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

H Y Li¹,², S E Li¹,², S Z Long³, F Z Wu¹,², T M Cui¹,² and X Z Zhou⁴

¹College of Materials and Metallurgy, Guizhou University, Guiyang, 550003, China
²Guizhou Province Key Laboratory of Metallurgical Engineering and Process Energy Saving, Guizhou University, Guiyang, 550003, China
³School of Marxism, Guizhou University, Guiyang, 550003, China
⁴Library, Guizhou University of Finance and Economics, Guiyang, 550003, China

E-mail: 568144269@qq.com

Abstract. Orthogonal experiments were conducted to study the effect of each single factor on the desulfurization rate and leaching rate of Mn²⁺ to obtain improved process parameters. The results showed that the use of pyrolusite flue gas and the process method of by-product MnSO₄ can not only effectively remove the sulfur in the gas, thereby controlling environmental pollution, but can also recover sulfur.

1. Introduction
The amount of SO₂ produced by iron and steel industry in China is second only to that of the coal power industry. And SO₂ 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 MnSO₄ 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 Mn²⁺ were performed in the absorber. The mother liquor was obtained.
via filtration, purification, crystallization, and drying to prepare the MnSO₄ products.

3. Experiment
The absorption temperature, liquid-solid ratio, pyrolusite granularity, and SO₂ inlet concentration have specific effects on the desulfurization rate and leaching rate of Mn²⁺. The first three factors have a direct impact on the desulfurization and leaching rate of Mn²⁺ in the pyrolusite pulp. The effect of SO₂ inlet concentration on the desulfurization and leaching rate of Mn²⁺ 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 Mn²⁺ 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 Mn²⁺. 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 Mn²⁺.

| Test number | Factor | Target | Average desulfurization rate η (%) | Total Mn leaching rate χ (%) |
|-------------|--------|--------|-----------------------------------|----------------------------|
| A           | B      | C      |                                   |                            |
| 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                      |

2
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 leaching rate (%) | Mn 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:

\[
\text{primary } \text{C} \text{ A} \text{ B} \quad \text{secondary}
\]

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:

\[
\text{primary } \text{A} \text{ C} \text{ B} \quad \text{secondary}
\]

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 SO\(_2\), 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 MnO\(_2\) 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, SO\(_2\) 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.

**Acknowledgments**

This work was financially supported by the National Natural Science Foundation of China (No. 51574094) and the Guizhou Provincial Department of Education Items (Qian Jiao He KYword[2014]222).

**References**

[1] Deng Z J 2015 Discussion on design parameters selection of sintering flue gas desulfurization Resource Economizatio Environmental Protection 3 19

[2] Pan D, Hao W and Yang L 2017 Investigation on the relationship between the fine particle emission and crystallization characteristics of gypsum during wet flue gas desulfurization process J Environ Sci 5 303-10

[3] Wu F Z, Li J Q, Cai J J, Jin H X and Chan X H 2009 Study on flue gas desulfurization of sintering in pilot-scale experiment J Chin Inst Eng 19 65-71

[4] Wu F Z, Cai J J and Li J Q 2008 Flue gas desulphurization of iron and steel industry and circular economy Industrial Furnace 30 8-12

[5] Dong J Q 2016 Study on operational parameters of wet flue gas desulfurization for sintering Science & Technology of Baotou Steel 2 75-7

[6] Dang Y H, Qi Y H and Wang H F 2010 Technology of flue gas desulfurization J Iron & Steel Res 22 1-6

[7] Yu Z Y, Fan X H, Gan M, *et al* 2016 Reaction behavior of SO$_2$ in the sintering process with flue gas recirculation Journal of the Air & Waste Management Association 66 687

[8] Liu Z J, Zhang J L and Yang T J 2009 Research and development of sintering flue gas desulphurization technology China Metallurgy 19 1-5

[9] Li S E, Li W, Pan FF, *et al* 2016 Enrichment and purification process of by-product manganese sulfate in the flue gas desulphurization Guangzhou Chemical Industry 1 53-5

[10] Wu F Z, Li S E and Jin H X 2014 Study on desulfurization of sintering flue gas with pyrolusite slurry Nonferrous Met (Metallurgy) 4 4-6