provided away from the inlet of the reflux liquid and ammonia intake; the reflux liquid from the primary

spray absorption section 8 and the reflux liquid from the secondary spray absorption section 9 are combined, wherein about 60-70 vol%, e.g. 65 vol%, of the total reflux liquid enters the ammonia-mixing chamber 6 and is mixed with liquid ammonia 5, while the remaining part of the reflux liquid enters the oxidation chamber 2; and based on the total amount of liquid ammonia fed to the ammonia-mixing chamber 6, for example, about 55% of liquid ammonia 5 is added directly to the ammonia-mixing chamber 6 (e.g. through a microporous distributor), the remaining 45% of liquid ammonia 5 is mixed with air 7 and then fed to the ammonia-mixing chamber 6, and the volume of air 7 is about 5%-about 10% of the volume of gaseous ammonia after liquid ammonia gasification. Valves may be set on each pipeline from/to the oxidation chamber 2 and the ammonia-mixing chamber 6 as required, to allow adjustment of the flows of materials from/to the two chambers, and in turn adjustment of the compositions of the liquid streams from/to the two chambers.

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### Technical Effects Achieved by the Invention

1. The present invention advantageously solves the problems of ammonia slip and aerosol formation in ammonia-based desulphurization, so as to meet more stringent discharge requirements. Under the conditions that the SO<sub>2</sub> concentration in the original flue gas is not more than 30000 mg/Nm<sup>3</sup>, and the concentration of total particulate matters is not more than 30 mg/Nm<sup>3</sup>, in the treated clean flue gas, the SO<sub>2</sub> content can be no more than 35 mg/Nm<sup>3</sup> and the total dust (including aerosols) content no more than 5 mg/Nm<sup>3</sup>.

2. In the process of the present invention, the ammonia slip in the treated clean flue gas is no more than 3 mg/Nm<sup>3</sup>, and the utilization rate of ammonia can reach 99% or more.

3. The apparatus of the present invention has a high purification efficiency, can be operated stably and reliably, avoids secondary pollution, and has a wide scope of adaptation.

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### Embodiments

#### Embodiment 1

Ammonia-based desulfurization of the flue gas from a coal combustion

process was carried out by using an apparatus of the present invention, wherein the apparatus is basically as shown in Figures 1-3, except that the oxidation chamber and the ammonia-mixing chamber are provided by 2 tanks outside the absorption tower, with a DN500 communication pipe being provided in the middle part of the two tanks; a circulating liquid from the outlet in the lower part of the ammonia-mixing chamber enters the upper part of the primary spray absorption section, and a circulating liquid from the outlet in the lower part of the oxidation chamber enters the upper part of the secondary spray absorption section; a reflux liquid from the primary spray absorption section and a reflux liquid from the secondary spray absorption section converge at a gas-liquid separator between the cooling-and-concentrating section and the primary spray absorption section with a total amount of 2700 m<sup>3</sup>/h, wherein 60 vol% of the reflux liquid enters the ammonia-mixing chamber, and 40 vol% of the reflux liquid enters the oxidation chamber; liquid ammonia is added to the ammonia-mixing chamber uniformly and gently at a flow of 204 kg/h through a microporous distributor, and additional liquid ammonia is added to air at 300 kg/h through a distributor, and the air volume is 10% of the volume of gaseous ammonia after liquid ammonia gasification, and then the mixed gas is fed to the ammonia-mixing chamber; the volume of the ammonia-mixing chamber is 27 m<sup>3</sup>; the volume of the oxidation chamber is 200 m<sup>3</sup>; and no stream is led to downstream units to recover ammonium sulfate.

The flow of the original flue gas is 600000 Nm<sup>3</sup>/h, and its temperature is 145 °C, the SO<sub>2</sub> concentration is 1600 mg/Nm<sup>3</sup>, and the concentration of total particulate matters is 21.3 mg/Nm<sup>3</sup>. The pH of the circulating liquid at the outlet in the lower part of the ammonia-mixing chamber is 6.1, and the oxidation rate in the ammonia-mixing chamber is 98%. The pH of the circulating liquid at the outlet in the lower part of the oxidation chamber is 5.3, and the oxidation rate in the oxidation chamber is 99.5%. The gas temperature at the outlet of the cooling-and-concentrating section is 51.4 °C.

In the clean flue gas from the secondary spray absorption section, the SO<sub>2</sub> content is 17.3 mg/Nm<sup>3</sup>, the content of total particulate matters (including aerosols) is 1.8 mg/Nm<sup>3</sup>, and the amount of entrained ammonia is 0.35 mg/Nm<sup>3</sup>.

## Embodiment 2

The experiment of embodiment 1 was repeated, expect that the oxidation

chamber and the ammonia-mixing chamber are provided in a same tank with a diameter of 5.5 m, the cross sectional area of the ammonia-mixing chamber is 18% of the cross sectional area of the tank, and the top of the ammonia-mixing chamber is 1 m lower than the liquid level in the oxidation chamber; 13 balancing holes are opened in the lower part on the side of the ammonia-mixing chamber, 22 balancing holes are opened on the roof, the size of each hole is 80 x 80 mm, and the balancing holes are provided away from the outlet of the circulating liquid and the ammonia intake; the volume of the ammonia-mixing chamber with a semi-cylindrical shape is 27 m<sup>3</sup>; the volume of the oxidation chamber is 220 m<sup>3</sup>; and the spray liquid from the primary spray absorption section and the spray liquid from the secondary spray absorption section are combined, wherein 70% of the combined reflux liquid is combined with 20% aqueous ammonia at 2522 kg/h and then enters the ammonia-mixing chamber, while the remaining reflux liquid enters the oxidation chamber.

The pH of the circulating liquid taken out from the ammonia-mixing chamber is 6.3, and the oxidation rate in the ammonia-mixing chamber is 98.6%. The pH of the circulating liquid taken out from the oxidation chamber is 5.4, and the oxidation rate in the oxidation chamber is 99.7%.

In the clean flue gas, the SO<sub>2</sub> content is 16.3 mg/Nm<sup>3</sup>, the content of total particulate matters (including aerosols) is 2.1 mg/Nm<sup>3</sup> and the amount of entrained ammonia is 0.42 mg/Nm<sup>3</sup>.

### Embodiment 3

The experiment was carried out by using the apparatus of embodiment 1, expect that the oxidation chamber and the ammonia-mixing chamber are provided in a same tank with a diameter of 6 m, the cross sectional area of the ammonia-mixing chamber is 20% of the cross sectional area of the tank, the top of the ammonia-mixing chamber is 1.5 m lower than the liquid level in the oxidation chamber; 8 balancing holes are opened in the lower part on the side of the ammonia-mixing chamber, 13 balancing holes are opened on the roof, the size of each hole is 100 x 100 mm, and the balancing holes are provided away from the outlet of the circulating liquid and the ammonia intake; the volume of the ammonia-mixing chamber is 25 m<sup>3</sup>, the ammonia-mixing chamber is located in the center of the tank, and is a horizontal tank; the volume of the oxidation chamber is

228 m<sup>3</sup>; the spray liquid from the primary spray absorption section and the spray liquid from the secondary spray absorption section are not combined, but are fed to the ammonia-mixing chamber and the oxidation chamber respectively, wherein the flow of the reflux liquid to the ammonia-mixing chamber is 1700 m<sup>3</sup>/h, and the flow of the reflux liquid to the oxidation chamber is 600 m<sup>3</sup>/h; and 20% aqueous ammonia used as an absorbent is added at a flow of 5432 kg/h to the reflux liquid entering the ammonia-mixing chamber, and at a flow of 1316 kg/h to the reflux liquid entering the oxidation chamber.

The flow of the original flue gas is 300000 Nm<sup>3</sup>/h, and its temperature is 145 °C, the SO<sub>2</sub> concentration is 8500 mg/Nm<sup>3</sup>, and the concentration of total particulate matters is 28.5 mg/Nm<sup>3</sup>.

The pH of the circulating liquid taken out from the ammonia-mixing chamber is 6.5, and the oxidation rate in the ammonia-mixing chamber is 96.8%. The pH of the circulating liquid taken out from the oxidation chamber is 5.3, and the oxidation rate in the oxidation chamber is 99%.

