Influence of SO$_2$ in the Medium to High Temperature Range of SO$_3$ Removal by CaO

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Abstract. Injecting sorbents can effectively decrease the SO$_3$ pollution, but its removal efficiency is reduced by the absorption owning to the abundant SO$_2$. Experiments were carried out on a fixed bed reactor to study the effect of SO$_2$ on the deSO$_3$ by CaO in the medium to high temperature range. The increase in temperature may obviously improve the removal efficiency of SO$_3$, but the conversion of SO$_2$ to CaO is much higher than SO$_3$, resulting the SO$_3$ selectivity decreases. Decreasing the SO$_2$ concentration or increasing the SO$_3$ concentration may increase conversion by CaO and SO$_3$ selectivity, but the former is less influential than the latter.

Keywords. SO$_2$; SO$_3$; CaO; absorption; conversion.

1. Introduction

Coal consumption in China is declining from year to year, but still represents 60% of China’s total energy consumption. Its combustion generates a series of polluting gases, particularly SO$_2$ and SO$_3$. SO$_3$ not only causes corrosion of equipment in power plants, but also highly jeopardizes the environment and human health, which has intrigued widespread discussion [1, 2].

There are three methods commonly used to control SO$_2$ emissions. One is reducing its generation via adjusting fuel and combustion methods [3, 4], but it is limited by controlling effect and low practicability. Another is the SO$_3$/H$_2$SO$_3$ removal with downstream equipment of power plant, such as precipitator [5-8] and wet flue gas desulfurization (WFGD) [7, 8], which usually are the heterogeneous condenses on the surface of fly ash or homogeneous condenses, but it is difficult to remove the ultrafine sulfuric acid mist [9]. Injecting alkaline absorbents is the most efficient way to remove SO$_3$ through a gas-solid reaction.

Alkaline absorbents commonly used in engineering, such as calcium-based, magnesium-based and Trona[10], are studied experimentally and have good deSO$_3$ performance. Chen [11] compared the absorption performance of Ca(OH)$_2$, Mg(OH)$_2$, MgO and CaO on SO$_3$, and found that the SO$_3$ efficiency all above 60% in 400$^\circ$C. And more researchers focused on the calcium-based sorbents taking into account the cost and the reactivity [12-15]. Wang [12] discovered that SO$_3$ removal efficiency by Ca(OH)$_2$ was approximately 92% with entrained flow reactors. But He [13] found that SO$_2$ has a competitive absorption against SO$_3$ when studied the SO$_3$ absorption of Ca(OH)$_2$ on at 200-350$^\circ$C, and the SO$_3$ selectivity at the initial moment is only 0.16 at 350$^\circ$C.

Increasing the temperature can promote the gas-solid reaction rate [14], so the SO$_3$ absorption performance of CaO is investigated at a higher temperature in this work. This study analyzed the influence of SO$_2$ on the removal performance of CaO in 400-900$^\circ$C with a fixed-bed reactor.
2. Experiment

2.1. Experiment Setup
Figure 1 shows the experimental system, it was consisted of a gas distribution system, SO$_3$ generation reactor, SO$_x$ absorption reactor and an analytical instrument. The SO$_3$ generation uses a catalyst to catalyze the SO$_2$ generation, and the catalytic temperature is 365°C. 100 mg absorbent is uniformly arranged on the quartz reactor, and the reaction gas penetrates the absorbent from the upstream and enters the gas analysis instrument.

2.2. Materials
The absorbent is from Sinopharm Group, and the CaO particles are crushed and sieved, with a particle size of 20-48 µm, and the adsorption was not in consideration resulted by particles size [10].

2.3. Method
The absorption of SO$_3$ and SO$_2$ at different reaction times detailed calculation method is in literature 15.

