

Analysis of Ammonia Content in Tail Gas of Plasma Flue Gas Desulfurization Technology and Its Application

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Abstract: Plasma flue gas desulfurization and deamination process has many advantages that traditional methods do not have, thus it has become one of the hot topics in recent years. In order to improve the desulfurization rate of plasma flue gas and better play the role of water and ammonia in the process, we propose a method of corona discharge steam activation to improve the desulfurization rate. Negative DC corona discharge and water absorption have a synergistic effect on flue gas desulfurization, which improves the desulfurization effect. The desulfurization efficiency of single discharge or water absorption is very low, and the desulfurization efficiency is greatly improved when water absorption and discharge work together. This paper also discusses key issues such as reduced energy consumption, residual ammonia treatment, and product collection in industrial applications of the technology. The effect of discharge on SO₂ removal and the combination of desulfurization and dust removal are discussed. The desulfurization rate of flue gas can be improved obviously by increasing corona discharge steam activation technology. The results show that the vapor activation technology of corona discharge is effective and feasible.

1. Introduction

Sulfur dioxide is a toxic gas, which is the main component of acid rain. It is harmful to the growth of crops and the physical and mental health of human beings. It will also destroy the relics of ancient culture and have a great impact on the environment [1]. Plasma flue gas desulfurization technology mainly refers to electron beam ammonia flue gas desulfurization technology and pulse discharge plasma flue gas desulfurization and denitration technology. Its treatment process is to treat flue gas containing sulfur dioxide and ammonia oxide with energy generated by electron accelerator or high voltage pulse power supply [2]. In the process of treating ammonia-containing waste gas, the soot, ammonia, and other pollutant molecules can be captured and degraded at the same time. Since sulfur in the flue gas is in the form of SO₂, technical desulfurization is possible [3]. Plasma dry desulfurization is a new technology developed in recent years. It has a series of advantages, such as investment, high-quality chemical products, no waste liquid treatment, etc., can simultaneously remove SO₂ and NO, simple operation, small size, etc. [4]. The technology realizes the comprehensive utilization of sulfur ammonia resources and natural ecological cycle, and is a green resource comprehensive utilization of flue gas purification technology, representing the development direction of flue gas desulfurization technology.

2. Experimental Part

2.1. Instruments and reagents

DX-320 ion chromatograph is composed of double plunger single channel reciprocating pump, CL20 chromatographic column box, CI25A chromatograph host, conductivity detector and PEAKNET.60 data processing system. The experimental reactor has a multi-needle and water film electrode structure. The reactor shell is cylindrical and made of polyethylene material. Methane sulfonic acid is analytically pure, NH₄Cl is of superior grade, and ammonia standard gas is prepared by Chemical Research Institute. During the experiment, if the water vapor is activated by corona discharge, the water vapor is injected into the reactor through needle electrodes. If the water

vapor is not treated by corona discharge, it is to let the water vapor enter the reactor through the front flue of the reactor. The activation and inactivation of water vapor in corona discharge can be realized by adjusting the gas commutation switch.

2.2. Principle of analytical method

The analyzer is based on the principle of non-dispersive infrared. After the pretreatment of the flue gas, the concentration of ammonia can be monitored in real time. Active species have strong oxidation, which can initiate oxidation reaction to oxidize SO_2 to SO_3 , generate H_2SO_4 in water and gas, and further produce ammonium sulfate when ammonia is injected as additive, which can be recovered as by-product. Since the concentration of SO_2 in the flue gas is on the order of 10^{-3} , the probability of direct dissociation by high-energy electrons is small. It reacts with the Nessler reagent to form a yellow-brown complex, and its absorbance is measured. Ion chromatography is the separation of ions by ion exchange between the mobile phase and the stationary phase.

2.3. Experimental method

Taking ammonia standard gas with a certain concentration and tail gas ammonia in desulfurization experimental equipment as samples, four different methods were used to test and compare the analysis results. Lime and other desulfurizing agents are added into the absorption tower, and the desulfurizing agent is fluidized by high-speed gas so as to be strongly mixed and contacted with flue gas, and acidic pollutants in the flue gas are neutralized and solidified with the desulfurizing agent so as to achieve the purpose of purifying the flue gas. And then cooling by a heat exchanger or/and a spray cooler. The cooled flue gas is mixed with stoichiometric ammonia and enters the plasma reactor. As the needle electrodes are evenly distributed on the needle plate, the gas passes through the circular discharge area in a radial shape and bypasses the needle plate electrode after discharge treatment, thus ensuring that the flue gas completely passes through the discharge area and the treated flue gas enters the gas outlet at the center of the cover plate on the reactor shell upwards. The desulfurization effect of ammonia activation is carried out under the condition that no pulse voltage is applied to the pulse discharge electrode system and the pulse discharge plasma does not work. Only the desulfurization rate and its influencing factors of applying positive DC voltage to the activation electrode are studied. The sampling methods of ion chromatograph and nessler's reagent spectrophotometry are as follows: dilute sulfuric acid is used as absorption liquid, and sampling method of nessler's reagent spectrophotometry is adopted.