In the clean flue gas, the SO<sub>2</sub> content is 31.4 mg/Nm<sup>3</sup>, the content of total particulate matters (including aerosols) is 2.8 mg/Nm<sup>3</sup>, and the amount of entrained ammonia is 0.7 mg/Nm<sup>3</sup>.

Comparative embodiment:

The experiment of embodiment 3 was repeated, except that the ammonia-adding in different chambers was not employed, that is, the ammonia-mixing chamber and the oxidation chamber are combined into one; the spray liquid from the primary spray absorption section and the spray liquid from the secondary spray absorption section are combined and then enter the oxidation chamber at 2300 m<sup>3</sup>/h, before which 20% aqueous ammonia is added at 6770 kg/h; and after oxidation, the spray liquids return to the primary and secondary spray absorption sections for absorption, with the pH of the oxidized circulating liquid being 5.9 and the oxidation rate being 98.3%.

In the clean flue gas, the SO<sub>2</sub> content is 67 mg/Nm<sup>3</sup>, the content of total particulate matters (including aerosols) is 12 mg/Nm<sup>3</sup>, the amount of entrained ammonia is 2.7 mg/Nm<sup>3</sup>, and consumption of 20% aqueous ammonia is increased by 22 kg/h. These indexes are inferior to those of embodiment 3.

The detection methods of some indexes and main instruments used in the

embodiments and the comparative embodiment are shown in Table 1 below.

Table 1. Detection methods of some indexes and main instruments

S/N	Monitoring items	Names and numbers of analysis method/standard	Instrument names and models	Instrument Nos.
1	Flue dust	Determination of particulates and sampling methods of gaseous pollutants emitted from exhaust of stationary source GB/T16157-1996	Laoying 3012H flue dust sampler Electronic balances BS224S and AB204-S	8042448, 08244496 18360886 and 1119051201
2	SO <sub>2</sub>	Determination of sulphur dioxide from exhaust of stationary source Fixed-potential electrolysis method HJ/T 57-2000	Testo 350 flue gas analyzer	10# and 1#
4	Ammonia	Air and exhaust -Determination of ammonia Nessler's reagent spectrophotometry HJ 533-2009	Laoying 3072H 722 spectrophotometer	02085809 and 2c5BP363
5	Flue gas oxygen content	Specification and test procedures for continuous emission monitoring systems of flue gas emitted from stationary sources-Electrochemical process (Appendix	Testo 350 flue gas analyzer	10# and 1#

		B) (HJ/T 76-2007)		
6	Flue gas temperature	Determination of particulates and sampling methods of gaseous pollutants emitted from exhaust gas of stationary source-Platinum resistance method (GB/T16157-1996)	TES-1310	/
7	Flue gas humidity	Specification and test procedures for continuous emission monitoring systems of flue gas emitted from stationary sources (Appendix B) (HJ/T 76-2007)	Laoying 3012H flue dust sampler	8042448 and 08244496

The patents, patent applications and test methods mentioned in the specification of this application are incorporated herein by reference.

While the present invention has been described with reference to exemplary embodiments, as will be appreciated by those skilled in the art, various alterations and modifications can be made without departing from the spirit and scope of the present invention. Therefore, the present invention is not limited to specific embodiments disclosed as the best implementation method of the present invention, but includes all embodiments falling within the scope of the appended claim.

Now, having described the various features of the desulfurization method and desulfurization apparatus, described herein in numbered paragraphs is:

1. An ammonia-based desulfurization process through ammonia-adding in different chambers, wherein an oxidation section comprises an oxidation chamber and an ammonia-mixing chamber in fluid communication with each other, and an ammonia absorbent is added to the ammonia-mixing chamber.

2. The process according to paragraph 1, wherein an absorption-oxidation cycle of the process comprises liquid circulation between the oxidation chamber and a secondary spray absorption section and liquid circulation between the ammonia-mixing chamber and a primary spray absorption section, and there is a communication between the two circulations at least through the fluid communication between the oxidation chamber and the ammonia-mixing chamber.

3. The process according to paragraph 1 or 2, comprising the following steps:  
providing a sulfur dioxide-containing gas stream to be treated;

feeding the sulfur dioxide-containing gas stream to be treated into a cooling-and-concentrating section, where the gas stream is washed and cooled using a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the gas stream;

allowing the gas stream from the cooling-and-concentrating section to enter the primary spray absorption section, where the gas stream is in countercurrent contact with a first spray absorption liquid;

allowing the gas stream from the primary spray absorption section to enter the secondary spray absorption section, where the gas stream is in countercurrent contact with a second spray absorption liquid;

feeding the liquid stream from the bottom of the primary spray absorption section and the liquid stream from the bottom of the secondary spray absorption section as a reflux liquid respectively into the ammonia-mixing chamber and the oxidation chamber, or combining the two liquid streams and then separately feeding the combined liquid stream into the ammonia-mixing chamber and the oxidation chamber, feeding an oxygen-containing gas into the oxidation chamber, and feeding an ammonia absorbent into the ammonia-mixing chamber, which is in fluid communication with the oxidation chamber;

feeding at least part of the liquid stream taken out from the lower part of the oxidation chamber as the second spray absorption liquid into the secondary spray absorption section, and optionally, feeding at least part of the liquid stream taken out from the lower part of the oxidation chamber into a subsequent unit to recover ammonium sulfate;

feeding the liquid stream taken out from the lower part of the

ammonia-mixing chamber as the first spray absorption liquid into the primary spray absorption section; and

venting the gas stream from the upper part of the secondary spray absorption section after removing droplets, optionally after further removal of fine particulate matters.

4. The process according to any one of paragraphs 1-3, which has at least one of the following characteristics:

- the sulfur dioxide-containing gas to be treated is a flue gas produced in coal combustion or a flue gas produced in a fluidized-bed catalytic cracking process or a flue gas produced in other industrial processes;

- the ammonia absorbent is in the form of liquid ammonia, gaseous ammonia, an aqueous ammonia or a combination thereof;

- the oxygen-containing gas is oxygen, air, oxygen-enriched air or oxygen-poor air;

- the ammonia absorbent is added to a liquid stream using a tubular distributor, a microporous distributor or a static mixer, and/or the ammonia absorbent is first mixed with an oxygen-containing gas, and then the mixed gas stream is directly added to the ammonia-mixing chamber;

- the pH of the circulating liquid withdrawn from the lower part of the ammonia-mixing chamber is in a range of 4.6-8.0;

- the pH of the circulating liquid withdrawn from the lower part of the oxidation chamber is in a range of 4.0-6.8;

- no additional ammonia absorbent is added to the oxidation chamber, except for the ammonia absorbent in the reflux liquid entering the oxidation chamber and the ammonia absorbent entering the oxidation chamber from the ammonia-mixing chamber;

- the oxidation rate in the ammonia-mixing chamber is in a range of 93%-99.5%;

- the oxidation rate in the oxidation chamber is not less than 98.5%;

- based on the total amount of the reflux liquid from the primary spray absorption section and the secondary spray absorption section, 30%-85% of the reflux liquid enters the ammonia-mixing chamber, and the remaining reflux liquid enters the oxidation chamber; and

- a valve-controlled pipeline is provided between a pipeline by which the circulating liquid is taken out from the lower part of the oxidation chamber and a pipeline by which the circulating liquid is taken out from the lower part of the ammonia-mixing chamber, so as to allow adjustment of the amounts and/or pH values of the circulating liquids entering the primary spray absorption section and the secondary spray absorption section respectively.

5 5. The process according to paragraph 3, wherein the spray liquid from the bottom of the primary spray absorption section and the spray liquid from the bottom of the secondary spray absorption section are combined, wherein about 10 30%-85% of the combined reflux liquid enters the ammonia-mixing chamber to be combined with the ammonia absorbent, and the remaining part of the combined reflux liquid enters the oxidation chamber.

6. The process according to paragraph 5, wherein at least part of the ammonia absorbent enters the reflux liquid part to be fed to the ammonia-mixing chamber through a microporous distributor or is fed directly to the ammonia-mixing chamber, and/or at least part of the ammonia absorbent is mixed with the oxygen-containing gas, and then added to the ammonia-mixing chamber.

7. The process according to any one of paragraphs 1-3, wherein liquid ammonia is used as an absorbent and the liquid ammonia is added to a solution through a mixer, and/or the liquid ammonia is first mixed with a gas and then added to the ammonia-mixing chamber, wherein the amount of the gas is 3%-10% of the volume of gaseous ammonia after liquid ammonia gasification.