The conversion of CaO by absorbing SO$_2$ ($X_{SO_2}$), SO$_3$ ($X_{SO_3}$) and SO$_x$ ($X_{SO_x}$) are defined as equations (1), (2) and (3):

\[
X_{SO_2} = \frac{N_{SO_2}}{N_{CaO}} \tag{1}
\]
\[
X_{SO_3} = \frac{N_{SO_3}}{N_{CaO}} \tag{2}
\]
\[
X_{SO_x} = \frac{N_{SO_2} + N_{SO_3}}{N_{CaO}} \tag{3}
\]

where $N_{SO_2}$ (mol) is the amount of SO$_2$ absorption; $N_{SO_3}$ (mol) is the amount of SO$_3$ absorption; and $N_{CaO}$ (mol) is the amount of CaO used in the experiment.

The SO$_3$ removal efficiency, $\alpha_{SO_3}$ is defined in equation (4):

\[
\alpha_{SO_3} = \frac{N_{SO_2} + N_{SO_3}}{N_{CaO}}
\]
\[ \alpha_{SO_3, (t_2 - t_1)}^2 = \frac{N_{SO_3,t_2} - N_{SO_3,t_1}}{C_{SO_3,in} \times Q \times (t_2 - t_1)} \]

where \( t_1, t_2 \) are the time between two adjacent samples; \( C_{SO_3,in} \) (g/m\(^3\)) is the inlet concentration of SO\(_3\) of the reactor; \( Q_s \) (m\(^3\)/s) is the total gas flow; \( m \) is the quality of CaO.

The SO\(_3\) selectivity, \( S_{SO_3} \), is defined in equation (5):

\[ S_{SO_3} = \frac{N_{SO_3}}{N_{SO_2} + N_{SO_3}} \] (5)

3. Results and Discussion

3.1. Influence of Temperature on Absorption of SO\(_3\) by CaO
Figure 2 shows the total conversion of SO\(_3\) by CaO (a), the conversion of SO\(_2\) (b) and SO\(_3\) (c) by CaO to 400/500/600/700/800/900°C. In the initial time, all conversions showed an obvious linear growth, and then slowly increasing as the reaction goes on. And with the temperature increases, the conversion of the absorbent exhibits two different changes. One is that the conversion increases, there is a significant increasing of three conversions, and the total conversion of SO\(_3\) absorbed by CaO increases from 0.093 to 0.56; another is that the rate of conversion increases. But increasing temperature the conversion of SO\(_2\) by CaO is larger than the conversion of SO\(_3\). In the latter stage, SO\(_3\) can continue to react with CaO through ionic diffusion [13, 16], while SO\(_2\) is molecular diffusion, so SO\(_3\) still maintains a good linear absorption and the conversion of SO\(_2\) increasing slowly. But when the temperature up to 700°C, the conversion of SO\(_2\) by CaO still have a good increase, the SO\(_2\) and O\(_2\) directly generate sulfate, the conversion of SO\(_2\) by CaO still increasing.

![Figure 2](image1.png)

**Figure 2.** The conversion of CaO by absorbing SO\(_3\) (a), SO\(_2\) (b), SO\(_3\) (c) at 400-900°C.

Figure 3 shows the SO\(_3\) selectivity of CaO at 400-900°C. Based on the above research, the absorbent will be affected by SO\(_2\) when removing SO\(_3\). The SO\(_3\) selectivity increases slowly with time. At the initial time, the concentration of SO\(_2\) is 20 times as much as the concentration of SO\(_3\), so that SO\(_2\) will react more with CaO. When the reaction progresses are controlled by the product layer, the molecular diffusion of SO\(_2\) is less than the ion diffusion of SO\(_3\), so the selectivity of SO\(_3\) increases in later times. By increasing the temperature, the SO\(_3\) selectivity decreases, particularly increasing temperature from 400°C to 700°C, the SO\(_3\) selectivity of CaO decreases from 0.29 to 0.10.
Figure 3. The SO$_3$ selectivity of CaO at 400-900°C.

Figure 4. The SO$_3$ removal efficiency by CaO at 400-900°C.

