

TITLE OF THE INVENTION

Ammonia Analyzer

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to an NH_3 analyzer for continuously measuring the concentration of ammonia (NH_3) contained in exhaust gas. Such an NH_3 analyzer is set on an outlet of a flue gas denitrator for exhaust gas treatment on a low temperature part subsequent to an air preheater of an oil burning boiler or on a outlet of a dust collector having an NH_3 injector, and utilized for measuring the NH_3 concentration in the treated exhaust gas.

Description of the Prior Art

Fig. 1 is a schematic block diagram showing an exemplary conventional NH_3 analyzer. Describing the measurement principle, NH_3 analyzers for flue gas employing catalysts include an oxidation type analyzer and a reduction type analyzer. Each NH_3 analyzer is formed by a sampling probe part 51 consisting of two sampling probe lines of NH_3 and NO_x passages, an analytic part 52 having analyzers for measuring the NO concentrations of the NH_3 and NO_x passages respectively, and an operation part 53 calculating the NH_3 concentration from the NO concentrations obtained from the two analyzers. NH_3 passage is provided with a catalyst C, which is prepared from an ammonia oxidation catalyst in the oxidation type analyzer or an ammonia reduction catalyst in the reduction type analyzer.

The oxidation type NH_3 analyzer oxidizes NH_3 contained in the NH_3 passage into equimolar NO and detects the concentration of NO, thereby measuring the NH_3 concentration. In other words, NO_x generally exists in the flue gas, and hence the NH_3 analyzer reduces NO_2 contained in the flue gas to NO by an NO_2 -NO converter upstream a detector. Since only the NO_x concentration is detected in the NO_x passage while the total concentration of NH_3 and NO_x is detected in the NH_3 passage, the NH_3 concentration is obtained as the difference between detection values of detectors in the two

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passages.

On the other hand, the reduction type NH_3 analyzer reacts NH_3 contained in the NH_3 passage with equimolar NO_x through action of the reduction catalyst and detects the concentration of NO_x defecting by the reaction thereby measuring the NH_3 concentration. In this case, the NO_x concentration decreased by the NH_3 concentration is detected in the NH_3 passage, and the NH_3 concentration is detected as the difference between detection values in the passages.

The conventional NH_3 analyzer inserts two sampling pipes for NH_3 and NO_x in a flue pipe and sucks sample gas from forward ends of the sampling pipes with a pump provided on the analytic part. The sampling pipes are heated to a temperature exceeding about 200°C for preventing dew condensation of moisture contained in the flue gas.

In order to prevent dust contained in the flue gas from reaching the NH_3 detection part with the flue gas, a filter for dust removal is previously set in a sampling probe passage subsequent to a suction port of the sampling pipe. The catalyst C is provided in the sampling pipe located in the flue pipe.

Fig. 2 is a partially fragmented side elevational view showing a sampling pipe 62 of a sampling probe of an NH_3 analyzer set on an outlet of a dust collector having an NH_3 injector for a heavy oil burning boiler in a state driving the boiler for a long time.

The sampling pipe 62 of metal is enclosed with a heater 66 and set at a temperature of 400°C for example. However, due to influence by the temperature (generally about 140 to 150°C) of flue gas, the temperature of the sampling pipe 62 gradually lowers toward its forward end. The temperature at the forward end of the sampling pipe 62 is about 140 to 150°C equally to the flue gas.

Dust 68 such as ammonium hydrogensulfate adheres to the forward end of the sampling pipe 62. It is known that the NH_3 analyzer indicates an abnormal value when the dust 68 adheres. The mechanism is as follows:

The dust 68 adheres to the forward end of the sampling pipe 62 since solid particulates of ammonium sulfate contained in the flue gas form acidic

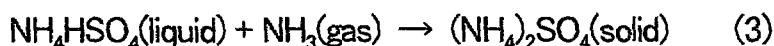
ammonium hydrogensulfate (liquid) at about 160 to 250°C, to adhere and sediment. The chemical formula for this is as follows:



When the flue gas temperature increases (the boiler load increases) or the NH_3 concentration decreases, the adhering and sedimenting ammonium hydrogensulfate partially decomposes and releases NH_3 , to increase the indicated value of the analyzer. The chemical formula for this is as follows:



When the flue gas temperature decreases (the boiler load decreases) or the NH_3 concentration increases on the contrary, the adhering and sedimenting ammonium hydrogensulfate partially absorbs NH_3 gas and is converted to ammonium sulfate, to decrease the indicated value of the analyzer. The chemical formula for this is as follows:



It is known that the equilibrium relation between ammonium sulfate and ammonium hydrogensulfate varies with the temperature and NH_3 partial pressure, as shown in Fig. 3 illustrating values measured by a flow method.

