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Dehumidification performance of the Nafion tube for SO2 at low concentration

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Abstract. Under the new situation of low emission standard for coal-fired power plants, improving sample dehumidification technology is the key to accurate monitoring of ultra-low concentration SO_2 flue gas. As a new dehumidification technology, Nafion membrane had been considered as a promising alternative to pretreatment for Continuous Emission Monitoring System (CEMS). The factors affecting the dehumidification efficiency of Nafion tube and the SO_2 preservation rate were investigated by simulating the flue gas experiment. The results showed that the gas flow rate and SO_2 concentration had no significant effect on Nafion dehumidification efficiency and preservation rate. The humidity increased correspondingly to the dehumidification rate, which increased by 0.3%, but when the humidity increased from 15% to 30%, the preservation rate decreased by 1%, and when the SO_2 concentration increases, the effect decreased.

1. Introduction

Ultra-low emission has become the national emission standard of flue gas from coal-fired power plant, which indicated that the concentration of atmospheric pollutants from coal-fired generating units basically reached the emission limit of gas turbine units (at baseline O_2 content 6%, soot, SO_2 and NO_x emission concentration were not higher than 10, 30, and 35 mg/L) [1]. SO_2 and NO_x, the main pollutants, could been removed more than 98% by flue gas desulphurization and denitrification processes with the development of technology. The sulfur content in flue gas has fallen below the standard, and the accuracy of online monitoring SO_2 concentration under ultra-low emission standards was the key to the control of flue gas emission. In order to realize the real-time and continuous monitoring of the above-mentioned pollutants, it is necessary to adopt the corresponding safety monitoring technology- Continuous Emission Monitoring System (CEMS) [2, 3]. The measurement data of the system can be used as the legal basis for the environmental protection departments to levy

pollutant discharge fees on enterprises, and it can be used to measure the environmental air and other pollution processes. Important basis for safety decision-making and effective management.

As an on-line emission monitoring and emission measurement system, CEMS mainly includes sample collection and processing system, analysis and measurement system, data transmission and processing system and auxiliary system. The analysis and measurement system are the core of CEMS [4]. In order to reach the standard of ultra-low emission, a low-range Nondispersive infrared (NDIR) analyzer (SO_2 measurement range 0-100 mg/m^3, detection limit as low as 1 mg/m^3) must be selected. The analyzer is susceptible to the interference of background gas such as moisture or impurities in the air, thus affecting the measurement accuracy [5]. The measured gas is required to be dust-free, anhydrous, room temperature and atmospheric pressure. In order to provide clean and dry gas for analytical instruments, higher requirements for sample handling system are put forward. Therefore, sample processing technology is one of the key technologies for real-time, continuous and on-line monitoring of ultra-low emission of flue gas pollutants, and plays an extremely important role in safety monitoring [6].

At present, the chilled-dry direct extraction method is mainly used to sample the flue gas samples in China. When the flue gas is condensed, it will produce condensate water (the water content of the general thermal power plant is 6-10%). Because the SO_2 content in ultra-low emission flue gas is very low (less than 35 mg/Nm^3), the traditional dehumidification technology cannot meet the demand of on-line detection of ultra-low emission flue gas, resulting in low concentration of SO_2 dissolved in condensate water, the detection value is very low, even lower than the detection limit of analytical instruments, and cannot be detected [7-9]. Therefore, further improving the dehumidification efficiency of CEMS pretreatment system and reducing the loss rate of SO_2 are of great importance to the accuracy and accuracy of on-line monitoring of flue gas pollutants. Based on the water absorption characteristics of Nafion membrane [10], the membrane gas-water separation technology was applied to CEMS pretreatment system to remove the moisture content of flue gas efficiently, which provided guarantee for the quality of monitoring data of ultra-low emission of flue gas pollutants, and provided important basis for the total discharge of pollutants, safety monitoring and supervision.

The main objective of this study was to evaluate the effect of Nafion membrane pretreatment system on efficiency and dehumidification preservation rate of SO_2.

2. Experiment of Nafion tube dehumidification

2.1. Mechanism of Nafion tube dehumidification

Nafion tube is a copolymer, which is a kind of membrane. The dehumidification property of Nafion membrane is attributed to its sulfonic group and strong hydrophilic property. When the gas containing moisture is blown into the Nafion tube, the water molecules will be attached to the sulfonate group, forming a water film on the membrane surface to prevent other substances through, water molecules gradually migrate to the membrane through the sulfonate group, and eventually to the other side of the membrane to play a dehumidification role. Nafion membrane dehumidifies flue gas based on the molecular transfer mechanism with nonporous structure. There is no gas leakage during dehumidification. The measurement error caused by condensation and dissolution of gas is greatly reduced. Therefore, the Nafion tube can be used as a good substitute for the gas pretreatment system in CEMS.