8. The process according to any one of paragraphs 3-7, wherein the ammonia absorbent is also added in at least one of the cooling-and-concentrating section, the primary spray absorption section and the secondary spray absorption section.

9. The process according to any one of paragraphs 1-8, wherein under the conditions that the SO<sub>2</sub> concentration in the original flue gas is not more than 30000 mg/Nm<sup>3</sup>, and the concentration of total particulate matters is not more than 30 mg/Nm<sup>3</sup>, in the clean flue gas, the SO<sub>2</sub> concentration can be no more than 35 mg/Nm<sup>3</sup>, the total particulate matters including aerosols no more than 5 mg/Nm<sup>3</sup>, and the ammonia slip no more than 3 mg/Nm<sup>3</sup>.

10. An apparatus for implementing the ammonia-based desulphurization process, comprising:

a primary spray absorption section, configured to allow countercurrent contact between a first spray liquid sprayed from the upper part thereof and the gas stream entering from the lower part thereof, allow to take out the contacted first spray liquid from the lower part thereof to provide a reflux liquid, and allow the preliminarily absorbed gas stream to enter a secondary spray absorption section;

the secondary spray absorption section, configured to allow countercurrent contact between a second spray liquid sprayed from the upper part thereof and the gas stream entering from the primary spray absorption section, and allow to take out the contacted second spray liquid from the lower part thereof to provide a reflux liquid; and

an oxidation section, comprising:

an oxidation chamber, configured to allow contact and reaction between at least part of the reflux liquid from the secondary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections and an oxygen-containing gas, and allow to take out at least part of the liquid phase from the lower part thereof for circulation to the secondary spray absorption section or both the secondary and primary spray absorption sections; and

an ammonia-mixing chamber, configured to be in fluid communication with the oxidation chamber on the top and/or side thereof, allow at least part of the reflux liquid from the primary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections to enter from the upper part thereof and mix with an ammonia absorbent, and allow to take out a liquid stream from the lower part thereof for circulation to the primary spray absorption section or both the secondary and primary spray absorption sections.

11. The apparatus according to paragraph 10, further comprising a cooling-and-concentrating section in the upstream of the primary spray absorption section, the cooling-and-concentrating section being configured to allow a gas stream to be treated to be washed and cooled by a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the gas stream, and allow the cooled gas stream to enter the primary spray absorption section.

12. The apparatus according to paragraph 10 or 11, which has at least one of

the following characteristics:

- the oxidation chamber and the ammonia-mixing chamber in the oxidation section are provided separately, for example, the oxidation chamber and the ammonia-mixing chamber are provided by two tanks in fluid communication with each other, or the oxidation chamber is provided in an absorption tower accommodating individual sections of the apparatus, and the ammonia-mixing chamber is provided in the absorption tower or outside the absorption tower; or the oxidation chamber and the ammonia-mixing chamber in the oxidation section are formed by partition of a tank; or both the oxidation chamber and the ammonia-mixing chamber in the oxidation section are provided in the absorption tower accommodating individual sections of the apparatus, and are formed by partition of the lower part of the absorption tower;

- the volume of the ammonia-mixing chamber is not less than the amount of the liquid taken out from the lower part over 2 minutes; and

- a valve-controlled pipeline is provided between a pipeline by which the circulating liquid is taken out from the lower part of the oxidation chamber and a pipeline by which the circulating liquid is taken out from the lower part of the ammonia-mixing chamber, so as to allow adjustment of the amounts and/or pH values of the circulating liquids entering the primary spray absorption section and the secondary spray absorption section respectively.

13. The apparatus according to paragraph 10, wherein the oxidation chamber and the ammonia-mixing chamber in the oxidation section are formed by partition of a tank, or both are provided in the absorption tower accommodating individual sections of the apparatus, and are formed by partition of the lower part of the absorption tower, wherein the cross sectional area of the ammonia-mixing chamber accounts for up to 85%, or no more than 60%, or no more than 50%, or no more than 40%, or from 5% to 50%, or from 7% to 40%, or from 10% to 35% of the cross sectional area of the tank/absorption tower, and wherein there are openings on the side and/or top of the ammonia-mixing chamber.

14. The apparatus according to paragraph 13, wherein the ammonia-mixing chamber is provided at least 20 cm, or at least 40 cm, or at least 60 cm, or at least 80 cm, or at least 100 cm, or 100-200 cm below the controlled level in the oxidation chamber.

15. The apparatus according to paragraph 10, wherein openings are provided on the side and/or top of the ammonia-mixing chamber to achieve fluid communication between the ammonia-mixing chamber and the oxidation chamber, and wherein the apparatus has at least one of the following characteristics:

- 5 - one or more holes are opened in the 1/3 lower part on the side of the ammonia-mixing chamber;
- there are one or more openings on the roof of the ammonia-mixing chamber;
- the area of each opening of the ammonia-mixing chamber is no more than 0.25 m<sup>2</sup>, or no more than 0.1 m<sup>2</sup>, or no more than 0.05 m<sup>2</sup>, or no more than 0.01  
10 m<sup>2</sup>;
- the one or more openings of the ammonia-mixing chamber are round, rectangular, square, oval or hexagonal; and
- the openings on the side and/or top of the ammonia-mixing chamber are provided away from the inlets and outlets of the individual streams.

15 16. The apparatus according to paragraph 10, wherein openings are provided at least on the side of the ammonia-mixing chamber to achieve fluid communication between the ammonia-mixing chamber and the oxidation chamber, and wherein the number of the openings on the side enables the total area of the openings to be equal to or larger than the cross sectional area required to reach the  
20 flow of the circulating pump between the ammonia-mixing chamber and the primary spray absorption section at a flow velocity of 4 m/s.

17. A method of ammonia-based oxidative desulfurization comprising:
- directing a current of sulfur dioxide containing gas through a vessel;
  - mixing, in an ammonia-mixing chamber, a liquid and an ammonia source to  
25 produce a first ammonia-containing liquid that has a first pH;
  - contacting, in an oxidation chamber, an oxygen-containing gas with a second ammonia-containing liquid that has a second pH that is lower than the first pH;
  - spraying the first ammonia-containing liquid in the vessel against the current;
  - after the spraying the first ammonia-containing liquid, recirculating the first  
30 ammonia-containing liquid to the ammonia-mixing chamber;
  - spraying the second ammonia-containing liquid in the vessel against the current; and
  - after the spraying the second ammonia-containing liquid, recirculating the

second ammonia-containing liquid to the oxidation chamber.

18. The method of paragraph 17 further comprising transferring materials between the oxidation chamber and the ammonia-mixing chamber through a balance hole defined in a partition between the oxidation chamber and the ammonia-mixing chamber.

19. The method of paragraph 18, characterized by at least one of the following features:

- the transferring includes transferring at a location in a top surface of the ammonia-mixing chamber and/or at a location in a lower third of a height of the ammonia-mixing chamber;

- the transferring includes transferring through a balance hole that is no more than  $0.25 \text{ m}^2$ , alternatively no more than  $0.1 \text{ m}^2$ , alternatively no more than  $0.05 \text{ m}^2$ , alternatively no more than  $0.01 \text{ m}^2$ ;

- the transferring includes transferring through a balance hole that is any of round, rectangular, square, oval, and hexagonal.

20. The method of paragraph 18 wherein:

the mixing comprises receiving in the ammonia-mixing chamber, at a material transfer port disposed in a surface of the ammonia-mixing chamber, ammonia; and

the spraying the first ammonia-containing liquid comprises drawing, from the ammonia-mixing chamber, the first ammonia-containing liquid;

wherein:

the material transfer port is in fluid communication with an elongated conduit leading away from the ammonia-mixing chamber; and

the surface is distant from the balance hole.

21. The method of paragraph 17 further comprising, before the spraying the first ammonia-containing liquid in the vessel against the current, cooling the current by contacting it with recirculated sprayed ammonia-containing liquid.

22. The method of paragraph 17 further comprising, before the spraying the first ammonia-containing liquid in the vessel against the current, cooling the current by contacting it with ammonium sulfate slurry.

