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Absorption of SO_2 with Sodium Humate and Seawater

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Abstract. In this paper, the effect of sodium humate (HA-Na) and seawater on the absorption of SO_2 in flue gas was investigated. At the same time, the effects of the initial pH value of seawater and SO_2 concentration on seawater desulfurization were also evaluated. The experimental results showed that seawater had the ability to absorb SO_2. SO_2 dissolved in seawater can react with HCO_3^- and CO_3^{2-} plasma to produce CO_2, which can prompt the absorption reaction. Besides, the addition of HA-Na can improve the performance of seawater desulfurization and increase the efficiency of seawater desulfurization. It also prolonged the desulfurization time and improved the problem of high usage amount of seawater in practical applications. With the increase of HA-Na addition, the desulfurization efficiency and the efficient desulfurization time of seawater increased. The efficiency of seawater desulfurization decreased with the initial pH value of seawater. The greater the concentration of SO_2, the faster the absorption efficiency of SO_2 by the solution decreased and the shorter the time for the solution to reach saturation.

Keywords. Sodium humate, seawater, desulfurization

1. Introduction

At present, the developed countries have made great progress in flue gas desulfurization (FGD) technology. Gas desulfurization technology has been applied industrially worldwide. It mainly includes wet FGD technology, dry FGD technology, absorber regeneration FGD technology, seawater FGD technology, electron beam FGD technology, pulse plasma FGD technology [1], etc. Depending on the combustion stage, FGD technologies can be classified into three types: pre-combustion FGD, in-combustion FGD and post-combustion FGD. FGD methods are divided into dry desulfurization, semi-dry desulfurization and wet desulfurization.

The limestone/gypsum wet FGD technology is relatively mature and is widely used for FGD [2]. This method is mainly used in the thermal power industry, whose principle is to use limestone or lime slurry as the absorbent in the spray tower. The spray droplets form $CaSO_3$ with the flue gas containing SO_2, which oxidizes to $CaSO_4$. Maina [3] used conventional limestone to mix iron wastes with lime by using wet mortar method to increase the absorption activity and improve the FGD efficiency. Aiumne [4]

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investigated the possibility of using marble waste as an absorbent in place of limestone. For limestone/gypsum wet FGD, the raw materials are readily available and the sulfate byproducts are easily stored. However, the process system has a large footprint and the pipes tend to become dirty and clogged.

Currently, the sodium-base method has become the focus of recent studies on the simultaneous removal of nitrogen oxides from flue gas along with FGD. Liu [5] studied the simultaneous removal of NO and SO_2 from flue gas by adding H_2O_2 to NaOH solution under UV radiation. Zhang [6] applied O_3 to FGD and denitrification in a glass furnace, who found that the presence of SO_2 promoted nitrogen uptake. The SO_2 removal efficiency is greater than 95%. However, its industrialization still needs time to be realized.

Humic acid (HA) molecule is a polymer compound composed of some structurally similar units and each structural unit consists of a nucleus, bridge bonds and reactive groups (mainly hydroxyl, carboxyl, methoxy). Each nucleus has one or more reactive groups, which makes it have many chemical and physical properties such as hydrophilicity, adsorption, ion exchange, complexation ability, etc. It opens up many possibilities for researchers, especially for the modification of HA, humates and their composites, giving them new properties such as adsorption, scale inhibition, flocculation, degradation, and photocatalysis.

Sun [7] studied the effect of the concentration of HA-Na solution on the desulfurization efficiency, which showed that the concentration of HA-Na had a greater effect on the desulfurization time but a smaller effect on the desulfurization efficiency. The optimal concentration was 0.06 g/mL. In order to maintain high desulfurization efficiency, the pH value of HA-Na solution should be kept above 4.5. Therefore, it is a good choice to use HA-Na as an additive to improve the performance of other absorbents. In this paper, the effect of HA-Na and seawater on the absorption of SO_2 in flue gas was investigated. The effects of the initial pH value of seawater and SO_2 concentration on seawater desulfurization were also evaluated.