Transfer mechanism of Nafion is different from conventional membrane processing technology. It does not require a large pressure pump as a driving force, only need to use the different water vapor pressure on both sides of membrane. With the water vapor gradient, water molecules are moved through the high-pressure side to the other side. During the process, the dehumidification effect is stable, there is no valve failure or aging decline caused by dehumidification. It is only needed to keep the air through the outer side of membrane during dehumidification process. Therefore, the maintenance cost and energy consumption are lessened largely.

2.2. Experimental method

The laboratory standard gas was humidified to simulate the actual flue gas. Then, the moisture gas was put through the Nafion membrane tube for the dehumidification pretreatment, and the dew point and the gas concentration were measured using the dew point thermometer and gas detector (PG-350) at the outlet. The effects of various factors on the dehumidification were investigated including the concentration, the flow and the humidity of gas. The specific experimental methods are as follows:

(1) The laboratory standard gas of N_2 and SO_2 were used to simulate flue gas based on the ultra-low emission limits, the SO_2 inlet concentration of 10, 20, 30 mg/L. The gas distribution method is shown in Table 1. The humidity of gas was obtained by humid generator, V_{water}/V_{gas} of 15%. In order to ensure the humidity in the allocated gas, a thermostat must be installed around the humidifier and the temperature must be above the dew point temperature of the humidity controlled. Otherwise, the loss will not be caused by the reduction of temperature and condensed water. The temperature of gas was kept at 80℃ and the flow of 2LPM. The humidity and SO_2 concentration were detected at the outlet after the gas through the Nafion tube.

Table 1. Gas mixture ratio

flow velocity (LPM)	SO_2 concentration （mg/L）	N_2 standard gas velocity （mL/min）	SO_2 standard gas velocity （mL/min）
	10.2	1980	20
2	20.6	1960	40
	31.2	1940	60
	10.3	2475	25
2.5	20.7	2450	50
	31.2	2425	75
	9.6	2970	30
3	20	2940	60
	30.9	2910	90
	10.3	3465	35
3.5	20.8	3430	70
	31.6	3395	105
	10.1	3960	40
4	20.9	3920	80
	31.5	3880	120

(2) The flow meter was used to adjust the flow rate of 2~4 LPM to investigate the effect of flow on dehumidification. The SO_2 inlet concentration was 30 mg/L, the temperature of gas at 80℃ and V_{water}

/ V_{gas} of 15%.

(3) The humidification parameters of the humidifier were changed to generate V_{water}/V_{gas} of 15% and 30% to investigate the effect of humidity. The SO_2 inlet concentration was verified at 10, 20, 30 mg/L. The flow rate of gas was kept at 3 LPM and the temperature at 80℃ as well.

3. Results and discussion

3.1. Effect of SO_2 inlet concentration

The dehumidification and preservation properties of Nafion membrane were studied in the condition of laboratory test. The effect of SO_2 inlet concentration on the dehumidification efficiency and the preservation rate is shown in Figure 1.
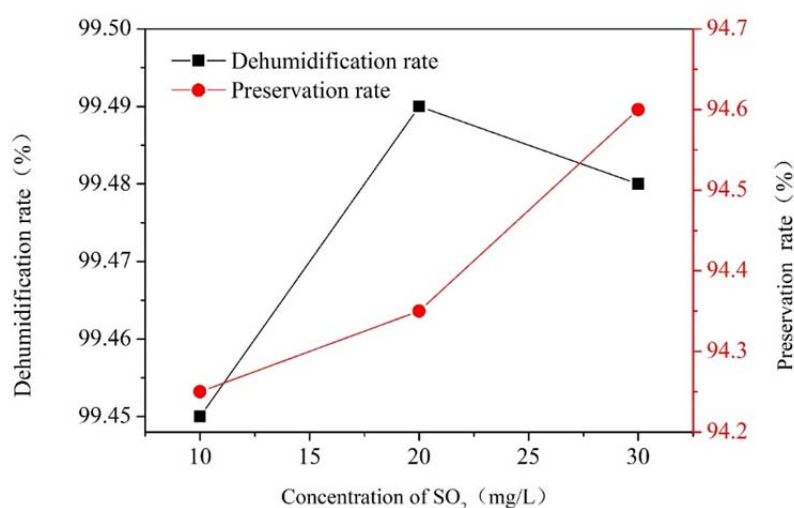
**Figure 1.** Effect of SO_2 inlet concentration on dehumidification efficiency and preservation rate