23. The method of paragraph 17 further comprising releasing the gas current from the vessel, wherein:

in the directing, the sulfur dioxide containing gas has an  $\text{SO}_2$  concentration no

more than 30000 mg/Nm<sup>3</sup> and a total particulate matter concentration no more than 30 mg/Nm<sup>3</sup>, and

the releasing includes releasing an exhaust gas having an SO<sub>2</sub> concentration no more than 35 mg/Nm<sup>3</sup> and a total dust, including aerosol, content 5 mg/Nm<sup>3</sup>.

5 24. The method of paragraph 17 further comprising, after the spraying the first and second ammonia-containing liquids, mixing the first and second ammonia-containing liquids to form a mixed reflux liquid.

25. The method of paragraph 24, characterized by at least one of the following features:

- 10 - the method further comprises circulating at least part, preferably between 70% and 15%, of the reflux liquid into the oxidation chamber;
- the method further comprises passing at least part, preferably between 30% and 85%, of the reflux liquid into the ammonia-mixing chamber; or
- the method further comprises contacting anhydrous ammonia with the reflux  
15 liquid via a microporous distributor and adding the resulting mixture into the ammonia-mixing chamber.

26. The method of paragraph 17, characterized by at least one of the following features:

- 20 - the method further comprises receiving the gas current from a coal combustion process or, alternatively, from a fluid catalytic cracking process;
- the ammonia source comprises anhydrous ammonia, gaseous ammonia, aqueous ammonia, or a combination thereof;
- the oxygen-containing gas is pure molecular oxygen, an oxygen-poor air, or an oxygen-enriched air;
- 25 - the method further comprises, prior to the mixing of the liquid and the ammonia source, mixing the ammonia source with the oxygen-containing gas;
- the pH of the first ammonia-containing liquid is in a range of 4.6-8.0;
- the pH of the second ammonia-containing liquid is in the range 4.0 to 6.8;
- the oxidation rate of the first ammonia-containing liquid within the  
30 ammonia-mixing chamber is in the range 93% to 99.5%, alternatively in the range 98.5% to 99.5%;
- the oxidation rate of the second ammonia-containing liquid within the oxidation chamber is greater than or equal to 98.5%;- the method further comprises,

prior to spraying the first ammonia-containing liquid, mixing the ammonia source with the first ammonia-containing liquid; or

5 - the method further comprises releasing the gas current from the vessel, wherein the released gas current has an entrained ammonia amount no more than 3 mg/Nm<sup>3</sup>.

27. The method of paragraph 17 further comprising adjusting, via a sealable valve, a fluid communication between a first conduit carrying the first ammonia-containing liquid and a second conduit carrying the second ammonia-containing liquid.

10 28. The method of paragraph 27 wherein the adjusting produces a change in pH of at least one of a liquid within the oxidation chamber and a liquid within the ammonia-mixing chamber.

29. The method of paragraph 17 wherein the ammonia-mixing chamber is disposed separately from the oxidation chamber, and wherein the oxidation  
15 chamber and the ammonia-mixing chamber are preferably in fluid communication via a conduit extending between the oxidation chamber and the ammonia-mixing chamber.30. The method of paragraph 17 wherein the ammonia-mixing chamber is disposed at least partly within the oxidation chamber.

31. The method of paragraph 17 wherein the spraying the first  
20 ammonia-containing liquid in the vessel against the current occurs before the spraying the second ammonia-containing liquid in the vessel against the current.32. An apparatus for removing sulfur oxides from a gas stream, the apparatus comprising:

25 a first sprayer circuit configured to spray a first liquid countercurrent to the gas stream, the first sprayer circuit including:

a first sprayer assembly;

an ammonia-mixing chamber including:

an ammonia input port;

a first-liquid return port; and

30 a first-liquid supply port configured to supply the first liquid to the first sprayer assembly, the ammonia-mixing chamber defining a balance hole that places material from inside the ammonia-mixing box in diffusive communication with material from outside the ammonia-mixing box; and

a second sprayer circuit configured to spray a second liquid countercurrent to the gas stream, the second sprayer circuit including:

a second sprayer assembly downstream, relative to the gas stream, from the first sprayer assembly;

5 an oxidation chamber having:

a gas input configured for contacting an oxygen-containing gas with an ammonia-containing liquid in the oxidation chamber;

a second-liquid return port configured to receive second liquid after the second liquid is sprayed; and

10 a second-liquid supply port configured to supply second liquid to the second sprayer assembly.

33. The apparatus of paragraph 32, characterized by at least one of the following features:

15 - the first-liquid return port is configured to receive first liquid after the first liquid is sprayed;

- the apparatus further comprises a cooling chamber in which the gas stream is cooled, before spraying the first liquid countercurrent to the gas stream, by contacting the gas stream with recirculated sprayed ammonia-containing liquid;

20 - the apparatus further comprises a conduit having a first end and a second end, the first end configured to be joined to a primary spray absorption section upstream from the first spray assembly, the second end being bifurcated and configured to be joined to the oxidation chamber and the ammonia-mixing chamber;

25 - the apparatus further comprises a gas cap configured to transfer the gas stream from the first sprayer assembly to the second sprayer assembly;

- the apparatus further comprises a sealable valve configured to adjust fluid communication between a first conduit carrying the first liquid from the first-liquid supply port and a second conduit carrying the second liquid from the second-liquid supply port;

30 - the ammonia-mixing chamber has a volume no less than a volume of the first liquid which is supplied to the first sprayer array over a period of two minutes;

- the ammonia-mixing chamber is disposed at least partly within the oxidation chamber; or

- the ammonia-mixing chamber has a first cross-sectional area, the oxidation chamber has a second cross-sectional area, and the second cross-sectional area is larger than the first cross-sectional area, preferably wherein the first cross-sectional area is within the range 8-50%, alternatively within the range 8-40%, alternatively within the range 10-35%, of the second cross-sectional area.

34. The apparatus of paragraph 32 wherein the ammonia-mixing chamber includes a surface that defines the balance hole, and preferably the balance hole is disposed in a lower third of a height of the ammonia-mixing chamber and/or on the top of the ammonia-mixing chamber. 35. The apparatus of paragraph 34, characterized by at least one of the following features:

-the ammonia-mixing chamber includes a material transfer port that is disposed in a surface of the mixing chamber and is distant from the balance hole, the material transfer port in fluid communication with an elongated conduit leading away from the mixing chamber,

- the balance hole is no more than  $0.25 \text{ m}^2$ , alternatively no more than  $0.1 \text{ m}^2$ , alternatively no more than  $0.05 \text{ m}^2$ , alternatively no more than  $0.01 \text{ m}^2$ , or

- the balance hole is any of round, rectangular, square, oval, and hexagonal.

36. The apparatus of paragraph 32 wherein the oxidation chamber and the ammonia-mixing chamber are in fluid communication via the balance hole, the balance hole disposed in a partition between the oxidation chamber and the ammonia-mixing chamber.

37. The apparatus of paragraph 32 wherein the oxidation chamber and the ammonia-mixing chamber are in fluid communication via a conduit extending between the oxidation chamber and the ammonia-mixing chamber.

## Claims

1. An ammonia-based desulfurization process through ammonia-adding in different chambers, wherein an oxidation section comprises an oxidation chamber and an ammonia-mixing chamber in fluid communication with each other, and an ammonia absorbent is added to the ammonia-mixing chamber.

2. The process according to claim 1, wherein an absorption-oxidation cycle of the process comprises liquid circulation between the oxidation chamber and a secondary spray absorption section and liquid circulation between the ammonia-mixing chamber and a primary spray absorption section, and there is a communication between the two circulations at least through the fluid communication between the oxidation chamber and the ammonia-mixing chamber.

3. The process according to claim 1 or 2, comprising the following steps:

providing a sulfur dioxide-containing gas stream to be treated;

feeding the sulfur dioxide-containing gas stream to be treated into a cooling-and-concentrating section, where the gas stream is washed and cooled using a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the gas stream;

allowing the gas stream from the cooling-and-concentrating section to enter the primary spray absorption section, where the gas stream is in countercurrent contact with a first spray absorption liquid;

allowing the gas stream from the primary spray absorption section to enter the secondary spray absorption section, where the gas stream is in countercurrent contact with a second spray absorption liquid;

feeding the liquid stream from the bottom of the primary spray absorption section and the liquid stream from the bottom of the secondary spray absorption section as a reflux liquid respectively into the ammonia-mixing chamber and the oxidation chamber, or combining the two liquid streams and then separately feeding the combined liquid stream into the ammonia-mixing chamber and the oxidation chamber, feeding an oxygen-containing gas into the oxidation chamber, and feeding an ammonia absorbent into the ammonia-mixing chamber, which is in fluid communication with the oxidation chamber;

feeding at least part of the liquid stream taken out from the lower part of the

oxidation chamber as the second spray absorption liquid into the secondary spray absorption section, and optionally, feeding at least part of the liquid stream taken out from the lower part of the oxidation chamber into a subsequent unit to recover ammonium sulfate;

feeding the liquid stream taken out from the lower part of the ammonia-mixing chamber as the first spray absorption liquid into the primary spray absorption section; and

venting the gas stream from the upper part of the secondary spray absorption section after removing droplets, optionally after further removal of fine particulate matters.

