

Study on optimum technological conditions of ore sintering flue gas desulfurization by using poor manganese

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Abstract. Orthogonal experiments were conducted to study the effect of each single factor on the desulfurization rate and leaching rate of Mn^{2+} to obtain improved process parameters. The results showed that the use of pyrolusite flue gas and the process method of by-product MnSO_4 can not only effectively remove the sulfur in the gas, thereby controlling environmental pollution, but can also recover sulfur.

1. Introduction

The amount of SO_2 produced by iron and steel industry in China is second only to that of the coal power industry. And SO_2 produced by sintering process accounts for more than 40% of iron and steel industry, while it is one of the main sources of air pollution [1-5]. Therefore, the research on how to develop a desulfurizing technique with less investment, less operating costs and resource regeneration, is very important [6-9]. It is certainly worth studying on optimum technological conditions of sintering flue gas desulfurization.

2. Materials

2.1. Materials

The composition and industrial analysis of the materials (pyrolusite, iron concentrate, and powdered coal).

- Mn is obtained from Mn ore, which was ground to an average particle size of 0.075 mm after breaking. The ore was obtained from a mountain in Guizhou province.
- Iron ore is the concentrate used in sintering in a domestic steel company.
- There is powdered coal and coke too.

2.2. Conditions and process

Pyrolusite slurry was used in flue gas desulfurization and to prepare the MnSO_4 products. Pyrolusite ore was crushed [10] into a specific particle size, and the pyrolusite slurry was prepared based on a particular proportion with water. Flue gas was applied to the absorber after dust removal. The desulfurization and leaching of Mn^{2+} were performed in the absorber. The mother liquor was obtained



via filtration, purification, crystallization, and drying to prepare the MnSO_4 products.

3. Experiment

The absorption temperature, liquid-solid ratio, pyrolusite granularity, and SO_2 inlet concentration have specific effects on the desulfurization rate and leaching rate of Mn^{2+} . The first three factors have a direct impact on the desulfurization and leaching rate of Mn^{2+} in the pyrolusite pulp. The effect of SO_2 inlet concentration on the desulfurization and leaching rate of Mn^{2+} can be controlled by changing the pH value of the slurry, the slurry circulation volume, and the length of absorption time. Therefore, we focused on studying the effects of the interaction of various factors, namely, absorption temperature, liquid-solid ratio, and particle size of pyrolusite. To perform the analysis with fewer tests and to determine the significance of each factor, the orthogonal table test was performed. Each experiment was conducted for 6 h. The desulfurization rate in the table is the average desulfurization rate, and the leaching rate of Mn^{2+} is the total leaching rate at the end of the cycle.

4. Results and discussion

Three factors were included in the orthogonal experiment. Each factor takes three levels, and their interactions with one another were excluded. The orthogonal table L9 (34) was selected to arrange the orthogonal test for the study of the desulfurization and leaching rates of Mn^{2+} . The factors and levels selected in the test are shown in table 1, and the orthogonal experiment table is shown in table 2. Variance analysis is shown in table 3.

Table 1. Factors in the orthogonal experiment.

Level	Impact factor		
	A (Absorbent temperature, °C)	B (liquid-solid ratio; kg water: kg ore)	C (Average Mn ore granularity, mm)
1	40	3:1	0.30
2	60	5:1	0.15
3	80	7:1	0.075

Table 2. Results of the experiment on the desulfurization and leaching rates of Mn^{2+} .

Test number	Factor			Target	
	A	B	C	Average desulfurization rate η (%)	Total Mn leaching rate χ (%)
1	40	3:1	0.300	70.13	67.56
2	40	5:1	0.150	74.57	76.20
3	40	7:1	0.075	76.48	71.45
4	60	3:1	0.150	65.57	69.93
5	60	5:1	0.075	77.33	74.52
6	60	7:1	0.300	61.43	64.56
7	80	3:1	0.075	72.45	63.34
8	80	5:1	0.300	56.66	58.42

9	80	7:1	0.150	61.38	73.35
η I	221.18	208.15	188.22	$T_{\eta}=616.00$	
II	204.33	208.56	201.52		
III	190.49	199.29	226.26	$\bar{\eta} = \frac{1}{9} \sum_{i=1}^9 \eta_i = 68.44$	
$\bar{I}$	73.73	69.38	62.74		
$\bar{II}$	68.11	69.52	67.17		
$\bar{III}$	63.49	66.43	75.42		
Range	10.23	3.09	12.68		
I^2	48920.5943326.4235426.77				
II^2	41750.7543497.2740610.31				
III^2	36286.4439716.5051193.59				
χ I	215.21	200.83	190.54	$T_{\chi}=619.33$	
II	209.01	209.14	219.48		
III	195.07	209.36	209.31	$\bar{\chi} = \frac{1}{9} \sum_{i=1}^9 \chi_i = 68.81$	
$\bar{I}$	71.74	66.94	63.51		
$\bar{II}$	69.67	69.71	67.17		
$\bar{III}$	65.04	69.79	69.77		
Range	6.70	2.85	6.26		
I^2	46315.3440332.6936305.49				
II^2	43685.1843739.5448171.47				
III^2	38067.9143831.6143810.68				

Table 3. Validated results of experiment of the optimum conditions.