Chen [8] evaluated the effects of carbonation temperature, reaction duration, and the addition amount of HA-Na on the carbonation rate of the CaO adsorbent. HA-Na/CaO is allowed to react 20 min at the optimum conditions for calcination (920°C, 100% N_2) and for carbonation (700°C, 15% CO_2, 85% N_2), respectively. The maximum conversion rate of HA-Na/CaO is 23% higher than that of CaO in the first cycle. After 20 cycles, the conversion rate of HA-Na/CaO is still 0.28, while that of CaO is only 0.15. The carbonation conversion rate for HA-Na/CaO is improved by 86% compared to CaO.

Zhou [9] put forward a novel method of improving the SO_2 absorption performance of sodium citrate (Ci-Na) by using HA–Na as an additive. The influence of different Ci-Na concentration, inlet SO_2 concentration and gas flow rate on desulfurization performance were studied. The consequence shows that the efficiency of SO_2 absorption by Ci-Na is above 90% and the desulfurization time adds with the Ci-Na concentration rising from 0.01 to 0.1 mol/L. Due to adding HA–Na, the desulfurization efficiency of Ci-Na increased from 90% to 99% and the desulfurization time increased from 40 to 55 min. Under the optimum conditions, the desulfurization time of Ci-Na can exceed 70 min because of adding HA–Na, which is nearly doubled.

2. Experimental Section

The SO_2 absorption experimental setup as shown in Figure 1 was used. The absorption substrate was seawater collected from the inlet of Shanghai Sanjia Port. The experiment was conducted with the prepared SO_2 in the concentration range of 1000 ppm-3000 ppm (the bottom gas was high-purity N_2).

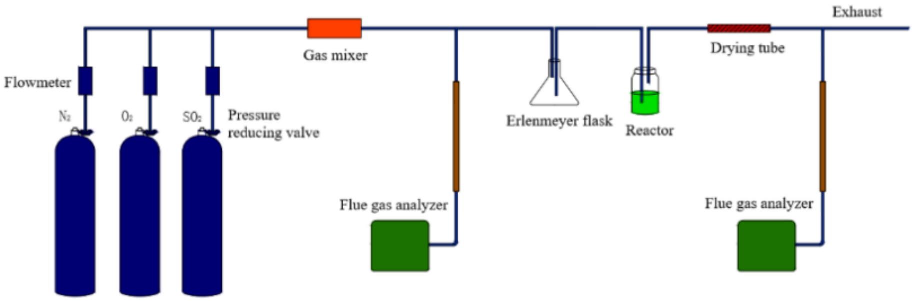

Figure 1. The SO_2 absorption experimental setup.

High-purity N_2 was introduced into the system for 10 minutes before the absorption started, and then the SO_2 cylinder was opened. SO_2 gas flowed out from the cylinder. SO_2 gas flow was decompressed by the pressure reducing valve. N_2 gas flow was controlled by the flowmeter to adjust the concentration of SO_2. The flue gas analyzer detected the concentration of SO_2 at the inlet. The gas was mixed well in a buffer erlenmeyer flask. Then they reacted in a reactor with an appropriate amount of pre-prepared HA-Na/seawater solution. The reacted gas was dried by the drying tube. The concentration of SO_2 at the outlet was detected by the flue gas analyzer. The experimental setup system needs to be tested for gas tightness to ensure that the system is well gasketed. The SO_2 absorption efficiency can be obtained from the following equation:

$$\eta = \frac{c_1 - c_2}{c_1} \times 100\% \tag{1}$$

where, η is the absorption efficiency of SO_2; c_1 is the concentration of SO_2 at the inlet; c_2 is the concentration of SO_2 at the outlet.

