Preparation and performance of sludge-based desulfurizer by calcification

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Abstract. The study used Ca/TS, water content, particle size and additives as control variables to prepare sludge-based desulfurizers. An experimental setup was built up to investigate the desulfurization effect. The 5-factor and 4-level orthogonal experimental scheme was designed to study the factors affecting the sulfur capturing efficiency of sludge-based desulfurizer. The effects of the types and ratios of additives on the sulfur capturing rate were studied with sodium carbonate, iron oxide and acetic acid as additives. The result showed that the optimal condition to produce calcification sludge desulfurizer (CSD) was: 0.425~0.6mm of diameter desulfurizer, moisture content of 30%, and ferric oxide ratio of 6%. The optimal desulfurization condition was the combustion temperature of 900 °C, calcium to sulfur molar ratio of 2.0 and the SO₂ concentration of 1%. In this case, the sulfur capturing ratio was 61.86%, higher than that of pure calcium oxide. The pore structure of the sludge-based desulfurizer showed that compared with the porosity of pure calcium oxide of 32.02% and the specific surface area of 19.80 m²/g, the sludge-based desulfurizers increased to 36.94% and 28.32 m²/g, respectively. The degree of irregularity is low, which greatly improves the sulfur-fixing effect of the sludge-based desulfurizer.

1. Introduction

In recent years, sludge disposal has become an important environmental protection issue that has been increasingly concerned by all countries in the world. At the same time, SO₂, a pollution gas produced by coal-fired power generation, has seriously threatened human health and ecological security. As a common desulfurizer in furnace [1], calcium oxide can react with the remaining water in dehydrated sludge to generate calcium hydroxide and realize sludge drying. On the other hand, sludge is formed by cementation and condensation of suspended solids in water, with loose structure, irregular shape, high specific surface area and porosity (usually more than 99%), and can be used as an adsorbent [2]. Calcium oxide is attached to the porous gap of dehydrated sludge and spreads through Knudsen Diffusion to increase the contact area between calcium oxide and sulfur dioxide, promote the reaction and improve the efficiency of sulfur fixation [3]. In this paper, the preparation of sludge-based desulfurizer is of great significance to solve the problems of sludge recycling and SO₂ emission reduction.
2. Materials and methods

2.1. The experimental materials
Initial sludge was taken from dehydrated sludge of a sewage treatment plant in Jiangning district, Nanjing city, with pH=6.8 and moisture content of 80.6%. See Table 1 for industrial analysis and element analysis of sludge. Compared with coal, the fixed carbon content of sludge is low, only 2.53%, but the volatile content is very high, up to 76.93%. Secondly, calcium oxide and iron oxide are the main components of sludge ash after combustion, accounting for 15.3% and 56.3%, respectively.

Quicklime, powder, purity ≥98%.
Additives. Iron oxide: analytical pure, deep red powder; Sodium carbonate: analytical pure, colorless crystal; Acetic acid: analytical pure, colorless transparent liquid.

| Sludge sample | Elemental analysis (%) | Industrial analysis (%) |
|---------------|------------------------|-------------------------|
|               | C  | H  | N  | S  | O  | Mad | Vad | FCad | Aad |
| Original sludge | 40.75 | 5.40 | 6.60 | 1.09 | 46.16 | 1.23 | 76.93 | 2.53 | 19.31 |

| Substance | Al₂O₃ | CaO | Fe₂O₃ | TiO | SiO₂ | K₂O | MgO | ZnO | SrO | PbO |
|-----------|-------|-----|-------|-----|------|-----|-----|-----|-----|-----|
| Original sludge | 7.55 | 15.34 | 56.27 | 2.36 | 9.05 | 4.96 | 1.60 | 2.23 | 0.21 | 0.43 |

2.2. The experimental devices
The main instruments are rapid moisture teste, standard sieve, tube furnace, magnetic stirrer, etc.

