Study on SO₂ Absorption Characteristics in Two-stage Wet Desulfurization Process

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Abstract. The effect of the inlet SO₂ concentration and the pH of the desulfurization slurry on the SO₂ absorption efficiency was systematically studied on a two-stage falling film reactor test system. Studies have shown that the SO₂ absorption efficiency has a positive correlation with the pH value of the slurry. In the entire pH range, the SO₂ absorption efficiency increases with the increase of the pH value and decreases with the increase of the SO₂ concentration, but in different pH value areas, the main influencing factors for controlling the SO₂ absorption efficiency are different. In the low pH range (3.5~5.5), the SO₂ absorption efficiency is mainly controlled by the inlet SO₂ concentration, and the pH value is a secondary factor. However, in the high pH area (5.5~6.5), the SO₂ absorption efficiency is mainly controlled by pH when the inlet SO₂ concentration is ≤4000mg/m³. When the inlet SO₂ concentration is >4000mg/m³, the SO₂ absorption efficiency is controlled by the inlet SO₂ concentration and pH value.

1.Introduction

In the limestone-gypsum wet desulfurization process of coal-fired units, when the inlet flue gas SO₂ concentration increases, the desulfurization efficiency can be improved by means of increasing the slurry circulation volume and slurry pH[1], but when the liquid-gas ratio increases to a certain degree, it is more difficult to improve the desulfurization efficiency[2], However, Too high slurry pH will lead to insufficient slurry oxidation and reduced limestone dissolution rate, affecting the desulfurization efficiency[3], especially when the boiler is burning high-sulfur coal, the contradiction is more prominent, therefore, it is necessary to take reasonable measures to improve the desulfurization efficiency and take into account the economics of operation.

Compared with the traditional wet desulfurization technology, the two-stage wet desulfurization technology has the advantages of high desulfurization efficiency and high applicability of high sulfur-fired thermal power units. It has a good adaptability to a wide range of changes in SO₂ concentration, greatly enhancing the reliability of the desulfurization system operation. This technology is widely used abroad, but because there are few high-sulfur coal-fired coal-fired units in China, the research into and application of this technology mainly focus on mechanism research, flow field optimization design of two-stage desulfurization system, and improvement of system layout. In this aspect[4-5], there is little research on the effect of operating parameters on desulfurization efficiency. The two-stage wet flue gas desulfurization process involves two reaction ranges with different pH values. In this paper, it is divided into two parts: low pH/high pH ranges. By studying the influence of relevant operating parameters on SO₂ absorption characteristics under different pH conditions, the two-stage wet desulfurization technology can be mastered as the operation characteristics of the
desulfurization reactor, which provides basic research data for the two-stage wet flue gas desulfurization technology.

2. Experimental

The two-stage falling film reactor test system consists of a simulated flue gas system consisting of the main body of the falling film reactor, a desulfurized slurry circulation system, a supplementary slurry system and an oxidation system. The test system is shown in Figure 1.

The simulated flue gas uses SO$_2$ standard gas with a concentration of 10000ppm as the gas source. The air passing through the blower is heated to 120°C by the heater and mixed with the SO$_2$ standard gas. By adjusting the flow rate of the CCS-5 mass meter, the flow rate of air and SO$_2$ standard gas is made into the simulated flue gas of the required concentration, which enters the two-stage falling film reactor and comes into contact with the falling film liquid film to be discharged into the atmosphere.

The falling film reactor is composed of an organic glass tube with an inner diameter of 29mm and a length of 2m, and a liquid distributor on the top. The lower part of the falling film reactor is connected to the transition liquid tank through a flange. The slurry in the circulating oxidation tank is driven by an electromagnetic diaphragm pump, the flow is controlled by a ball valve, measured by a glass rotor flowmeter, and discharged into the liquid distributor on the top of the falling film reactor. The slurry then passes through the liquid distributor and the main body of the falling film. The gap between them forms a uniform slurry film and exchanges with the flue gas for mass transfer, then enters the transition liquid tank, and then returns to the circulating slurry tank.