4. The process according to any one of claims 1-3, which has at least one of the following characteristics:

- the sulfur dioxide-containing gas to be treated is a flue gas produced in coal combustion or a flue gas produced in a fluidized-bed catalytic cracking process or a flue gas produced in other industrial processes;

- the ammonia absorbent is in the form of liquid ammonia, gaseous ammonia, an aqueous ammonia or a combination thereof;

- the oxygen-containing gas is oxygen, air, oxygen-enriched air or oxygen-poor air;

- the ammonia absorbent is added to a liquid stream using a tubular distributor, a microporous distributor or a static mixer, and/or the ammonia absorbent is first mixed with an oxygen-containing gas, and then the mixed gas stream is directly added to the ammonia-mixing chamber;

- the pH of the circulating liquid withdrawn from the lower part of the ammonia-mixing chamber is in a range of 4.6-8.0;

- the pH of the circulating liquid withdrawn from the lower part of the oxidation chamber is in a range of 4.0-6.8;

- no additional ammonia absorbent is added to the oxidation chamber, except for the ammonia absorbent in the reflux liquid entering the oxidation chamber and the ammonia absorbent entering the oxidation chamber from the ammonia-mixing chamber;

- the oxidation rate in the ammonia-mixing chamber is in a range of 93%-99.5%;

- the oxidation rate in the oxidation chamber is not less than 98.5%;
- based on the total amount of the reflux liquid from the primary spray absorption section and the secondary spray absorption section, 30%-85% of the reflux liquid enters the ammonia-mixing chamber, and the remaining reflux liquid enters the oxidation chamber; and
- a valve-controlled pipeline is provided between a pipeline by which the circulating liquid is taken out from the lower part of the oxidation chamber and a pipeline by which the circulating liquid is taken out from the lower part of the ammonia-mixing chamber, so as to allow adjustment of the amounts and/or pH values of the circulating liquids entering the primary spray absorption section and the secondary spray absorption section respectively.

5. The process according to claim 3, wherein the spray liquid from the bottom of the primary spray absorption section and the spray liquid from the bottom of the secondary spray absorption section are combined, wherein about 30%-85% of the combined reflux liquid enters the ammonia-mixing chamber to be combined with the ammonia absorbent, and the remaining part of the combined reflux liquid enters the oxidation chamber.

6. The process according to claim 5, wherein at least part of the ammonia absorbent enters the reflux liquid part to be fed to the ammonia-mixing chamber through a microporous distributor or is fed directly to the ammonia-mixing chamber, and/or at least part of the ammonia absorbent is mixed with the oxygen-containing gas, and then added to the ammonia-mixing chamber.

7. The process according to any one of claims 1-3, wherein liquid ammonia is used as an absorbent and the liquid ammonia is added to a solution through a mixer, and/or the liquid ammonia is first mixed with a gas and then added to the ammonia-mixing chamber, wherein the amount of the gas is 3%-10% of the volume of gaseous ammonia after liquid ammonia gasification.

8. The process according to any one of claims 3-7, wherein the ammonia absorbent is also added in at least one of the cooling-and-concentrating section, the primary spray absorption section and the secondary spray absorption section.

9. The process according to any one of claims 1-8, wherein under the conditions that the SO<sub>2</sub> concentration in the original flue gas is not more than 30000 mg/Nm<sup>3</sup>, and the concentration of total particulate matters is not more than

30 mg/Nm<sup>3</sup>, in the clean flue gas, the SO<sub>2</sub> concentration can be no more than 35 mg/Nm<sup>3</sup>, the total particulate matters including aerosols no more than 5 mg/Nm<sup>3</sup>, and the ammonia slip no more than 3 mg/Nm<sup>3</sup>.

10. An apparatus for implementing the ammonia-based desulfurization process, comprising:

a primary spray absorption section, configured to allow countercurrent contact between a first spray liquid sprayed from the upper part thereof and the gas stream entering from the lower part thereof, allow to take out the contacted first spray liquid from the lower part thereof to provide a reflux liquid, and allow the preliminarily absorbed gas stream to enter a secondary spray absorption section;

the secondary spray absorption section, configured to allow countercurrent contact between a second spray liquid sprayed from the upper part thereof and the gas stream entering from the primary spray absorption section, and allow to take out the contacted second spray liquid from the lower part thereof to provide a reflux liquid; and

an oxidation section, comprising:

an oxidation chamber, configured to allow contact and reaction between at least part of the reflux liquid from the secondary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections and an oxygen-containing gas, and allow to take out at least part of the liquid phase from the lower part thereof for circulation to the secondary spray absorption section or both the secondary and primary spray absorption sections; and

an ammonia-mixing chamber, configured to be in fluid communication with the oxidation chamber on the top and/or side thereof, allow at least part of the reflux liquid from the primary spray absorption section or part of the combined reflux liquid from the primary and secondary spray absorption sections to enter from the upper part thereof and mix with an ammonia absorbent, and allow to take out a liquid stream from the lower part thereof for circulation to the primary spray absorption section or both the secondary and primary spray absorption sections.

11. The apparatus according to claim 10, further comprising a cooling-and-concentrating section in the upstream of the primary spray absorption section, the cooling-and-concentrating section being configured to allow a gas

stream to be treated to be washed and cooled by a circulating washing liquid in the cooling-and-concentrating section whilst concentrating the circulating washing liquid in the cooling-and-concentrating section using the heat in the gas stream, and allow the cooled gas stream to enter the primary spray absorption section.

12. The apparatus according to claim 10 or 11, which has at least one of the following characteristics:

- the oxidation chamber and the ammonia-mixing chamber in the oxidation section are provided separately, for example, the oxidation chamber and the ammonia-mixing chamber are provided by two tanks in fluid communication with each other, or the oxidation chamber is provided in an absorption tower accommodating individual sections of the apparatus, and the ammonia-mixing chamber is provided in the absorption tower or outside the absorption tower; or the oxidation chamber and the ammonia-mixing chamber in the oxidation section are formed by partition of a tank; or both the oxidation chamber and the ammonia-mixing chamber in the oxidation section are provided in the absorption tower accommodating individual sections of the apparatus, and are formed by partition of the lower part of the absorption tower;

- the volume of the ammonia-mixing chamber is not less than the amount of the liquid taken out from the lower part over 2 minutes; and

- a valve-controlled pipeline is provided between a pipeline by which the circulating liquid is taken out from the lower part of the oxidation chamber and a pipeline by which the circulating liquid is taken out from the lower part of the ammonia-mixing chamber, so as to allow adjustment of the amounts and/or pH values of the circulating liquids entering the primary spray absorption section and the secondary spray absorption section respectively.

13. The apparatus according to claim 10, wherein the oxidation chamber and the ammonia-mixing chamber in the oxidation section are formed by partition of a tank, or both are provided in the absorption tower accommodating individual sections of the apparatus, and are formed by partition of the lower part of the absorption tower, wherein the cross sectional area of the ammonia-mixing chamber accounts for up to 85%, or no more than 60%, or no more than 50%, or no more than 40%, or from 5% to 50%, or from 7% to 40%, or from 10% to 35% of the cross sectional area of the tank/absorption tower, and wherein there are openings

on the side and/or top of the ammonia-mixing chamber.

14. The apparatus according to claim 13, wherein the ammonia-mixing chamber is provided at least 20 cm, or at least 40 cm, or at least 60 cm, or at least 80 cm, or at least 100 cm, or 100-200 cm below the controlled level in the oxidation chamber.

