Ore sintering flue gas desulfurization and its resourecilization by using pyrolusite

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Abstract. Flue gas desulfurization (FGD) has been implemented for sulfur dioxide gas emission reduction by pyrolusite in iron ore sintering. However, the mechanism of SO₂ reduction through FGD is still not fully clear. And in present work, the effects of operating conditions on desulfurization rate and Mn²⁺ leaching rate of pyrolusite were investigated. Six hours later, the desulfurization rate and Mn²⁺ leaching rate all can be higher than 70%. And a higher absorption temperature was good for desulfurization rate, while a middle temperature was good for Mn²⁺ leaching rate. A higher manganese ore granularity and SO₂ concentration were good for desulfurization rate and Mn²⁺ leaching rate. However, a higher liquid-solid rate was only good for desulfurization rate, but Mn²⁺ leaching rate. The results demonstrate that the pyrolusite is a kind of very promising adsorbent in industrial flue gas desulfurization application due to its low cost and good desulfurization capacity.

1. Introduction
China’s western regions, such as Sichuan, Guangxi, Guizhou, Yunnan, Gansu, Ningxia, and Qinghai, have vast deposits of pyrolusite. A large number of pyrolusite is found in the area of Hunan and Guangdong. The characteristics of pyrolusite resources in our country are poor, miscellaneous, and fine. The proportion of poor Mn is large, which is about 93% of the country’s total reserve. The direct industrial application of these low-grade Mn ore resources is difficult. In the production process, iron and steel enterprises consume large amounts of sulfur resources and energy. Meanwhile, SO₂ emissions from these industries have important effects on the environment. The use of pyrolusite leads to SO₂ absorption and by-product MnSO₄ and other products that are widely used and have a good market value. Therefore, the technique in China can not only effectively remove sulfur and control pollution but also can recover and result in resource optimization. Numerous studies have been conducted on flue gas desulfurization by using Mn [1-9], but only a few studies have been conducted on sintering flue gas desulfurization.

2. Materials and process

2.1. Materials
The composition and industrial analysis of the materials (pyrolusite, iron concentrate, and powdered
coal) are given in tables 1 to 3.

2.1.1. Pyrolusite. Mn is obtained from manganese ore, which was ground to an average particle size of 0.075 mm after being broken. The ore was obtained from a mountain in Guizhou Province.

| Ingredient                  | MnO₂ | SiO₂ | Al₂O₃ | Fe  | CaO | Others |
|-----------------------------|------|------|-------|-----|-----|--------|
| Quality content of low-grade pyrolusite (%) | 35.20 | 28.22 | 11.90 | 11.52 | 5.63 | 8.6    |

2.1.2. Iron ore. Iron ore is the concentrate used in sintering in a domestic steel company.

| Ingredient                  | TFe  | SiO₂ | H₂O   | Al₂O₃ | CaO | S     | MgO   |
|-----------------------------|------|------|-------|-------|-----|-------|-------|
| Quality content (%)         | 67.64| 3.75 | 8.29  | 0.32  | 0.59| 0.049 | 0.48  |

2.1.3. Powdered coal and coke.

| Material       | Quality content (wt.%) | Industrial analysis (wt.%) |
|----------------|------------------------|---------------------------|
|                | Ash content | Moisture | Fixed carbon | S   | C   | H   | N   | O   |
| Coke powder    | 9.59        | 11.5     | 77.1          | 0.63| 77.1| 4.31| 0.8 | 4.86|
| Steam coal     | 20.86       | 7.66     | 59.35         | 0.54| 59.38| 3.88| 0.56| 7.12|

2.2. Conditions and process

The experimental conditions are shown in table 4.

| Order number | Project                                           | Parameter                      |
|--------------|---------------------------------------------------|--------------------------------|
| 1            | Concentration of sulfur dioxide in flue gas       | ~3000 mg/m³                   |
| 2            | Temperature (°C)                                  | 20                             |
| 3            | Stirring speed (r/min)                            | 300                            |
| 4            | Liquid-solid ratio (kg water/kg ore)              | 5:1                            |
| 5            | Average mineral powder particle size (mm)         | 0.075                          |
| 6            | Fume volume (m³/h)                                | 10                             |
| 7            | Ore grade (%)                                     | Low grade, 35.20% MnO₂        |
| 8            | Pulp total volume (L)                             | 5                              |

Pyrolusite slurry was used in flue gas desulfurization and to prepare the MnSO₄. Pyrolusite ore was
crushed [10] into a specific particle size, and the pyrolusite slurry was based on a particular proportion with water. Flue gas flowed into the absorber after removing dust. The desulfurization and leaching of Mn\(^{2+}\) were performed in the absorber. The mother liquid was used to prepare the MnSO\(_4\) by filtering, purifying, crystallizing, and drying.