From the experimental data, it can be seen that the Nafion membrane can still maintain a high dehumidification efficiency under the condition of high humidity and constant flow rate, and the dew point temperature of the outlet gas can be around -20 ℃. SO_2 inlet concentration had unsignificant effect on dehumidification performance, which indicated that Nafion membrane was suitable for gas dehydration in a wide range of SO_2 concentration. The slight effect of concentration changes may be due to the accompanying dissolution of SO_2 and the loss of gases during the experiment. To the preservation rate of SO_2, when the inlet concentration was low, the loss was about 6%, which was higher than the 5% stipulated by the state. However, the increase in concentration was a gradual decrease in the loss rate. Therefore, in the practical application of flue gas detection pretreatment, Nafion membrane has high preservation rate and dehumidification capacity for flue gas pretreatment containing sulfur dioxide of 10-30 mg/L, which fully meeted the pretreatment requirements of ultra-low emission standards.

During experiment, the possible causes of SO_2 loss were: (i) there were some problems in the valve distribution accuracy of mass flowmeter. When 10 mg/L SO_2 was prepared, the inlet flow rate of SO_2 was controlled at 20 mL/min, and there were some problems in the accuracy. (ii) because SO_2 is a dissolved gas, there was a leakage in humidifier humidifying pipe due to the solubility of SO_2, which resulted in gas loss. (iii) there was a huge temperature difference between the pipe thermostat and the

inlet pipe, which may produce condensate and lead to SO_2 loss.

3.2. *Effect of gas flow*

The effect of SO_2 flow on the dehumidification efficiency and SO_2 preservation rate is shown in Figure 2.
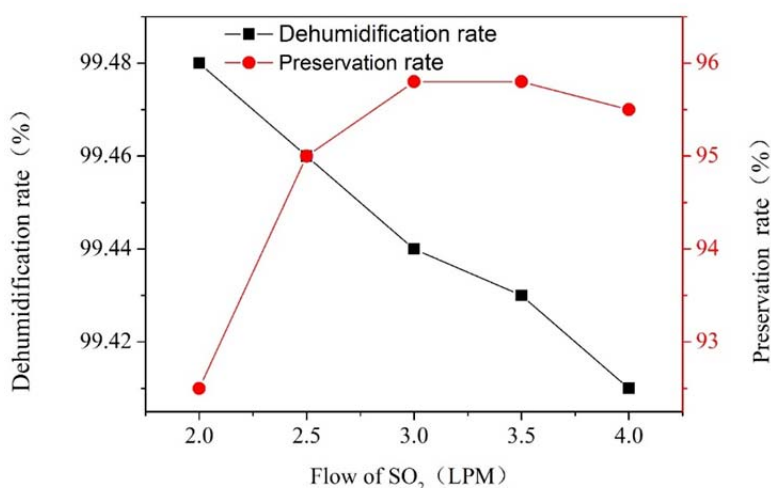

Figure 2. Effect of gas flow on dehumidification rate and preservation rate
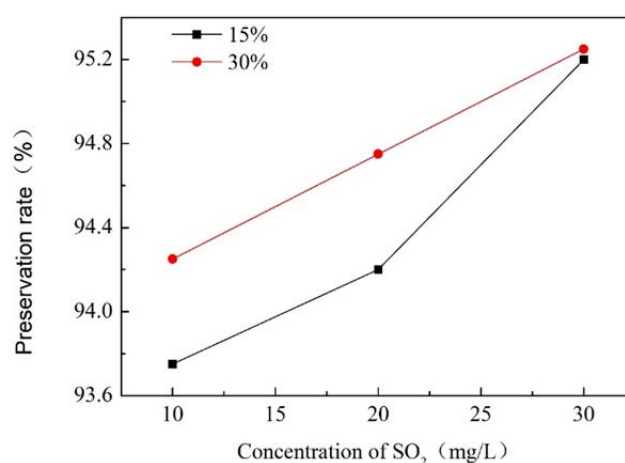
As shown in Figure 2, the dehumidification effect decreased slightly with the increase of flow rate as the SO_2 concentration was 30 mg/L, and the gas preservation rate was stable at a high level. The reasons for the loss of SO_2 can be briefly summarized as follows: (i) the accuracy of mass flowmeter was not enough. When the inlet flow rate was low, the inaccuracy of the inlet flow rate would result in the high loss rate of SO_2. The main reason was the accuracy of the valve train rather than the leakage of Nafion membrane. (ii) water vapor in gas caused SO_2 to dissolve. Longitudinal comparison showed that when SO_2 passes through GASS-6000 at low concentration, its preservation rate is significantly higher than that at high concentration. Therefore, there may be a loss of dissolved SO_2. In order to make up for the loss, we had done many repetitious tests and obtained accurate data. This type of error was significantly improved at higher flow rates. Under the flow rate greater than 2LPM, it had no effect on the dehumidification and preservation rate of Nafion tube. In order to get better pretreatment effect, we can choose about 2LPM flow to carry out experiments.