15. The apparatus according to claim 10, wherein openings are provided on the side and/or top of the ammonia-mixing chamber to achieve fluid communication between the ammonia-mixing chamber and the oxidation chamber, and wherein the apparatus has at least one of the following characteristics:

- one or more holes are opened in the 1/3 lower part on the side of the ammonia-mixing chamber;
- there are one or more openings on the roof of the ammonia-mixing chamber;
- the area of each opening of the ammonia-mixing chamber is no more than 0.25 m<sup>2</sup>, or no more than 0.1 m<sup>2</sup>, or no more than 0.05 m<sup>2</sup>, or no more than 0.01 m<sup>2</sup>;
- the one or more openings of the ammonia-mixing chamber are round, rectangular, square, oval or hexagonal; and
- the openings on the side and/or top of the ammonia-mixing chamber are provided away from the inlets and outlets of the individual streams.

16. The apparatus according to claim 10, wherein openings are provided at least on the side of the ammonia-mixing chamber to achieve fluid communication between the ammonia-mixing chamber and the oxidation chamber, and wherein the number of the openings on the side enables the total area of the openings to be equal to or larger than the cross sectional area required to reach the flow of the circulating pump between the ammonia-mixing chamber and the primary spray absorption section at a flow velocity of 4 m/s.

17. A method of ammonia-based oxidative desulfurization comprising:  
directing a current of sulfur dioxide containing gas through a vessel;  
mixing, in an ammonia-mixing chamber, a liquid and an ammonia source to produce a first ammonia-containing liquid that has a first pH;  
contacting, in an oxidation chamber, an oxygen-containing gas with a second ammonia-containing liquid that has a second pH that is lower than the first pH;  
spraying the first ammonia-containing liquid in the vessel against the current;

after the spraying the first ammonia-containing liquid, recirculating the first ammonia-containing liquid to the ammonia-mixing chamber;

spraying the second ammonia-containing liquid in the vessel against the current; and

after the spraying the second ammonia-containing liquid, recirculating the second ammonia-containing liquid to the oxidation chamber.

18. The method of claim 17 further comprising transferring materials between the oxidation chamber and the ammonia-mixing chamber through a balance hole defined in a partition between the oxidation chamber and the ammonia-mixing chamber.

19. The method of claim 18, characterized by at least one of the following features:

- the transferring includes transferring at a location in a top surface of the ammonia-mixing chamber and/or at a location in a lower third of a height of the ammonia-mixing chamber;

- the transferring includes transferring through a balance hole that is no more than  $0.25 \text{ m}^2$ , alternatively no more than  $0.1 \text{ m}^2$ , alternatively no more than  $0.05 \text{ m}^2$ , alternatively no more than  $0.01 \text{ m}^2$ ;

- the transferring includes transferring through a balance hole that is any of round, rectangular, square, oval, and hexagonal.

20. The method of claim 18 wherein:

the mixing comprises receiving in the ammonia-mixing chamber, at a material transfer port disposed in a surface of the ammonia-mixing chamber, ammonia; and

the spraying the first ammonia-containing liquid comprises drawing, from the ammonia-mixing chamber, the first ammonia-containing liquid;

wherein:

the material transfer port is in fluid communication with an elongated conduit leading away from the ammonia-mixing chamber; and

the surface is distant from the balance hole.

21. The method of claim 17 further comprising, before the spraying the first ammonia-containing liquid in the vessel against the current, cooling the current by contacting it with recirculated sprayed ammonia-containing liquid.

22. The method of claim 17 further comprising, before the spraying the first

ammonia-containing liquid in the vessel against the current, cooling the current by contacting it with ammonium sulfate slurry.

23. The method of claim 17 further comprising releasing the gas current from the vessel, wherein:

in the directing, the sulfur dioxide containing gas has an SO<sub>2</sub> concentration no more than 30000 mg/Nm<sup>3</sup> and a total particulate matter concentration no more than 30 mg/Nm<sup>3</sup>, and

the releasing includes releasing an exhaust gas having an SO<sub>2</sub> concentration no more than 35 mg/Nm<sup>3</sup> and a total dust, including aerosol, content 5 mg/Nm<sup>3</sup>.

24. The method of claim 17 further comprising, after the spraying the first and second ammonia-containing liquids, mixing the first and second ammonia-containing liquids to form a mixed reflux liquid.

25. The method of claim 24, characterized by at least one of the following features:

- the method further comprises circulating at least part, preferably between 70% and 15%, of the reflux liquid into the oxidation chamber;
- the method further comprises passing at least part, preferably between 30% and 85%, of the reflux liquid into the ammonia-mixing chamber; or
- the method further comprises contacting anhydrous ammonia with the reflux liquid via a microporous distributor and adding the resulting mixture into the ammonia-mixing chamber.

26. The method of claim 17, characterized by at least one of the following features:

- the method further comprises receiving the gas current from a coal combustion process or, alternatively, from a fluid catalytic cracking process;
- the ammonia source comprises anhydrous ammonia, gaseous ammonia, aqueous ammonia, or a combination thereof;
- the oxygen-containing gas is pure molecular oxygen, an oxygen-poor air, or an oxygen-enriched air;
- the method further comprises, prior to the mixing of the liquid and the ammonia source, mixing the ammonia source with the oxygen-containing gas;
- the pH of the first ammonia-containing liquid is in a range of 4.6-8.0;
- the pH of the second ammonia-containing liquid is in the range 4.0 to 6.8;

- the oxidation rate of the first ammonia-containing liquid within the ammonia-mixing chamber is in the range 93% to 99.5%, alternatively in the range 98.5% to 99.5%;

- the oxidation rate of the second ammonia-containing liquid within the oxidation chamber is greater than or equal to 98.5%;- the method further comprises, prior to spraying the first ammonia-containing liquid, mixing the ammonia source with the first ammonia-containing liquid; or

- the method further comprises releasing the gas current from the vessel, wherein the released gas current has an entrained ammonia amount no more than 3 mg/Nm<sup>3</sup>.

27. The method of claim 17 further comprising adjusting, via a sealable valve, a fluid communication between a first conduit carrying the first ammonia-containing liquid and a second conduit carrying the second ammonia-containing liquid.

28. The method of claim 27 wherein the adjusting produces a change in pH of at least one of a liquid within the oxidation chamber and a liquid within the ammonia-mixing chamber.

29. The method of claim 17 wherein the ammonia-mixing chamber is disposed separately from the oxidation chamber, and wherein the oxidation chamber and the ammonia-mixing chamber are preferably in fluid communication via a conduit extending between the oxidation chamber and the ammonia-mixing chamber.

30. The method of claim 17 wherein the ammonia-mixing chamber is disposed at least partly within the oxidation chamber.

31. The method of claim 17 wherein the spraying the first ammonia-containing liquid in the vessel against the current occurs before the spraying the second ammonia-containing liquid in the vessel against the current.

32. An apparatus for removing sulfur oxides from a gas stream, the apparatus comprising:

a first sprayer circuit configured to spray a first liquid countercurrent to the gas stream, the first sprayer circuit including:

a first sprayer assembly;

an ammonia-mixing chamber including:

an ammonia input port;  
a first-liquid return port; and  
a first-liquid supply port configured to supply the first liquid to the first sprayer assembly, the ammonia-mixing chamber defining a balance hole that places material from inside the ammonia-mixing box in diffusive communication with material from outside the ammonia-mixing box; and

a second sprayer circuit configured to spray a second liquid countercurrent to the gas stream, the second sprayer circuit including:

a second sprayer assembly downstream, relative to the gas stream, from the first sprayer assembly;

an oxidation chamber having:

a gas input configured for contacting an oxygen-containing gas with an ammonia-containing liquid in the oxidation chamber;

a second-liquid return port configured to receive second liquid after the second liquid is sprayed; and

a second-liquid supply port configured to supply second liquid to the second sprayer assembly.