3. Experimental

Flue gas desulfurization by pyrolusite is based on the reducibility of SO\(_2\) and the oxidation of MnO\(_2\). The effects of absorption temperature, liquid-solid ratio, particle size of pyrolusite, and SO\(_2\) concentration on the desulfurization rate and Mn\(^{2+}\) leaching rate were determined.

4. Results and discussion

4.1. Absorption temperature

The temperature is 20\(^{\circ}\)C, 30\(^{\circ}\)C, 40\(^{\circ}\)C, 50\(^{\circ}\)C, and 60\(^{\circ}\)C. The other conditions are the same as those in table 4. The effects of temperature on the desulfurization rate and Mn\(^{2+}\) leaching rate were determined.

Figure 1. Temperature influence on desulfurization rate.

During the desulfurization by pyrolusite, the initial effect is almost unnoticeable in figure 1. When the temperature is 30\(^{\circ}\)C~40\(^{\circ}\)C, the desulfurization effect is improved, but the difference is not significant. With the decrease (e.g., at 20\(^{\circ}\)C) or increase (e.g., at 50\(^{\circ}\)C and 60\(^{\circ}\)C), the desulfurization rate decreases to a particular extent. This phenomenon is mainly due to the two aspects of temperature on flue gas desulfurization by pyrolusite. When the temperature increases, SO\(_2\) solubility in the liquid phase makes it difficult to the reaction of MnO\(_2\) and SO\(_2\). On the other hand, the high temperature is favorable for desulfurization with reduced liquid viscosity, increasing diffusion coefficient, and increasing reaction rate constant. It shows that the temperature has a similar effect on both the desulfurization rate and Mn\(^{2+}\) leaching rate in figure 2.

4.2. Liquid-solid ratio

The liquid-solid ratio in pyrolusite pulp is the ratio of the quantity of water and mineral powder, which is expressed in kg water/kg mine. The liquid-solid ratio is an important parameter, which has an effect on the desulfurization rate, the leaching rate of Mn\(^{2+}\), as well as the equipment investment costs and operating expenses, and so on. The condition of the liquid-solid ratio was 3:1, 5:1, and 7:1. The effects of liquid-solid ratio at these three conditions on the desulfurization rate and Mn\(^{2+}\) leaching rate were investigated; other conditions were the same as those in table 4. The results are shown in figures 3 and 4.
Figure 3. Rate of liquid quantity and solid quantity influence on desulfurization rate.

The desulfurization rate gap is significantly small in the initial stage in figure 3. The desulfurization rate decreases with increasing liquid-solid ratio of the pyrolusite system after 1 h. When the liquid-solid ratio is 3:1, the desulfurization rate is higher in a significantly longer period of time than those of 5:1 and 7:1. When the liquid-solid ratio is 5:1 and 7:1 and after 4.5 h, the desulfurization rate decreases observably. When the variation is mainly due to the low liquid-solid ratio, both the proportion of MnO₂/SO₂ in the liquid phase and the concentration of reactants increase. These are favorable to the absorption of SO₂. Meanwhile, the numerous particles are suspended in the liquid phase of packed column, which increase the contact area of gas-liquid. It is conducive for SO₂ to permeate through the liquid and solid phases. So, the absorption rate of SO₂ is improved.

The leaching rate of Mn²⁺ decreases when the liquid-solid ratio increases in the same reaction time in figure 4. This phenomenon is mainly due to the high liquid-solid ratio (7:1), in which the molar concentration of MnO₂ in the pulp is low, the proportion of MnO₂/SO₂ is small, and both the reaction rate of MnO₂ in the pulp and the depletion rate is slow. Thus, the leaching rate of Mn²⁺ decreases.

4.3. Manganese ore granularity

The average particle size of mineral powder was 0.30 mm, 0.15 mm, and 0.075 mm. The other conditions are the same as those in table 4. The effects of the particle size on the desulfurization rate and leaching rate of Mn²⁺ were studied. The results are shown in figures 5 and 6.