The oxidized air is pressurized by an electromagnetic compression aeration pump, measured by an LZB-10 float flowmeter, and then blown into the aeration device in the circulating slurry tank. The pH of the slurry passes through two PHS-3C pH meters For measurement, the experimental instrument parameters are shown in Table 1.

The pH of this experiment is set at 4.0, 4.5, 5.0, 6.0, 6.5, SO$_2$(dry basis, standard state). Under the above pH conditions, the simulated flue gas velocity is designed to be 3.5m/s, and the flue gas volume is 8.5m$^3$/h. After the ultra-low emission reconstruction, the liquid-vapor ratio of the desulfurization system is generally 18-22L/m$^3$, so the liquid-vapor ratio is chosen to be 20L/Nm$^3$ in this paper. The calculation of the liquid-vapor ratio is shown in equation 1, the slurry density is designed to be 1100kg/m$^3$, using The density meter is calibrated. The SO$_2$ concentration is set at 2000 mg/m$^3$, 3000 mg/m$^3$, 4000 mg/m$^3$, 5000 mg/m$^3$, 6000 mg/m$^3$, and 8000 mg/m$^3$. The SO$_2$ concentration at the inlet and outlet of the anti-desulfurization reactor is tested by the Ecom-J2KN flue gas analyzer.

The calculation method for defining the sulfur fixation efficiency $\eta$ is shown in Equation 1.

$$\eta = \frac{C_{in} - C_{out}}{C_{in}}$$  \hspace{1cm} (1)

In the formula: $C_{in}$ and $C_{out}$ respectively represent the SO$_2$ concentration at the inlet and outlet of the fixed bed reactor.
3. Experimental results and discussion

3.1 Effect of pH value and inlet SO$_2$ concentration on SO$_2$ absorption efficiency

3.1.1 Effect of slurry pH on SO$_2$ absorption efficiency

It can be seen from Figures 2 and 3 that the SO$_2$ absorption efficiency has a positive correlation with the slurry pH. Whether in the low pH range or the high pH range, the SO$_2$ absorption efficiency increases with the increase of the pH value. In the low pH range, the pH value increases from 4.0 to 5.5, and the SO$_2$ absorption efficiency increases by about 1%-5%; in the high pH range, the pH value increases from 5.8 to 6.5, and the SO$_2$ absorption efficiency increases by about 3.5% to 5.6%. This is mainly because the rate of absorption of SO$_2$ by the limestone slurry is controlled by the gas film and the liquid film [6]. The increase of the pH value of the slurry is beneficial to enhance the liquid phase mass transfer of SO$_2$ and directly affects the efficiency of SO$_2$ removal. As the pH value of the desulfurization slurry increases, the pH value of the desulfurization slurry entering the falling film reactor increases accordingly. According to the double-membrane theory [7], the pH of the slurry in the liquid membrane at the junction of the gas and liquid membranes also increases as the pH of the circulating slurry increases, which promotes the hydrolysis of sulfur dioxide gas at the surface of the
liquid membrane and improves the sulfur dioxide gas and increases the mass transfer driving force in the mass transfer liquid membrane. As the pH value of the circulating slurry increases, the hydrolysis rate of sulfuric acid and sulfite in the mass transfer liquid membrane will be accelerated, thereby increasing the mass transfer coefficient of sulfur dioxide during the liquid membrane transfer process, and thus increasing the total mass transfer coefficient.