Figure 3 shows the removal efficiency trend of CaO to SO$_3$ at 400-900°C in 2000 ppm SO$_2$ and 100 ppm SO$_3$. At first the SO$_3$ removal efficiency reached about 90%, then showed a rapid decline in 15 minutes. Subsequently, the removal efficiency began to decrease slowly, and after 30 minutes, the removal efficiency was slightly decreased. The SO$_3$ removal efficiency increases significantly with increasing temperature, it increased from 0.29 to 0.46, so the temperature is a prime factor on the removal of SO$_3$.

3.2. Influence of SO$_2$ Concentration on Absorption of SO$_3$ by CaO

Figure 5 shows the total conversion of SO$_3$ by CaO (a), the conversion of SO$_2$ by CaO (b) of and SO$_3$ (c) under 2000 ppm SO$_2$/1000 ppm SO$_2$/2000 ppm SO$_2$/100 ppm SO$_2$/200 ppm SO$_3$ at 800°C. After increasing the concentration of SO$_3$, the total conversion increases. Increasing the concentration of SO$_2$ or decreasing SO$_3$, the conversion of SO$_3$ by CaO decreases. Changing the concentration of SO$_2$ has a smaller impact than directly changing SO$_3$ concentration. Since the conversion of absorption of SO$_2$ CaO is greater than the conversion of absorption of SO$_3$, because the proportion of SO$_2$ is much higher than SO$_3$. At 800°C, the conversion of SO$_2$ by CaO is 0.43, and the conversion of SO$_3$ is 0.038 in 2000 ppm SO$_2$ and 100 ppm SO$_3$.

Figure 6 shows the SO$_3$ selectivity of CaO in different flue gas components at 800°C. The SO$_3$ selectivity of different atmospheres have the same trend, which is small in the early stage and then increasing moderate with the reaction time. When increasing the concentration of SO$_3$ or decreasing the concentration of SO$_2$, the SO$_3$ selectivity will increase. Reducing the concentration of SO$_3$ without changing SO$_2$ concentration, the SO$_3$ selectivity of CaO increases from 0.082 to 0.14.
Figure 6. The SO$_3$ selectivity of CaO (a) at 800°C.

Figure 7. The SO$_3$ removal efficiency by CaO at 800°C.

Figure 7 shows the SO$_3$ removal efficiency of CaO at 2000 ppm SO$_2$/1000 ppm SO$_2$+100 ppm SO$_3$/2000 ppm SO$_2$+100 ppm SO$_3$/2000 ppm SO$_2$+200 ppm SO$_3$. Changing the concentration of SO$_2$ and SO$_3$ will alter the SO$_3$ removal efficiency, but it is smaller than directly increasing the concentration of SO$_3$. The SO$_2$ has a large proportion, so changing the concentration of SO$_2$ its influence on the SO$_3$ removal efficiency is small, but there still have a good SO$_3$ removal efficiency, basically remains at 0.42.

4. Conclusion
The influence of SO$_2$ on the SO$_3$ absorption performance of CaO was studied in the middle and high temperature range. Increasing the experimental temperature increased the amount of conversions and conversion rate of the absorbent, but the conversion for absorbing SO$_2$ was significantly higher than SO$_3$. The SO$_3$ selectivity of CaO decreased from 0.29 to 0.075 when the temperature increased from 400°C to 900°C. Therefore, rising temperature, although the utilization of the absorbent increases, the influence of SO$_2$ on removing SO$_3$ by the absorbent also increases.

Changing the flue gas composition at 800°C, the reduction of SO$_2$ play a smaller role on the conversion of SO$_3$ than directly increasing the concentration of SO$_3$. The conversion of the absorbent to SO$_3$ and selectivity was enhanced through decreasing the SO$_2$ concentration or increasing the SO$_3$ concentration, but the selectivity relative amount of increase is not large. At 800°C, the absorbent has little influence on the removal of SO$_3$, which is all about 40% at last.

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