Figure 5. Granularity of manganese influence on desulfurization rate.  

Figure 6. Granularity of manganese influence on the rate of leaching Mn²⁺.

From kinetics, the particle size of pyrolusite has a relatively significant impact on the reaction rate.
Therefore, it is also an important factor that affects the desulfurization rate and leaching rate of Mn$^{2+}$. The desulfurization rate and leaching rate of Mn$^{2+}$ increase with decreasing particle size in figures 5 and 6. When the concentration is constant, finer particles provide larger liquid-solid contact area. The large contact area is conducive to mass transfer, in which the internal diffusion resistance from the gas phase to the solid particles is reduced, thereby the reaction rate is accelerating. So, the finer the size of manganese ore is, the higher the rate of desulphurization and leaching of Mn$^{2+}$ is.

4.4. SO$_2$ concentration

Experiments with the control samples of SO$_2$ concentration (3000, 4000, and 5000 mg/m$^3$) were conducted. The other conditions are the same as those in table 4. The effects of SO$_2$ concentration on the desulfurization rate and leaching rate of Mn$^{2+}$ were investigated, and the results are shown in figures 7 and 8.

![Figure 7: Inlet concentration influence on desulfurization rate.](image1)

![Figure 8: Inlet concentration influence on the rate of leaching Mn$^{2+}$.](image2)

In the initial reaction, the difference in desulfurization rates is low in figures 7 and 8. The flue gas desulfurization rate decreases with increasing SO$_2$ concentration for 1.5 h. While the SO$_2$ concentration increases, the gas-liquid mass transfer force also increases. Thus, the transmission rate of SO$_2$ to the liquid phase increases, Mn consumption is fast, the desulfurization rate rapidly decreases, and the leaching rate of Mn$^{2+}$ rapidly increases. These phenomena are due to the continuous cycle of SO$_2$. The total amount of MnO$_2$ in the slurry is constant. At the same desulfurization rate, the higher SO$_2$ concentration needs more consumption of MnO$_2$. In the late reaction, while the quantity of MnO$_2$ decreases, both the pH value and the desulfurization rate significantly decreases. When the SO$_2$ concentration of the reaction tower is low, the Mn/S value in the liquid phase becomes relatively large and the consumption of MnO$_2$ becomes slower. Thus, the time for the same desulfurization rate is longer. Some MnO$_2$ particles exist in the later period, wherein the curve of desulfurization rate slightly declines. On the other hand, for the leaching rate of Mn$^{2+}$, a higher concentration of inlet SO$_2$ results in a faster consumption of MnO$_2$. Therefore, to achieve the same leaching rate of Mn$^{2+}$ for SO$_2$ at a higher inlet concentration, the required time must be shortened.

This test does not limit the SO$_2$ content but deepens the understanding of the mechanism of desulfurization. The high concentration of SO$_2$ is advantageous for pyrolusite because the high SO$_2$ concentration increases mass transfer force, thereby increasing the amount of dissolved SO$_2$ in the liquid phase per unit time, both the reaction rate of MnO$_2$ and the leaching rate of Mn$^{2+}$ increase. In addition, the purification and crystallization of the by-product of desulfurization has specific requirements on the concentration of MnSO$_4$. Therefore, the high SO$_2$ concentration may be appropriate in increasing the circulation amount and pH value of the slurry. Meanwhile, it is high for desulfurization rate and leaching rate of Mn$^{2+}$ to reduce the liquid-solid ratio, increase the MnO$_2$ content in the pulp, and prolong the absorption time.
5. Conclusions
When the temperature decreases (e.g., 20°C) or increases (e.g., 50°C and 60°C), the desulfurization rate decreases, and temperature has no significant effect on the desulfurization rate and leaching rate of Mn²⁺. When the temperature is at 40°C, desulfurization and leaching rate of Mn²⁺ are slightly higher than those at 30°C. At the same reaction time, the desulfurization rate of pyrolusite slurry system decreases and the leaching rate of Mn²⁺ increases with increasing liquid-solid ratio. When the reaction proceeds within the same reaction time, the finer the size of manganese ore is, the higher the rate of desulphurization and leaching of Mn²⁺ is. The Desulfurization rate in the flue gas decreases with increasing inlet SO₂ concentration, whereas the leaching rate of Mn²⁺ rapidly increases. Six hours later, the desulfurization rate and Mn²⁺ leaching rate all can be higher than 70%.

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).

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