In a region where the gas temperature is in excess of about 250°C, particulates of ammonium sulfate contained in the flue gas decompose and release NH_3 gas through the formulas (1) and (2). For example, it can be theoretically said that an ammonium sulfate component of 10 mg/m³N existing in dust from an outlet of a dust collector having an NH_3 injector increases the indicated value of an NH_3 analyzer by about 3 ppm if the analyzer has no filter. The inventors have experienced in an experiment that, even if a filter is provided, ammonium sulfate adhering thereto adsorbs/desorbs NH_3 depending on the temperature or the NH_3 concentration to cause abnormality on the indicated value of the analyzer.

While the NH_3 analyzer of the NO reduction system is applied on its principle to the case where the NO concentration in gas is higher than the NH_3 concentration, the NH_3 concentration may temporarily exceed the NO concentration in starting of a boiler or the like. It has been proved that the reduction catalyst absorbs NH_3 in this case to thereafter increase the NH_3

indicated value. In this regard, the inventors have investigated the relation between the catalytic temperature and the amount of adsorbed NH_3 , to confirm that a larger amount of NH_3 is adsorbed when the heater temperature (catalytic temperature) is as low as shown in Fig. 4. When the catalyst is
5 provided in the sampling pipe, the catalytic temperature may change due to influence by change of the flue gas temperature.

Thus, the conventional NH_3 analyzer is inferior in measurement accuracy for the NH_3 concentration in the flue pipe, and extremely deteriorated in responsiveness particularly when the NH_3 concentration
10 changes due to change of the flue gas temperature.

SUMMARY OF THE INVENTION

Accordingly, the objective of the present invention is to improve the measurement accuracy of an NH_3 analyzer employed for the measurement of
15 the NH_3 concentration in flue gas.

An ammonia analyzer according to an aspect of the present invention, comprising a sampling probe inserting a sampling pipe into a flue pipe and guiding flue gas out from the flue pipe and an ammonia detection part measuring the ammonia concentration in the flue gas directly or through a
20 catalyst, comprises a temperature control part keeping the temperature of a flue gas passage between a flue gas suction port of the sampling pipe and the ammonia detection part in the range of 250 to 400°C.

In order to prevent adhesion/sedimentation of ammonium hydrogensulfate in the flue gas passage, particularly in the flue gas suction port,
25 the inventors have examined the decomposition temperature of ammonium sulfate. Fig. 5(A) is a model diagram showing an apparatus for a visual decomposition test of ammonium sulfate, Fig. 5(B) is a model diagram showing state change of a sample, and Fig. 5(C) illustrates the test result. Referring to Fig. 5(C), the vertical axis shows the temperature and the horizontal axis
30 shows the elapsed time. In this test, about 5 mg of powdery ammonium sulfate was placed on a heating part of metal and state change of the sample was observed while monitoring the temperature of the heating part. The

ambient temperature was 20°C.

Ammonium hydrogensulfate did not decompose but remained in an adhering and sedimenting state under 250°C, while decomposition of ammonium hydrogensulfate took place at a temperature exceeding 250°C.

- 5 The decomposition rate gradually increased from 250°C, and it has been confirmed that ammonium hydrogensulfate immediately decomposes at a temperature in excess of about 300°C.

This result suggests that adhesion/sedimentation of ammonium hydrogensulfate can be prevented when the temperature is in excess of 250°C.

- 10 The inventors have further found in the process of a probe improvement test that NH_3 is oxidized and converted to NO at a temperature exceeding 400°C to decrease the NH_3 indicated value.

- Therefore, when keeping the temperature of the flue gas passage between the flue gas suction port and the ammonia detection part in the range of 250 to 400°C, the NH_3 concentration can be correctly measured.
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- An ammonia analyzer according to another aspect of the present invention, comprising a sampling probe inserting a sampling pipe into a flue pipe and guiding flue gas out from the flue pipe and an ammonia detection part measuring the ammonia concentration in the flue gas directly or through a catalyst, comprises a filter for dust removal provided on a flue gas suction port of the sampling pipe to be exposed to a flue gas flow in the flue pipe.
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- If the concentration of particulates of ammonium sulfate contained in the flue gas is so high that the concentration of NH_3 generated by decomposition of ammonium sulfate cannot be neglected, the particulates of ammonium sulfate must be removed through a filter. It has been confirmed that, when providing a filter on a forward end of the sampling pipe to expose the overall filter to the flue gas flow in the flue pipe, adsorption/desorption of NH_3 in dust adhering to the filter is saturated in a short time so that its influence on the response speed of the ammonia detection part is substantially negligible. This is because the amount of flue gas coming into contact with the filter in a constant time is several 100 to several 1000 times as compared with the case of providing the filter in the probe.
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The filter is preferably prepared from a bag filter of cloth. The bag filter flutters due to the flue gas flow in the flue pipe to brush off the adhering dust and decrease adhesion of the dust.