3. Results and Discussion

3.1. Determination of ammonia standard gas

Different methods were used to determine ammonia standard gas with a certain concentration, and the determination results are listed in Table 1. As can be seen from the table, the push-pull speed, visual error, etc. will cause differences due to the need to use the push-pull handle for sampling in the detection tube method. After being heated, the flue gas is mixed with sulfur dioxide and sent to the reactor. Ammonia gas is mixed with compressed air and added from the hollow electrode. Molecules that pass through N_2 excited states have a much higher probability of dissociation than molecules that pass through electron collisions. The emission spectra of SO fragments produced by collision have been detected in experiments. Flue gas enters directly from one end of the reactor wall, passes through the discharge area between the needle electrode and the water surface, and then is discharged from the other end of the reactor wall. The desulfurization rate increases with the increase of activation voltage when water vapor or ammonia are activated separately and water vapor and ammonia are activated simultaneously. At the same activation voltage, the desulfurization rate when water vapor and ammonia are activated simultaneously is higher than that when they are activated separately. Therefore, the corona current increases with the increase of activation voltage. Ammonia molecule is an electronegative gas. It is easy to combine with electrons to form ions with low mobility. Therefore, the corona current caused by ammonia

injection is slightly lower than that without injection. In this experiment, the dosage of sulfur dioxide and ammonia is controlled by mass flow controller. A flue gas parameter measurement outlet is set before and after the reactor and after the bag filter.

Table 1 Comparison of test values of pure ammonia standard gas side

	Ammonia analyzer	Ion chromatography	Nessler's reagent method
Ammonia concentration(mg/m ³)	70.36	73.94	76.03
Average value(mg/m ³)	75.24	77.82	74.28

3.2. Determination of ammonia content in tail gas of desulfurization unit

Ammonia analyzer can monitor ammonia concentration change online, but it is easily disturbed by moisture and sulfur dioxide in flue gas. Therefore, Nessler reagent spectrophotometry is generally used for calibration. At the same time, the alkaline water of slag ash flushing is used to supplement the water of dust collector, which can make the wastewater reused and save water. There are two ways to remove SO₂, one is first to form salt and then to oxidize, the other is to oxidize and then to form salt. In DC corona discharge plasma flue gas desulfurization, the first way is the main way. SO₂ is oxidized by free radical reaction to form acid mist, which is separated from the gas phase [5]. The high-energy active particles generated by low-temperature plasma can reduce the activation energy of the catalytic reaction, so that the catalyst originally used at high temperature can be used at lower temperature [6]. The experimental results are shown in Figure 1. From the figure, it can be seen that the measured value of ammonia analyzer can reflect the change of ammonia content in flue gas, but it is quite different from the measured result of Nash reagent method. When humidity increases, corona current activated by ammonia decreases under the same activation voltage. The reason is that water vapor is an electronegative gas, which easily adsorbs electrons to generate ions, resulting in a decrease in mobility, which leads to a decrease in corona current. The results show that the simultaneous activation of steam and ammonia is effective.