2.3. The experimental methods

2.3.1. Calcify sludge to prepare desulfurizer. The sludge was placed in a pneumatic filter press, and the water content of the sludge was about 65% when the sludge was pressed and filtered under the pressure of 1.2 Mpa for 30 minutes, then add CaO and additives, stir for 2 min at a rotating speed of 8 r/min, and the sludge and quicklime will fully contact and react. After the sludge temperature drops to room temperature, the moisture content will be measured. After drying and vibration screening, sludge-based desulfurizers with different moisture content (15%, 20%, 25%) and different particle size (20 mesh, 30 mesh, 40 mesh and 60 mesh) were obtained.

2.3.2. Performance test of desulfurizers. After setting the temperature in the tubular furnace, the mixed gas of SO₂, O₂, CO₂ and N₂ was injected into the quartz heating tube, and the total gas volume was 1.5L/min. The reaction atmosphere was changed to be 5% O₂+15% CO₂+(1.0%~2.5%) SO₂, N₂ as the equilibrium gas. After the temperature and atmosphere in the furnace reach the set value and remain constant for 10 min, the sludge-based desulfurizer is rapidly pushed into the furnace for sulfur fixation reaction experiment. The tail gas was injected into the NaOH solution containing 10% concentration to neutralize the acid gas SO₂ contained in the tail gas. After the reaction, the desulfurizer was sealed and stored.
3. Results and discussion

3.1. Characterization analysis of desulfurizer

3.1.1. Microstructure analysis of desulfurizer. SEM images were obtained by SEM analysis of morphology and porosity of pure calcium oxide (A), sludge-based desulfurizer (B) and the sludge-based desulfurizer with iron oxide (C), as shown in Figure 1. As can be seen in the figure, the pure calcium oxide particles are small spherical particles that aggregate into a group. The surface of pure sludge particles is uneven, and the specific surface area and porosity are large. The calcium oxide particles in the sludge-based desulfurizer adhere to the irregular surface of the dehydrated sludge, showing a layered appearance, which is conducive to contact and react with SO2 gas. After addition of additives, porosity and specific surface area were increased [4].

![Figure 1. SEM image of four materials](image)

3.1.2. Microscopic pore characteristics. Microscopic pore characteristics of desulfurizer can be obtained by using porosity and specific surface area analyzer [5], as shown in Table 2.

| Desulfurizer                        | Porosity (%) | Specific surface area (m²/g) | Average microscopic aperture (nm) |
|-------------------------------------|--------------|------------------------------|----------------------------------|
| Pure calcium oxide                  | 32.02        | 19.80                        | 1.97                             |
| Sludge-based desulfurizer           | 36.94        | 28.32                        | 1.63                             |
| Sludge-based desulfurizer with iron oxide | 37.11        | 28.95                        | 1.49                             |

The internal porosity and specific surface area of the sludge-based desulfurizer particles with iron oxide were the largest, followed by the sludge-based desulfurizer, and the lowest is pure calcium oxide. Microscopic pore characteristics of pure calcium oxide (A), sludge-based desulfurizer (B) and the sludge-based desulfurizer with iron oxide (C) can be obtained by using porosity and specific surface area analyzer, as shown in Figure 2. The pore diameter of pure calcium oxide particles is mainly distributed at 1.5 ~ 2.0 nm, while the microscopic pore diameter of sludge-based desulfurizer is mainly distributed at 1.0 ~ 1.5 nm.
3.1.3. **Macroscopic pore characteristics.** SEM images [6] were analyzed by Image-Pro Plus software to obtain the maximum pore diameter, minimum pore diameter and average pore diameter of the material particles, as shown in Table 3.

| Desulfurizer                          | Max   | Min   | Average |
|---------------------------------------|-------|-------|---------|
| Pure calcium oxide                    | 100.88| 0.22  | 0.78    |
| Sludge-based desulfurizer             | 520.24| 3.08  | 8.83    |
| Sludge-based desulfurizer with iron oxide| 540.82| 3.16  | 9.03    |

Pure calcium oxide particles are compact spherical particles. The size of pure calcium oxide particles is small and the aggregation degree between particles is large. The macroscopic average pore diameter is 0.78 microns. Sludge, as the adhesion carrier of calcium oxide particles, greatly improves the porosity of calcium oxide [7], which increases the average pore diameter of the sludge base sulfur fixation agent by 11.5 times. In addition to autocatalysis, the loose lattice structure formed at high temperature [8] increased the average pore diameter of the sludge-based desulfurizer particles with iron oxide by 2.3%, and the increase of interparticle aperture can reduce the diffusion resistance of SO$_2$ gas and improve the efficiency of sulfur fixation.