5 The sampling pipe is preferably provided with a coiled sheath heater and increased in thickness on its forward end portion (flue gas suction port side). Consequently, the heat capacity of the forward end portion can be increased to keep the sampling pipe at a prescribed temperature between the flue gas suction port and the ammonia detection part.

10 The heater provided on the forward end portion of the sampling pipe is preferably increased in density. Consequently, the forward end portion of the sampling pipe, which is readily decreased in temperature due to influence by the flue gas temperature, can be kept at a prescribed temperature.

15 An ammonia analyzer according to still another aspect of the present invention, comprising a sampling probe inserting a sampling pipe into a flue pipe and guiding flue gas out from the flue pipe and an ammonia detection part having two passages for ammonia and a nitrogen oxide with an ammonia oxidation catalyst or an ammonia reduction catalyst in the ammonia passage for measuring the nitrogen monoxide concentrations in the respective passages and obtaining the ammonia concentration from the concentration
20 difference therebetween, comprises a heating box set outside the flue pipe for keeping the ammonia oxidation catalyst or the ammonia reduction catalyst at a constant temperature.

25 Adsorption of NH_3 to the ammonia oxidation catalyst or the ammonia reduction catalyst increases when the catalytic temperature lowers while the amount of adsorption of NH_3 varies with the catalytic temperature. Therefore, when setting the catalyst in the heating box not influenced by change of the flue gas temperature and keeping the same at a constant temperature, it is possible to suppress an error in the value indicated by the analyzer depending on the amount of adsorption of NH_3 .

30 In this case, the analyzer preferably comprises a temperature control part keeping the temperature of the flue gas passage between the flue gas suction port of the sampling pipe and the ammonia conversion catalyst in the

range of 250 to 400°C.

Furthermore, the analyzer preferably comprises a filter for dust removal on the flue gas suction port of the sampling pipe, to be exposed to the flue gas flow in the flue pipe.

- 5 The foregoing along with other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawing.

10 BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic block diagram of a conventional NH_3 analyzer,

- Fig. 2 is a partially fragmented side elevational view showing a sampling pipe of a sampling probe of an NH_3 analyzer set on an outlet of a dust collector having an NH_3 injector for a heavy oil burning boiler in a state after driving the boiler for a long time;
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Fig. 3 illustrates the equilibrium relation between ammonium sulfate and ammonium hydrogensulfate;

Fig. 4 illustrates the ratio of NH_3 adsorption to a catalyst with respect to a heater temperature;

- 20 Fig. 5(A) is a model diagram showing an apparatus for a visual deposition test of ammonium sulfate, Fig. 5(B) is a model diagram showing state change of a sample, and Fig. 5(C) illustrates the test result;

Fig. 6 is a front sectional view showing a sampling probe according to an embodiment of the present invention;

- 25 Fig. 7 is a sectional view taken along the line A-A in Fig. 6;

Fig. 8 is an enlarged sectional view of a part enclosed with a circle in Fig. 6; and

Fig. 9 is a block diagram showing the concept of the embodiment.

30 DESCRIPTION OF THE PREFERRED EMBODIMENT

Fig. 6 is a front sectional view showing a sampling probe according to an embodiment of a reduction type ammonia analyzer for flue gas according to

the present invention, Fig. 7 is a sectional view taken along the line A-A in Fig. 6, and Fig. 8 is an enlarged sectional view of a part enclosed with a circle in Fig. 6. Fig. 6 is a sectional view taken along the line B-B in Fig. 7. Fig. 9 is a conceptual diagram of this embodiment.

