Study on Desulfurization of SO_2 by Attapulgite Compond Calcium Oxide Desulfurizaiton Agent

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Abstract: Attapulgite (ATP), produced in Gansu Linze, and metal oxides CaO, which was used as a conventional desulfurizer, were used to prepare a kind of new desulfurizer. The influences of water content rate of desulfurization, desulfurizer particle dimeter and bed temperature had been studied. As a rusult, the sulfur tolerance of the desulfurizer reached 17.12%, when water content rate of desulfurization is about 20 %, particle diameter to reactor diameter ratio is1/10 and the bed temperature is nomal.

Keywords: Attapulgite; CaO; desulfurization; SO_2; adsorption; catalysis

1 Introduction

CaO was a conventional desulfurizer, which was used in a mature method of lime/gyp. It was thought the lime/gyp method was more effect and cheaper than other methods, such as acitiviate carbon adsorption and Claus recycle, etc.. But the calcium desulfurizer is ready to scaling in the process of desulfurization reaction, because $CaSO_4$ was generated, molar volume of which is three times as much as CaO, and the micro pore of desulfurizer will soon jammed by $CaSO_4$, thus prevent the reaction and decrease SO_2 removal efficiency [1 ~ 3].

The attapulgite (ATP) is a new material of multi-porous which has special tunnel, a lot of activation center and larger superficial area ratio. The researchers native and overseas had studied its properties[4-6], and mainly concerned about the aspect of modifying material of compound material[7,8]. The studies of using attapulgite as a desulphurizer had less reported except that our team used attapulgite and activated aluminum as a supporter, and activated metal oxide compound as absorbent to remove high concentration SO_2[9].

In this study, ATP and metal oxides CaO were used to prepare a kind of new desulfurizer. And the influences of water content of desulfurizer, particle size and bed temperture on desulfurization had been studied.

2 Experimental

2.1 Preparation of the desulphurizer

CaO, ATP(produced in Gansu Linze) which has been grinded and sieved by 60 eyes sieves, and some water were mixed and well-distributed at a certain ratio. The mixture was aged, shaped and then dried in the oven at the temperature of 105℃, and roasted in the high temperature oven at 600℃ for 2 hours, cooled in the ambient. After that, the samples were immersed in 1mol/L NaOH solution for 1h, then dried. The CaO/ATP desulfurizer samples were obtained.

2.2 Determining the Properties of the CaO/ATP Desulphurizer

The ability of desulphurization of CaO/ATP desulphurizer was determined by the experiment equipment showed in **Figure 1**. SO_2 gas had gone through the little desulphurizing tower continuously until the adsorbent supporter was penetrated. The inlet SO_2 gas concentration and outlet SO_2 concentration were determined ever few minutes when it went through the little desulphurizing tower until the desulphurizer was penetrated. Then the penetrating curves were obtained and the sulfur tolerance(S) were calculated by following formula:

$$S = \frac{(G_a - G_b)}{G_b} \times 100\%$$

G_a—the weight of the desulphurizer after desulphurization

G_b—the weight of the desulphurizer before desulphurization.

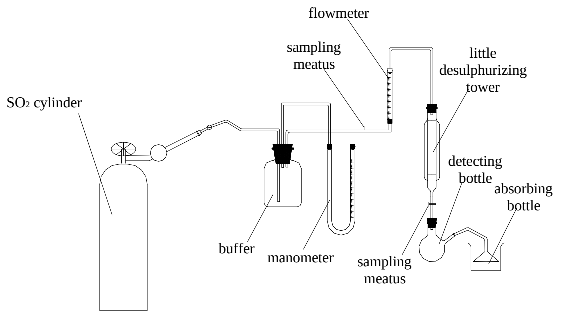

Figure 1 Experiment equipment

3 Results and Discussion

3.1 Influence of Water Content of CaO/ATP Desulphurizer on Desulfurization Capability

The influences of water content on desulfurization ablity

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were presented in **Figure 2** and **Figure 3**.