Test number	Reaction temperature(°C)	liquid-solid ratio(kg/kg)	Mn ore granularity (mm)	Average desulfurization rate (%)	Total Mn leaching rate (%)
1	40	5□1	0.075	78.30	77.35
2	40	5□1	0.075	78.26	77.52
3	40	5□1	0.075	79.15	78.64
Average value	—			78.57	77.84

4.1. Effects of various factors on the indicators

For the average desulfurization rate, the range R of the data in the third column of the orthogonal experimental results is at maximum (table 2), followed by the first column and the second column. The

orthogonal test describes that the effect on the desulfurization rate of pyrolusite system is at maximum when the process conditions of the particle size of Mn changes. By contrast, the effect on desulfurization rate is at minimum when the liquid-solid ratio changes. Thus, the primary and secondary orders of the factors that affect the desulfurization rate can be arranged as follows:

$$\text{primary} \xrightarrow{\text{C} \quad \text{A} \quad \text{B}} \text{secondary}$$

For the total leaching rate of Mn^{2+} , the range of the data of the third column in the orthogonal experimental results (table 2) is at maximum, followed by the first column and the second column. The orthogonal test describes that the effect on desulfurization rate of the pyrolusite system is at maximum when the process conditions of the particle size of Mn^{2+} changes. By contrast, the effect on desulfurization rate is at minimum when the reaction temperature changes. Thus, the primary and secondary orders of the factors that affect the total leaching rate of Mn^{2+} can be arranged as follows:

$$\text{primary} \xrightarrow{\text{A} \quad \text{C} \quad \text{B}} \text{secondary}$$

4.2. Analysis of the optimal reaction conditions

Comparisons among the values I, II, and III in table 2 show that for the average desulfurization rate, the reaction temperature level A1 is better than A2 and A3, the liquid-solid ratio level B2 is slightly better than B1 and B3, and the granularity level of the Mn ore C3 is better than C1 and C2. Therefore, the optimal factor combination in this experiment is A1B2C3, that is, a reaction temperature of 40°C, a liquid-solid ratio of 5:1, and a particle size of Mn ore of 0.075 mm. For the total leaching rate of Mn^{2+} , the reaction temperature level A1 is slightly better than A2 and A3, the level of liquid-solid ratio B2 is better than B1 and B3, and the granularity level of Mn ore C3 is better than C1 and C2. Therefore, the optimal factor combination in this experiment is A1B2C3, which is the same with that for the desulfurization rate.

This group of tests does not appear in the orthogonal experiment. Additional experiments are needed for verification. The verification tests were repeated for three times, and the experimental results are shown in table 3.

The verification results of the optimum technological experiments show that the average desulfurization rate and the total leaching rate of Mn^{2+} are higher than the test results of each group in the orthogonal tests. Thus, the level of the derived A₁B₂C₃ combination guarantees higher desulfurization and leaching rates of Mn^{2+} .

Further analysis was conducted at the temperature of the slurry cycle (40°C) because the average outlet temperature of the flue gas is at ~140°C. Therefore, at 40°C, when pyrolusite was used to absorb SO₂, the slurry does not need additional heating. For wet desulfurization, the liquid-solid ratio is essentially the content indicator of the desulfurizing agent in a liquid phase. The desulfurizing agent in the pyrolusite desulfurization system is not only MnO₂ but also CaO, MgO, or other substances. Therefore, the selection of the liquid-solid ratio cannot guarantee a high desulfurization rate. And, process conditions and equipment choice should also be considered. The optimum liquid-solid ratio obtained from the orthogonal experimental results is 5:1, which was determined and based on the composition of low-grade pyrolusite. The economic and safe operation of the absorption tower and the recycling equipment were also considered. If the particle size of pyrolusite is too small, the ore reduction and grinding times both increase, thereby increasing power consumption. In addition, liquid-solid separation also becomes more difficult. Considering the grinding, solid-liquid separation, SO₂ absorption rate, and leaching rate of Mn^{2+} , the most appropriate average particle size of Mn is 0.075 mm.

5. Conclusion

The optimum process parameters, which were obtained from orthogonal and optimal experiments, for the flue gas desulfurization of pyrolusite slurry in the packed column are as follows: the temperature is

at 40°C, liquid–solid ratio is 5:1, and the average particle size of Mn is 0.075 mm. In these conditions, higher desulfurization rate and leaching rate of Mn^{2+} can be achieved.

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