33. The apparatus of claim 32, characterized by at least one of the following features:

- the first-liquid return port is configured to receive first liquid after the first liquid is sprayed;

- the apparatus further comprises a cooling chamber in which the gas stream is cooled, before spraying the first liquid countercurrent to the gas stream, by contacting the gas stream with recirculated sprayed ammonia-containing liquid;

- the apparatus further comprises a conduit having a first end and a second end, the first end configured to be joined to a primary spray absorption section upstream from the first spray assembly, the second end being bifurcated and configured to be joined to the oxidation chamber and the ammonia-mixing chamber;

- the apparatus further comprises a gas cap configured to transfer the gas stream from the first sprayer assembly to the second sprayer assembly;

- the apparatus further comprises a sealable valve configured to adjust fluid communication between a first conduit carrying the first liquid from the first-liquid

supply port and a second conduit carrying the second liquid from the second-liquid supply port;

- the ammonia-mixing chamber has a volume no less than a volume of the first liquid which is supplied to the first sprayer array over a period of two minutes;

- the ammonia-mixing chamber is disposed at least partly within the oxidation chamber; or

- the ammonia-mixing chamber has a first cross-sectional area, the oxidation chamber has a second cross-sectional area, and the second cross-sectional area is larger than the first cross-sectional area, preferably wherein the first cross-sectional area is within the range 8-50%, alternatively within the range 8-40%, alternatively within the range 10-35%, of the second cross-sectional area.

34. The apparatus of claim 32 wherein the ammonia-mixing chamber includes a surface that defines the balance hole, and preferably the balance hole is disposed in a lower third of a height of the ammonia-mixing chamber and/or on the top of the ammonia-mixing chamber.

35. The apparatus of claim 34, characterized by at least one of the following features:

- the ammonia-mixing chamber includes a material transfer port that is disposed in a surface of the mixing chamber and is distant from the balance hole, the material transfer port in fluid communication with an elongated conduit leading away from the mixing chamber,

- the balance hole is no more than  $0.25 \text{ m}^2$ , alternatively no more than  $0.1 \text{ m}^2$ , alternatively no more than  $0.05 \text{ m}^2$ , alternatively no more than  $0.01 \text{ m}^2$ , or

- the balance hole is any of round, rectangular, square, oval, and hexagonal.

36. The apparatus of claim 32 wherein the oxidation chamber and the ammonia-mixing chamber are in fluid communication via the balance hole, the balance hole disposed in a partition between the oxidation chamber and the ammonia-mixing chamber.

37. The apparatus of claim 32 wherein the oxidation chamber and the ammonia-mixing chamber are in fluid communication via a conduit extending between the oxidation chamber and the ammonia-mixing chamber.