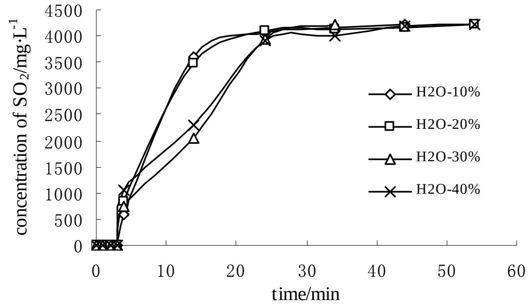

Figure 2 Influences of water content on penetrating curves

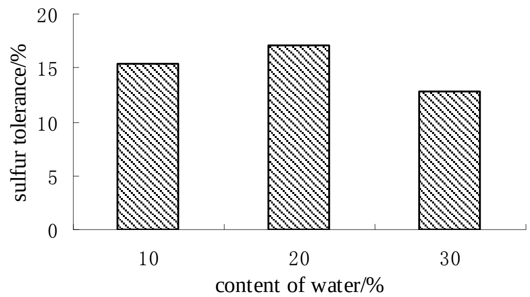

Figure 3 Influences of water content on sulfur tolerance

As shown in **Figure 2**, water containing rate of the sample was higher, penetrating time was longer. It was because the CaO/ATP desuulfurizer had the ability of both physical adsorption and chemical adsorption. The existence of water was one of important elements for chemical adsorption. The sample's surface atom structure and surface lectric charge imbalance formed the adsorbing center, when SO_2 passed through the desulphurizer, it was adsorbed by the activate site, and reacted with O_2 and H_2O adsorbed, and generated H_2SO_4, which is stored in micro holes or middle holes of the desulphurization agent. The reaction equation is as follow:

$$SO_2 + H_2O + 1/2O_2 \rightarrow H_2SO_4$$

Except that, another reaction also happened:

$$CaO + SO_2 + 2H_2O \rightarrow CaO_3 \cdot 2H_2O$$

Sulfur tolerance was becoming higher when water containing rate was increasing, but it went down when water content was beyond 20%, as shown in **figure 3**. It was because the generated H_2SO_4 and $CaSO_4$ were still on the surface of the desulfurizer, which hindered the reactions to go on. The more water just prolonged the penetrating time to some extent. As a result, the water content should better be 20%, more water will decrease its sulfur torlerance.

3.2 Influence of Particle Diameter of CaO/ATP Desulphurizer on Desulfurization Capability

The influences of particle diameter on desulfurization ablity were presented in **Figure 4** and **Figure 5**.

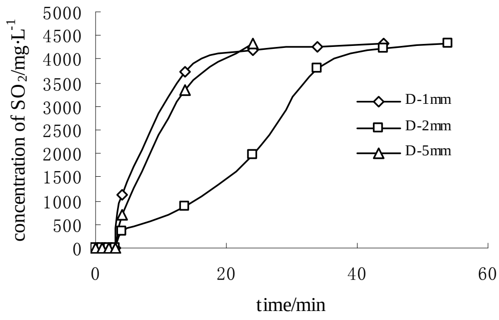

Figure 4 Influences of particle diameter on penetrating curves

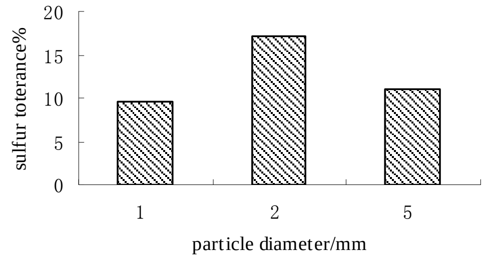

Figure 5 Influences of particle diameter on sulfur tolerance

Desulfurization effect had some relationship with particle size, particle size should not be too big or too small, as shown in **Figure 4** and **Figure 5**. Small particles had big superficial area, but too small particles would lead to short penetrating time and low sulfur tolerance. The particle diameter to reactor diameter should be a proper ratio, not too small and not too big, otherwise it will lessen the effectiveness of desulurization of the agent. According to the experiment, 1/10 is a good ratio of particle diameter to reactor diameter.

3.3 Influence of bed temperature on desulfurization capability

The influences of bed temperature on desulfurization ablity were presented in **Figure 6** and **Figure 7**.