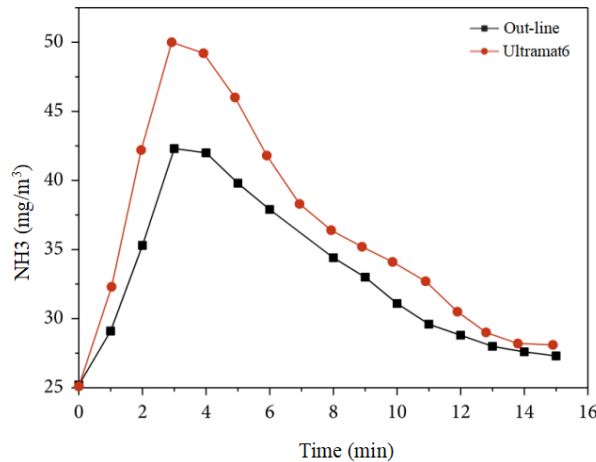


Fig.1. Nessler reagent method and ammonia analyzer tail gas ammonia sample

Because the Nessler reagent spectrophotometry requires the preparation of reagent solution without ammonia, the steps are complicated and time consuming. Moreover, mercury diamide, a highly toxic reagent, must also be used for color development in the analysis, causing certain pollution to the environment. Because the energy consumption index is related to the future operation cost of the technology and also to the manufacturing cost of DC high voltage power supply. Therefore, the energy consumption must reach an acceptable level for practical application, otherwise the technology will not be adopted. The oxidation and reduction paths exist only under the condition of discharge and are parallel paths [7]. However, both the experimental results and the simulation results of microscopic reaction kinetics show that the oxidation path is the main path. Therefore, we introduce ion chromatography into the determination of ammonia concentration in

tail gas, and compare the results with those determined by Nessler reagent in order to establish a rapid, accurate and environmentally friendly analytical method. The experimental results are listed in Table 2. Because of the same flue gas flow rate and different discharge gap, the residence time of flue gas in the corona zone also changes. The longer the discharge gap is, the more conducive to SO₂ removal. The number of free radicals produced by the collision of high energy electrons with water molecules and ammonia molecules produced by corona discharge is higher than that produced by the injection of water vapor and ammonia alone. In this way, when injected simultaneously, the number of oxidized SO₂ molecules is large and the desulfurization rate is high. Therefore, under the same electric field intensity, ammonia gas injected through activated electrode produces more free radicals and ions than that injected from the front end of the reactor, and the desulfurization efficiency is improved.

Table 2 Analysis results of ammonia content in desulfurization tail gas

Sample number	Sample 1	Sample 2
The content of ammonia was determined by ion chromatography(mg/m ³)	198.36	135.38
The content of ammonia was determined by Nessler's reagent method(mg/m ³)	203.77	145.62

3.3. The influence of flue gas flow rate on removal efficiency

Under the condition that the initial concentration of SO₂ in flue gas is 1200×10^{-6} , the desulfurization efficiency can reach 85% when the positive high pressure is 30V and the flue gas flow rate is 15 Nm³·h⁻¹. The generation of excitation and ionization must be the part of electrons whose energy is equal to the excitation energy and ionization energy. Electrons larger than and smaller than the corresponding energy cannot emit excitation and ionization. Moreover, the electron energy required for the excitation and ionization of water molecules and ammonia molecules are different [8]. The reason is that when ammonia is activated, ammonia moves from high-energy electron region to low-energy electron region. When ammonia gas is not activated, ammonia molecules uniformly enter the electric field region, so compared with the activation, the probability of collision between ammonia gas and high-energy electrons is smaller, and less amino radicals are generated, so the desulfurization efficiency is higher when ammonia gas is activated. The residence time of flue gas in the reactor is 5-6 seconds, the stoichiometric ratio of SO₂ to NH₃ is 1.5:1, and the energy consumption of corona is 1.0-2.5Wh/Nm³. Under these operating conditions, the removal rate of SO₂ with initial concentration of 1000-2000PPm can reach more than 85%. In addition, when the flue gas flow rate is less than 25Nm³/h, the desulfurization efficiency decreases very slowly. Considering the flue gas treatment capacity and removal efficiency, the flue gas flow rate is generally selected as 20Nm³/h, and the desulfurization efficiency is about 75%.

4. Conclusion

Experiments show that Nessler reagent spectrophotometry has strong applicability and can truly reflect the ammonia content in the exhaust gas because it eliminates the interference of other components in the flue gas. However, this method requires a high level of operation and stability of working conditions for analysts, and takes a long time, so it is not suitable for continuous monitoring. Therefore, as a designer, in the selection of boilers, we must proceed from the actual situation of the project, consider comprehensively and select a reasonable desulfurization process. If the reactor is omitted and the dust collector is powered by positive pulse, the desulfurization rate will be low, the residual ammonia leakage and the proportion of positive salt in the reaction product will be low. When measuring single component ammonia, the ammonia on-line analyzer has rapid reaction and high accuracy. However, under actual working conditions, due to the influence of instrument design and structure, the anti-interference ability is poor, and the measurement results are quite different from the real values. Desulfurization efficiency of single discharge or water absorption is very low, while desulfurization efficiency is greatly improved when water absorption

and discharge act together. During the test, flue gas enters from the axis of the high voltage electrode, which is more conducive to the improvement of desulfurization efficiency. Compared with Nessler's reagent colorimetric method, ion chromatography saves a lot of manpower and time, is faster and more convenient, and can be used for analysis of tail gas ammonia in desulfurization experiments.

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