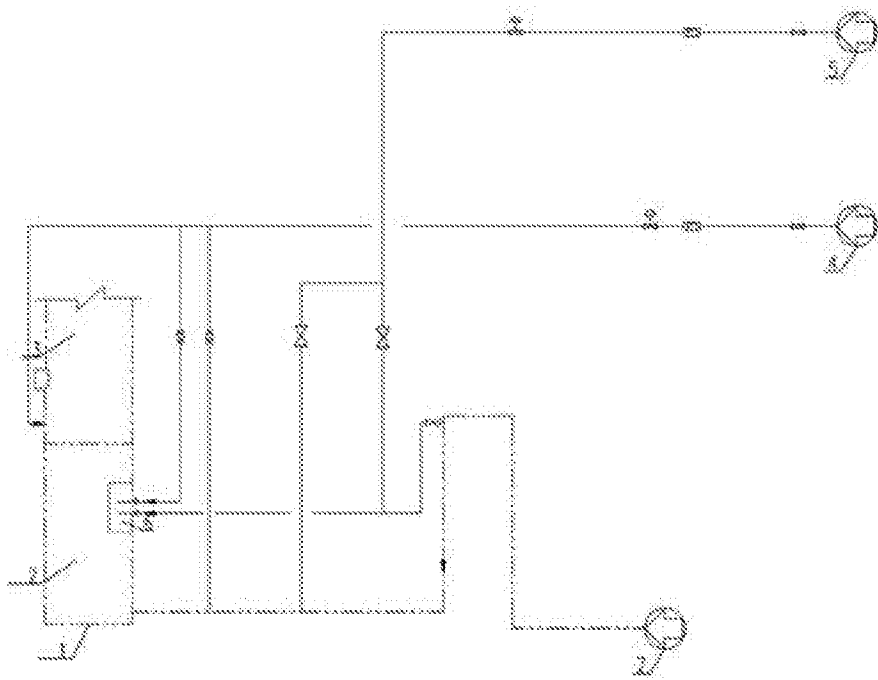


Fig 1

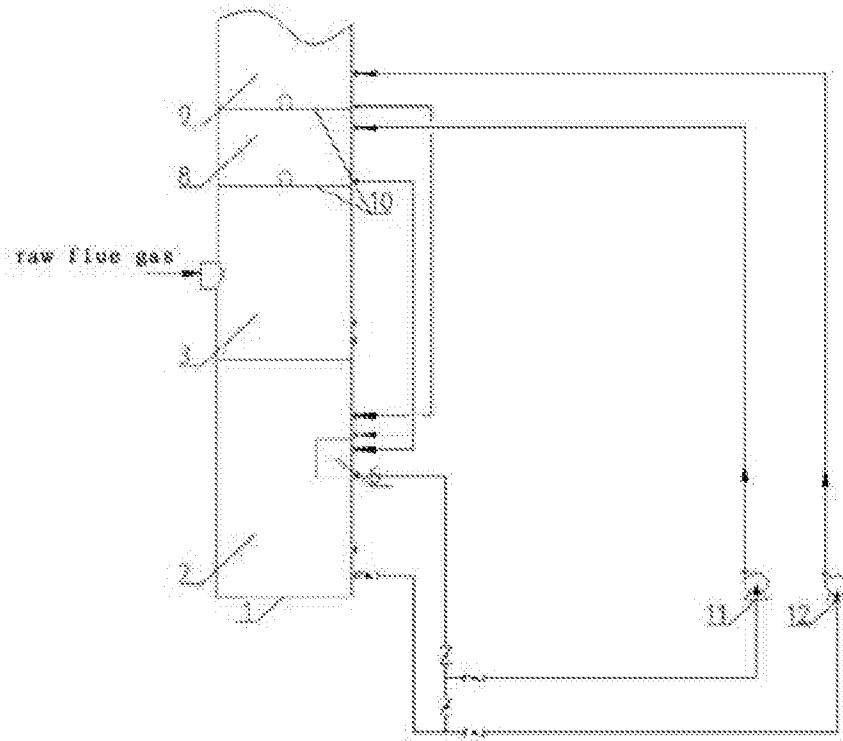


Fig 2

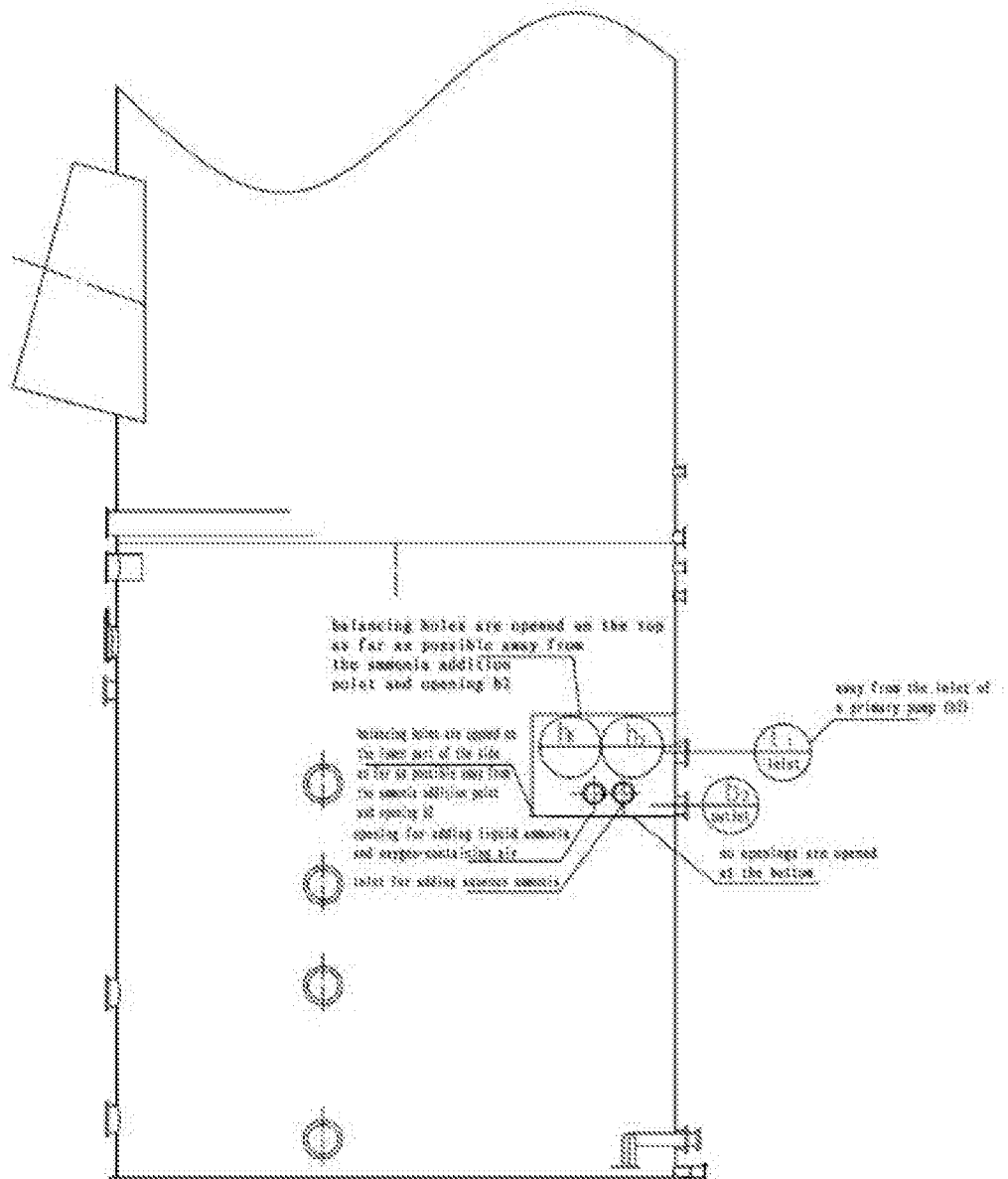


Fig 3

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/096797

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
B01D 53/78(2006.01)i; B01D 53/50(2006.01)i; B01D 53/76(2006.01)i		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
CNABS,CNTXT,CNKI,VEN: ammonia, ammonium, desulfur+, desulphur+, spray, +jet+, scrub+, +ject+, oxidat+, oxygen+, circulat+, cycl+, return, recycl+		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 107213769 A (JIANGSU NEW CENTURY JIANGNAN ENVIRONMENTAL PROT CO LTD) 29 September 2017 (2017-09-29) claims 1-16	1-16
X	CN 205760547 U (WEIFANG SPECIAL STEEL GROUP CO LTD) 07 December 2016 (2016-12-07) claims 1-4, description, paragraphs [0004] to [0008], [0015] and figures 1-2	1, 4, 7
Y	CN 205760547 U (WEIFANG SPECIAL STEEL GROUP CO LTD) 07 December 2016 (2016-12-07) claims 1-4, description, paragraphs [0004] to [0008], [0015] and figures 1-2	2-31 and 33-37
Y	CN 103301736 A (JIANGSU NEW CENTURY ENVIRONMENTAL PROT CO LTD) 18 September 2013 (2013-09-18) claims 1-4, description, paragraphs [0003] to [0005], [0007] and figure 1	2-31 and 33-37
Y	CN 203264545 U (JIANGSU NEW CENTURY ENVIRONMENTAL PROT CO LTD) 06 November 2003 (2003-11-06) claims 1-4, description, paragraphs [0025]-[0031] and figure 1	2-31 and 33-37
Y	CN 1211464 A (LENTJES BISCHOFF GMBH) 24 March 1999 (1999-03-24) claims 1-5, description, page 2, line 6 – page 6, line 6 and figure 1	2-31 and 33-37
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “E” earlier application or patent but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
13 September 2018		09 October 2018
Name and mailing address of the ISA/CN		Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA 6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China		LIU,Tianzuo
Facsimile No. (86-10)62019451		Telephone No. 86-010-62084793

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/096797

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 205730861 U (ANHUI TONGXING ENV PROT ENG CO LTD) 30 November 2016 (2016-11-30) claims 1-7, description, paragraphs [0026]-[0038] and figure 1	2-31 and 33-37
Y	CN 105749704 A (ZHANG BO) 13 July 2016 (2016-07-13) claims 1-10, description, paragraphs [0045]-[0054] and figure 1	2-31 and 33-36
A	US 9370745 B2 (JIANGSU NEW CENTURY JIANGNAN ENVIRONMENTAL PROT CO LTD) 21 June 2016 (2016-06-21) the whole document	1-31 and 33-37

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

- [1] Claim 1 relates to an ammonia-based desulfurization process.
- [2] Claim 10 relates to an apparatus for implementing the ammonia-based desulphurization process.
- [3] Claim 17 relates to a method of ammonia-based oxidative desulfurization.
- [4] The same or corresponding technical features are that: an oxidation chamber, an ammonia absorbent is added to an ammonia-mixing chamber and ammonia-based desulfurization.
- [5] D1 (CN 205760547 U) discloses a desulfurizing tower and process (see claims 1-4, description, paragraphs [0004] to [0008], [0015] and figures 1-2). From top to bottom, a reaction section is provided with an absorbing section, a condensing section and an oxidation section with an ammonia adding chamber located inside. The ammonia adding chamber is connected with an ammonia adding pipe through a three-way pipe with a plurality of overflow holes. Ammonia is mixed with a solution in the ammonia adding chamber.
- [6] Hence, all the same or corresponding technical features are disclosed by D1.
- [7] Therefore, the same or corresponding technical features are not the special technical features that define a contribution which the invention makes over the prior art. Therefore, claims 1, 10 and 17 lack unity and do not meet the requirements of PCT Rule 13.2.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
  - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
  - No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2018/096797**

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	107213769	A	29 September 2017	CL	2017001697	A1	15 December 2017
				BR	102017013602	A2	26 September 2017
				CA	2971657	A1	25 August 2017
				US	10016721	B1	10 July 2018
				CA	2971657	C	19 June 2018
				JP	2018023967	A	15 February 2018
CN	205760547	U	07 December 2016	None			
CN	103301736	A	18 September 2013	CN	102908890	A	06 February 2013
				CN	103301736	B	25 February 2015
CN	203264545	U	06 November 2003	None			
CN	1211464	A	24 March 1999	EP	0891804	B1	27 August 2003
				DK	0891804	T3	22 December 2003
				RU	2166355	C2	10 May 2001
				DE	59809384	D1	02 October 2003
				ID	20592	A	21 January 1999
				HU	9801539	A3	28 September 2001
				HU	9801539	A2	28 June 1999
				PL	191238	B1	28 April 2006
				EP	0891805	B1	27 August 2003
				HU	9801541	A3	28 March 2002
				HU	9801541	A2	28 June 1999
				CN	1211465	A	24 March 1999
				US	6063352	A	16 May 2000
				ES	2205332	T3	01 May 2004
				CN	1101720	C	19 February 2003
				CA	2263739	C	12 February 2002
				CA	2264261	A1	24 September 2000
				PL	327489	A1	01 February 1999
				CZ	291531	B6	12 March 2003
				JP	4057705	B2	05 March 2008
				DE	19731062	A1	21 January 1999
				CZ	290230	B6	12 June 2002
				CZ	9802261	A3	17 February 1999
				PL	327490	A1	01 February 1999
				HU	221175	B1	28 August 2002
				RU	2176543	C2	10 December 2001
				CZ	9802260	A3	17 February 1999
				EP	0891804	A2	20 January 1999
				CA	2263739	A1	17 September 2000
				CA	2264261	C	06 August 2002
HU	9801539	D0	28 September 1998				
JP	3538547	B2	14 June 2004				
EP	0891805	A2	20 January 1999				
DE	19731062	C2	12 July 2001				
HU	9801541	D0	28 September 1998				
CN	1104935	C	09 April 2003				
EP	0891804	A3	03 November 1999				
PL	191530	B1	30 June 2006				
EP	0891805	A3	03 November 1999				

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2018/096797**

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
				JP	H1199318	A	13 April 1999
				ID	20587	A	21 January 1999
				ES	2201376	T3	16 March 2004
				JP	H1176748	A	23 March 1999
				DK	0891805	T3	15 December 2003
				US	6139807	A	31 October 2000
				DE	59809385	D1	02 October 2003
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CN	205730861	U	30 November 2016	None			
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CN	105749704	A	13 July 2016	CN	105749704	B	26 December 2017
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US	9370745	B2	21 June 2016	US	2015352486	A1	10 December 2015
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