As we seen, penetrating time and sulfur torlerance all decreased with bed temperature became higher. It was shown that the de-SO_2 reaction by the CaO/ATP desulfurizer was a heat-release reaction, low temperature was good for the reaction. Physical adsorption was main process of that. So the experiments of dusulfurization can

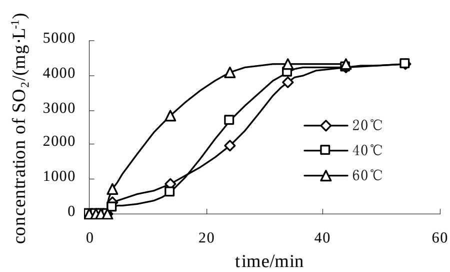

Figure 6 Influences of bed temperature on penetrating curves

be operated at normal temperature and do not need any-heating equipment, as to simplify the experiments.

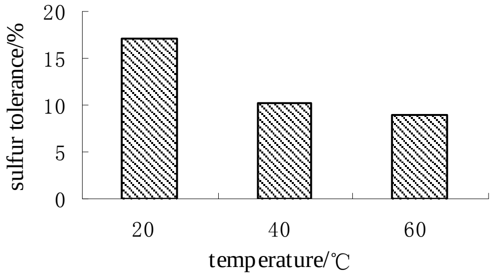

Figure 7 Influences of bed temperature water content on sulfur tolerance

3.4 Component Analysis comparison of CaO/ATP before and after desulfurization

JSM 5600LV(Japan) / K1VE2 EDS(US) were used for Component Analysis comparison of CaO/ATP before and after desulfurization, the results were showed in **figure 8**, **figure 9** and **table 1**. As we see, after desulfurization, the sulfur content of sample was much higher than that before desulfurzation.

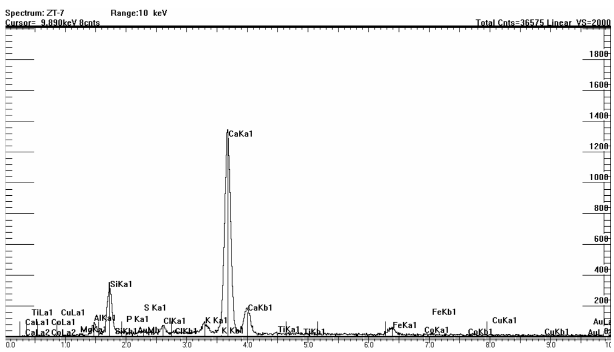

Figure 8 Component analysis of CaO/ATP before desulfurization

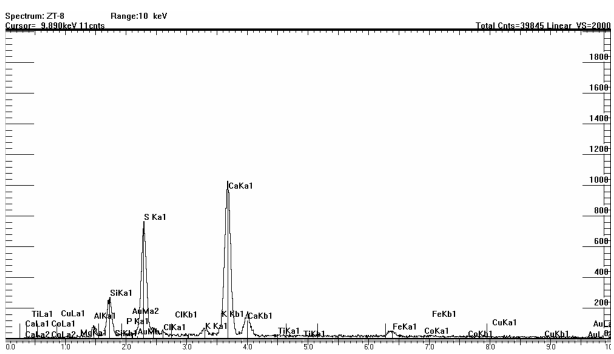

Figure 9 Component analysis of CaO/ATP after desulfurization

Table 1 Component analysis of CaO/ATP before and after desulfurization

Element	*Na*	*Mg*	*Al*	*Si*	*P*	*S*
Before	0	0.66	4.61	15.76	0.84	1.22
After	0.95	0.62	3.33	10.58	0.83	28.56
Element	Cl	K	Ca	Ti	Fe	I
Before	2.51	3.40	66.41	0.59	3.35	0.65
After	1.70	2.32	47.26	0.39	2.79	0.68

4. Conclusions

A kind of new compond desulfurizationf agent, which was composed by CaO and attapulgite produced in Gansu, was studied. The experiments result showed that, water containing rate, desulfurizer particle dimeter and bed temperature had much influence on effectiveness of dusulfurization. water containing rate of the sample was higher, penetrating time was longer, but the sulfur tolerance went down when water content was beyond 20%, so water content had better to be 20%. Particle diameter to reactor diameter should be a proper ratio(1/10), otherwise the effectiveness of desulurization of the agent will be lessened. Penetrating time and sulfur torlerance all decreased with bed temperature became higher; the normal temperature is a good choice for the reaction. At the conditions of above, the sulfur tolerance of the desulfurizer reached 17.12%.

Acknowledgment

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