5 A sampling pipe 1, which is inserted in a flue pipe for sampling flue gas, has a flue gas suction port 1a on an end thereof. The sampling pipe 1 is formed by welding and integrating an outer metal cover 6 with an inner metal tube 2. The tube 2 is increased in thickness on its forward end portion. A heater 3, which is coiled around the tube 2 of the sampling pipe 1, is covered
10 with a heat insulator 4. The heater 3 is increased in density on the forward end of the tube 2. A temperature control part 31 controls the heater 3 to keep the temperature around the gas suction port 1a of the sampling pipe 1 at 300°C for example, so that the temperature is not in excess of 400°C on any position of the sampling pipe 1.

15 The flue gas suction port 1a is provided with a filter support 5, and a 3 μ m-mesh bag filter 7 for dust removal, for example, is provided to cover the filter support 5. The bag filter 7 is exposed to a flue gas flow in the flue pipe. A backwash air mechanism (not shown) is provided for feeding air into the sampling pipe 1 backward and removing dust adhering to the bag filter 7, to
20 backwash the bag filter 7 periodically or at need.

 The base end of the sampling pipe 1 is inserted in a heating box 9, branched into an NO_x passage 11 and an NH₃ passage 13 in the heating box 9 and guided out from the heating box 9. The NH₃ passage 13 passes through an NH₃ reduction electric furnace unit 15 in the heating box 9, and is guided
25 out from the heating box 9. The NH₃ passage 13 located between the sampling probe 1 and the NH₃ reduction electric furnace unit 15 is covered with a heat insulator 17 and its temperature is kept at 300°C for example, by a furnace inlet heater 19 provided in the heat insulator 17. The temperature control part 31 controls the furnace inlet heater 19.

30 The NH₃ passage 13 is provided with a catalytic reaction tube charged with an NH₃ reduction catalyst 21 for reacting NH₃ and NO and converting the same to nitrogen (N₂) and water (H₂O) in the NH₃ reduction electric furnace

unit 15. The NH_3 reduction electric furnace unit 15 heats the NH_3 reduction catalyst to about 400°C and keeps the same at a constant temperature.

The heating box 9 is provided therein with a space heater 23 keeping the internal temperature thereof at 150°C for example. The temperature control part 31 controls the space heater 23 as well.

The NO_x passage 11 and the NH_3 passage 13 guided out from the heating box 9 are connected to an NO_x -system NO detector 25 and an NH_3 -system NO detector 27 respectively. The NO detectors 25 and 27 are of chemiluminescent types, for example. Passages downstream the NO detectors 25 and 27 are guided to an outlet through a pump 29 sucking the flue gas.

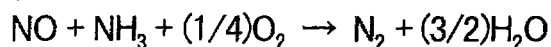
As to the measurement principle, the reduction type NH_3 analyzer to which the present invention is applied divides a sample collected from the flue pipe into two systems, i.e., an NH_3 system measuring the $(\text{NO}-\text{NH}_3)$ concentration and an NO_x system measuring the NO concentration, detects the concentrations by the NO detectors 25 and 27 provided downstream the respective systems and calculates the difference between two output signals, thereby measuring the NH_3 concentration.

With reference to Figs. 6 to 9, the flow of the flue gas shall now be described.

The pump 29 is driven to introduce the flue gas in the flue pipe into the sampling pipe 1 from the flue gas suction port 1a through the bag filter 7. The bag filter 7 removes dust from the flue gas. The bag filter 7, exposed to the flue gas flow in the flue pipe, flutters to brush off the dust adhering to the bag filter 7. The heater 3 keeps the internal temperature of the sampling pipe 1 at 300°C , whereby adhesion/sedimentation of ammonium hydrogensulfate caused by a slight amount of dust contained in the flue gas passing through the bag filter 7 can be prevented.

The sampled flue gas is fed to the heating box 9 through the sampling pipe 1, and divided into the two systems of the NO_x passage 11 and the NH_3 passage 13. NH_3 contained in the sample fed to the NH_3 passage 13 reacts with equimolar NO due to action of the NH_3 reduction catalyst 21 provided in

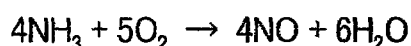
the NH_3 reduction electric furnace unit 15 as follows:



The NO concentration in the flue gas in the NH_3 passage 13 downstream the NH_3 reduction catalyst 21 is at a value obtained by
 5 subtracting NO reacting with NH_3 from NO having been originally contained in the flue gas.

NO_x generally exists in the flue gas in addition to NH_3 . Therefore, when reducing NO_2 contained in the flue gas into NO by an NO_2 -NO converter upstream the detector and detecting the NO concentration with the NO
 10 detector, the NO concentration decreased by the NH_3 concentration is detected in the NH_3 passage 13, whereby the NH_3 concentration is obtained as the difference between detection values of detectors in the passages 11 and 13.