3.3. *Effect of gas humidity*

The actual flue gas humidity of coal-fired power plants has a certain range of fluctuations, different humidity will produce different loads, affecting the dehumidification capacity of Nafion membrane. In order to investigate the effect of different loads on dehumidification and retention rate in actual operation, a humidity factor analysis experiment was designed. The effect of different humidity on SO_2 dehumidification efficiency and its preservation rate in Nafion membrane is shown in Figure 3 and Figure 4.
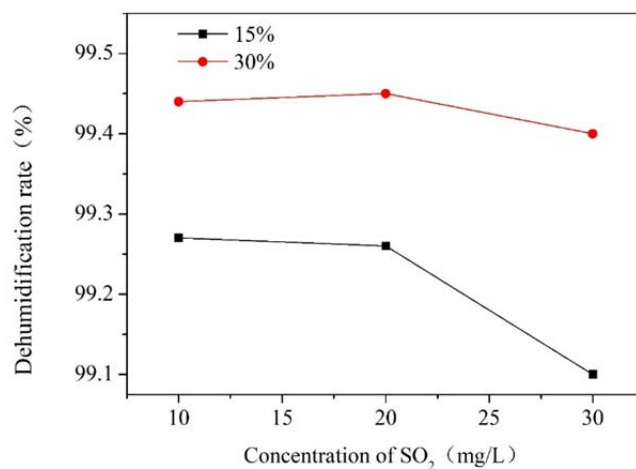
Figure 3. Effect of humidity on SO_2 dehumidification efficiency in different concentration

Figure 4. Effect of humidity on SO_2 preservation rate in different concentration

As shown in Figure 3, the dehumidification increased with the increase of humidity. It was because that water vapor pressure increased with the increasing humidity, which enhanced humidity difference and dehumidification effect increased. Humidity was proportional to the dehumidification performance of Nafion membranes. Figure 4 showed that preservation rate gradually decreased with the increase of humidity and increased with the SO_2 concentration.This was due to the high sample temperature, SO_2 solubility decreased, loss of dissolution decreased. Therefore, in order to ensure the best dehumidification effect, avoid excessive humidity. But compared with the traditional process, the dehumidification and preservation rate of Nafion membrane is far superior to that of the former. Moreover, even if acidic liquids appear in Nafion film, because of its good corrosion resistance, corrosion problems will not occur.

4.   Summary of conclusions

(1) There was no significant effect of flow rate on dehumidification rate and preservation rate. It was found that the effect of flow rate on dehumidification rate was 0.2%, while the influence rate of preservation rate was 1%.

(2) SO_2 concentration did not have a significant effect on its dehumidification rate. Under the condition of constant humidity and flow rate, the dehumidification rate of 30 ppm SO_2 was only 0.04% lower than that of 10 ppm, even if there was partial dissolution loss. But SO_2 concentration had a certain effect on its preservation rate. With the increase of SO_2 concentration from 10 mg/L to 30 mg/L, the preservation rate increased from 93.5% to 95%. SO_2 is required to be less than 50 mg/L in the flue gas emission standard, so the loss of SO_2 in the dehumidification process of Nafion tube was very small.

(3) Humidity had an effect on the preservation rate of SO_2. When the humidity was 15%, the preservation rate of SO_2 was 94.5%, which was higher than 93.7% when the humidity was 30%. But when the concentration was increased to 30 mg/L, the effect of humidity was close to zero. They had reached over 95.5% respectively. In order to prevent the influence of humidity on Nafion, in practical use, it is necessary to avoid the generation of cold-temperature zone and increase the temperature of high-temperature zone according to the actual situation.

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