3. Results and Discussion

3.1. Comparison of Seawater and Sodium Humate /Seawater Desulfurization Efficiency

Keeping other conditions unchanged, as can be seen from Figure 2, the desulfurization efficiency and desulfurization time increased significantly after adding 1.2 g HA-Na. The efficiency of seawater desulfurization was increased from 86% to 96%-99%, and the time of seawater desulfurization was extended from 6 min to 24 min.

There was also a significant increase in the desulfurization efficiency when compared with HA-Na/pure water. It indicates that HA-Na can improve the desulfurization efficiency of seawater.

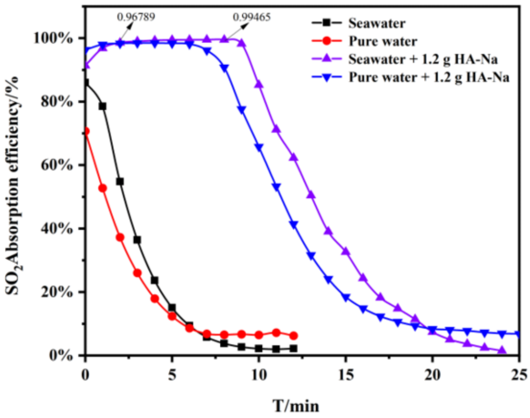

Figure 2. The desulfurization efficiency of seawater, pure water, HA-Na/seawater and HA-Na/pure water.

3.2. Different Concentrations of Sodium Humate /Seawater on the Effect of Desulfurization

The SO_2 gas of 2300 ppm was prepared as the simulated flue gas. The total gas flow rate was controlled at 1.68 L/min. For each group of experiments, 60 mL of seawater was taken. And 0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.8 g, 1.2 g and 2.4 g of HA-Na were added to it respectively. The SO_2 concentration at the inlet and outlet was measured by the flue gas analyzers. A set of data was recorded every minute at 25°C.

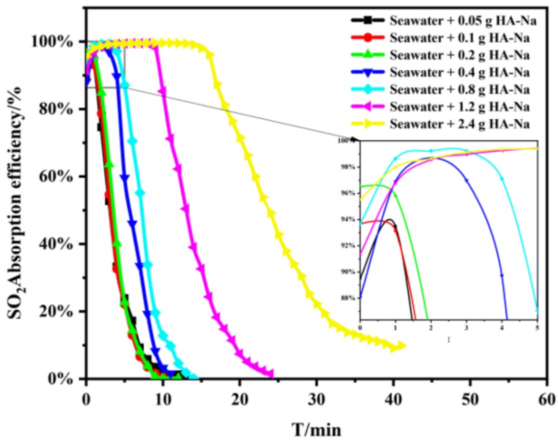

Figure 3. Different concentrations of HA-Na/seawater on the effect of desulfurization efficiency.

Figure 3 shows the relationship between different concentrations of HA-Na/seawater and SO_2 desulfurization efficiency. As we can see from Figure 3, the efficiency of HA-Na/seawater desulfurization increased in a certain interval with the increase of HA-Na addition.

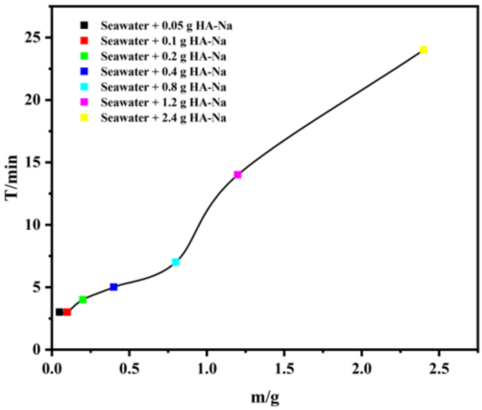

Figure 4. Different concentrations of HA-Na/seawater on the effect of desulfurization time.