Based on the theoretical efficiency of the two-stage desulfurization and the actual efficiency of the experiment, the SO\textsubscript{2} concentration at the inlet of the high pH value range was determined, and the effect of the SO\textsubscript{2} concentration and pH at the inlet on the desulfurization efficiency was further studied. It can be seen from Figure 4 that in the low pH area, the effect of inlet SO\textsubscript{2} concentration on SO\textsubscript{2} absorption efficiency is greater than that caused by pH, the SO\textsubscript{2} concentration increases from 2000 mg/m\textsuperscript{3} to 4000 mg/m\textsuperscript{3}, the SO\textsubscript{2} absorption efficiency decreases by 11.5%, and the pH value from 3.5 to 5.5, the desulfurization efficiency increased by 3.6%. In the high pH area, there is a different trend. When the inlet SO\textsubscript{2} concentration≤4000mg/m\textsuperscript{3}, the pH value increases from 5.5 to 6.5, the desulfurization efficiency increases by 10.8%, and the SO\textsubscript{2} concentration increases from 2000mg/m\textsuperscript{3} to 4000mg/m\textsuperscript{3}, SO\textsubscript{2} absorption efficiency only increased by 4.5%, SO\textsubscript{2} absorption efficiency is mainly controlled by pH. However, when the inlet SO\textsubscript{2} concentration≥4000 mg/m\textsuperscript{3}, the SO\textsubscript{2} concentration increased from 4000 mg/m\textsuperscript{3} to 8000 mg/m\textsuperscript{3}, the SO\textsubscript{2} absorption efficiency decreased by 9.8%, and when the pH value increased from 5.5 to 6.5, the desulfurization efficiency increased by 5.5%. In this pH range, the SO\textsubscript{2} absorption efficiency is controlled by both the SO\textsubscript{2} concentration and the pH, but the influence of the SO\textsubscript{2} concentration on the SO\textsubscript{2} absorption efficiency dominates. Furthermore, with the increase of SO\textsubscript{2} concentration, the improvement of desulfurization efficiency by the way of increasing pH becomes slower. In general, in the high pH range, the effect of pH on absorption efficiency is much greater than the effect of pH on absorption efficiency in the low pH section.

3.1.2. Effect of inlet SO\textsubscript{2} concentration on SO\textsubscript{2} absorption efficiency
It can be seen from Figure 4 that in the low pH range, the SO\textsubscript{2} concentration at the inlet of the desulfurization reactor increases from 2000mg/m\textsuperscript{3} to 8000mg/m\textsuperscript{3}, and the SO\textsubscript{2} absorption efficiency generally decreases by more than 13%. In the high pH range, the SO\textsubscript{2} absorption efficiency generally decreases by more than 11%, as the SO\textsubscript{2} concentration increasing from 2000mg/m\textsuperscript{3} to 8000mg/m\textsuperscript{3}. This is due to the increase in the concentration of SO\textsubscript{2} in the gas phase, the slurry at the same position in the falling film reactor absorbs more SO\textsubscript{2}, resulting in a faster rate of decrease in the pH of the slurry, and a decrease in the liquid phase enhancement coefficient of SO\textsubscript{2} absorption in the mass transfer liquid film, resulting in The overall mass transfer coefficient drops. The accelerated rate of decrease in pH causes the relative solubility of SO\textsubscript{2} on the gas-liquid contact surface to decrease, and the proportion of H\textsubscript{2}SO\textsubscript{3} in the system in the slurry increases, resulting in a relative decrease in the gas and liquid mass transfer power. At the same time, the inlet SO\textsubscript{2} concentration increases, increasing the SO\textsubscript{2} partial pressure in the flue gas, thereby increasing the liquid phase reaction kinetics, and increasing the mass transfer rate, but the increase in mass transfer is less than the inlet SO\textsubscript{2} concentration, which makes the entire falling film The desulfurization rate in the reaction tower drops.
4. Conclusion

(1) The absorption efficiency of SO₂ increases with the increase of pH value and decreases with the increase of SO₂ concentration at the inlet; no matter in low pH or high pH range, the influence of inlet SO₂ concentration on the absorption efficiency is greater than that of pH value.

(2) In the low pH range, the effect of inlet SO₂ concentration on SO₂ absorption efficiency is
greater than that caused by pH, and SO$_2$ absorption efficiency is mainly controlled by inlet SO$_2$ concentration.

(3) In the high pH range, the SO$_2$ absorption efficiency is mainly controlled by pH when the inlet SO$_2$ concentration is $\leq 4000$mg/m$^3$, and the SO$_2$ absorption efficiency is controlled by the inlet SO$_2$ concentration and pH when the inlet SO$_2$ concentration is $>4000$mg/m$^3$. The effect of pH changes on absorption efficiency is much greater than the effect of pH on absorption efficiency in the low pH range.

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