While the NH_3 reduction catalyst is employed in the embodiment, the
 15 present invention is also applicable to an oxidation type NH_3 analyzer when substitutionally employing an NH_3 oxidation catalyst. As to the measurement principle, the oxidation NH_3 analyzer brings NO and NH_3 contained in flue gas into contact with the catalyst and detects the concentration of NO generated by reaction thereby equivalently detecting the NH_3 concentration. The
 20 reaction formula is as follows:



In the flue gas in the NH_3 passage 13 downstream the NH_3 oxidation catalyst, NO generated by oxidation of NH_3 is added to initial NO. The analyzer reduces NO_2 into NO by an NO_2 -NO converter and detects NO by
 25 NO detectors provided downstream the NO_x passage 11 and the NH_3 passage 13 respectively, so that the NH_3 concentration is obtained as the difference between detection values of these passages 11 and 13.

If the amount of dust contained in the flue gas in the flue pipe is small, the flue gas may be sampled without the bag filter 7.

30 While the NH_3 analyzer according to the embodiment employs a catalyst, the present invention is not restricted to this but is also applicable to an NH_3 analyzer employing no catalyst. In this case, it is preferable to keep

the temperature of the flue gas passage between the sampling pipe and the NH_3 detector at a constant temperature in the range of 250 to 400°C.

While the chemiluminescent detectors are employed in the embodiment, the present invention is not restricted to this but is also
5 applicable to an NH_3 analyzer employing other types of detectors such as those of wavelength modulation type ultraviolet systems or secondary differential absorption spectrophotometric systems.

While the bag filter is employed in the embodiment, the present invention is not restricted to this but another filter such as a metal filter is also
10 employable.

The inventive NH_3 analyzer comprising a sampling probe is employable for managing the concentration of NH_3 injected for denitrating flue gas from an oil burning boiler or collecting dust for example, and controlling the NH_3 injection rate.

15 Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, as the spirit and scope of the present invention is limited only by the terms of the appended claims.

WE CLAIM:

1. An ammonia analyzer comprising a sampling probe inserting a sampling pipe into a flue pipe and guiding flue gas out from said flue pipe and an ammonia detection part measuring the ammonia concentration in said flue gas guided by said sampling pipe directly or through a catalyst, said ammonia analyzer comprising
a temperature control part keeping the temperature of a flue gas passage between a flue gas suction port of said sampling pipe and said ammonia detection part in the range of 250 to 400°C.
2. The ammonia analyzer in accordance with claim 1, wherein said ammonia detection part has two passages for ammonia and an nitrogen oxide with an ammonia oxidation catalyst or an ammonia reduction catalyst in said ammonia passage for measuring nitrogen monoxide concentrations of respective said passages and obtaining the ammonia concentration from the concentration difference therebetween.
3. The ammonia analyzer in accordance with claim 1, wherein said sampling pipe is provided on its flue gas suction port with a filter for dust removal to be exposed to a flue gas flow in said flue pipe.
4. The ammonia analyzer in accordance with claim 2, wherein said sampling pipe is provided on its flue gas suction port with a filter for dust removal to be exposed to a flue gas flow in said flue pipe.
5. The ammonia analyzer in accordance with claim 3, wherein said filter is a bag filter.
6. The ammonia analyzer in accordance with claim 1, wherein said sampling pipe is provided with a heater as said temperature control part, with a forward end portion of said sampling pipe increased in



thickness for increasing heat capacity.

7. The ammonia analyzer in accordance with claim 6, wherein
said heater is a sheath heater increased in density on said forward end
5 portion of said sampling pipe.

8. An ammonia analyzer comprising a sampling probe inserting a
sampling pipe into a flue pipe and guiding flue gas out from said flue pipe and an
ammonia detection part measuring the ammonia concentration in said flue gas
10 guided by said sampling pipe directly or through a catalyst, said ammonia
analyzer comprising:

a filter for dust removal provided on a flue gas suction port of said
sampling pipe to be exposed to a flue gas flow in said flue pipe.

9. The ammonia analyzer in accordance with claim 8, wherein
said ammonia detection part has two passages for ammonia and an
nitrogen oxide with an ammonia oxidation catalyst or an ammonia reduction
catalyst in said ammonia passage for measuring nitrogen monoxide
concentrations of respective said passages and obtaining the ammonia
20 concentration from the concentration difference therebetween.

10. The ammonia analyzer in accordance with claim 8, wherein
said filter is a bag filter.