According to Figure 4, it can be seen that its efficient desulfurization time also keeps increasing. This is due to the weak alkaline nature of HA-Na. The amount of ionized OH^- increases with the addition of HA-Na. This leads to the ionization of more CO_3^{2-} and HCO_3^- in seawater, which makes the continuous absorption of the acidic SO_2 gas dissolved in the solution. Thus, HA-Na improves the desulfurization efficiency and desulfurization time.

3.3. Effect of the Initial pH of Seawater on Desulfurization Efficiency

Figure 5 shows the effect of different initial pH on seawater desulfurization. It can be seen that the initial pH of seawater has an obvious effect on the desulfurization efficiency of seawater. The desulfurization efficiency decreases with the decrease of pH value.

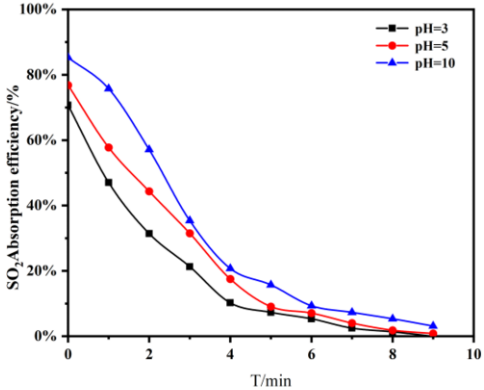

Figure 5. The effect of different initial pH on seawater desulfurization.

Therefore, alkalinity is an important factor affecting seawater desulfurization, and increasing the alkalinity of seawater can improve the efficiency of seawater desulfurization. Alkaline substances can be added to the application of seawater desulfurization to improve its desulfurization capacity. And HA-Na is weakly alkaline, which is a good additive to improve the desulfurization efficiency of seawater (e.g. Figure 2).

3.4. Effect of SO_2 Concentration on Desulfurization Efficiency

The total gas flow rate was controlled at 1.68 L/min at room temperature. High-purity nitrogen was used as the carrier gas. The simulated flue gas with SO_2 concentration of 1000 ppm, 2000 ppm and 3000 ppm were configured respectively. In each group of experiments, 60 mL of seawater and 1.2 g of HA-Na were used to configure the absorption solution. The obtained results are shown in Figure 6.

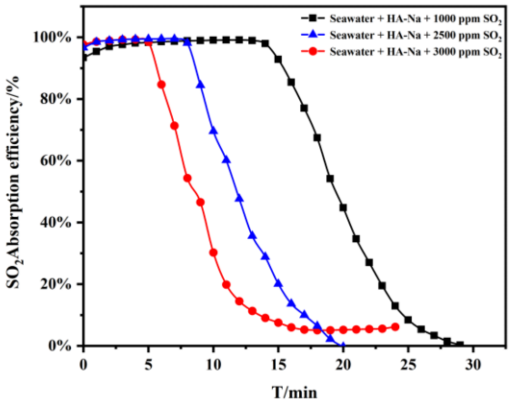

Figure 6. Different concentrations of SO_2 on the effect of desulfurization efficiency.

As can be seen from Figure 6, the larger the SO_2 concentration in the inlet flue gas, the faster the SO_2 absorption efficiency decreases and the shorter the time for the solution to absorb SO_2 to reach saturation. This is due to the fact that the amount of SO_2 absorbed by per unit volume of solution is quantitative. Increasing the SO_2 concentration in the inlet flue gas means an increase in the amount of SO_2 per unit volume of flue gas. Thus, the time to saturation of the solution is shortened.

4. Conclusion

The effect of HA-Na and seawater on the absorption of SO_2 in flue gas was investigated in this paper. The effects of the initial pH and SO_2 concentration of seawater on seawater desulfurization were also evaluated. The performance of seawater desulfurization was improved with the addition of HA-Na to improve the efficiency of seawater desulfurization. The seawater desulfurization time was extended. Moreover, the problem of high seawater usage in practical applications was alleviated.

Acknowledgments

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