3.2. **Performance of sulfur fixation in tube furnace**

In this experiment, L$_{16}$ ($4^5$) orthogonal experiment [9] was selected to study the influence degree of each factor and to select the best matching combination.

The experimental factors change as follows: the furnace temperature is A1 ~ A4 is 800, 850, 900, 950°C respectively; the concentration of SO$_2$ B1 ~ B4 is 1.0, 1.5, 2.0, 2.5% respectively, Ca/S ratio C1 ~ C4 is 1.0, 1.5, 2.0, 2.5 respectively; particle diameter D1 ~ D4 is 0.30 ~ 0.425, 0.425 ~ 0.60, 0.60 ~ 0.85, 0.85 ~ 2.0mm respectively; water content is 15, 20, 25, 30% respectively. Table 4 lists the results of orthogonal experiments. The sulfur fixation rates are all higher than 46.37%, and the maximum is 56.70%. The best condition is combustion temperature 950°C, SO$_2$ concentration 1.0%, Ca/S=2.5, particle size 0.60-0.85mm, and moisture content 30%. Perform range analysis on the data in figure 4, the range of temperature, SO$_2$ concentration, Ca/S ratio, particle diameter and water content were 7.03, 0.50, 2.82, 1.26 and 0.22, respectively. The results showed that the combustion temperature and the ratio of calcium to sulfur had the greatest influence on the effect of sulfur fixation, followed by the particle size of desulfurizer, the concentration of SO$_2$ had little influence on the effect of sulfur fixation, and the moisture content of desulfurizer had the least influence.
Table 4. Experimental plan and results $L_{16}(4^5)$

| Number | Group               | Sulfur capturing ratio(%) |
|--------|---------------------|---------------------------|
| 1      | A_1B_1C_1D_1E_1     | 46.37                     |
| 2      | A_1B_2C_2D_2E_2     | 47.53                     |
| 3      | A_1B_3C_3D_3E_3     | 49.48                     |
| 4      | A_1B_2C_2D_2E_4     | 49.97                     |
| 5      | A_2B_1C_1D_1E_4     | 52.11                     |
| 6      | A_2B_2C_2D_2E_3     | 51.08                     |
| 7      | A_2B_2C_2D_2E_2     | 52.78                     |
| 8      | A_2B_2C_2D_2E_1     | 52.86                     |
| 9      | A_1B_2C_3D_4E_4     | 56.24                     |
| 10     | A_1B_1C_2D_3E_4     | 56.25                     |
| 11     | A_1B_1C_2D_3E_3     | 53.24                     |
| 12     | A_1B_2C_3D_3E_3     | 52.84                     |
| 13     | A_1B_2C_2D_4E_3     | 56.70                     |
| 14     | A_1B_2C_2D_4E_4     | 55.64                     |
| 15     | A_1B_2C_2D_4E_3     | 55.38                     |
| 16     | A_1B_2C_2D_3E_2     | 53.75                     |

3.3. Analysis of factors affecting sulfur fixation efficiency

In order to understand the influence degree of each factor on the sulfur fixation rate of the sludge-based desulfurizer, the influence of each factor on the sulfur fixation rate was studied at the working temperature of 900 ℃, SO$_2$ concentration of 1.5%, calcium sulfur ratio of 1.5, water content of 25%, particle size of 0.6~0.85mm, as shown in figure 3.

Figure 3 shows that the moisture content of sulfur fixation agent and the SO$_2$ inlet concentration in flue gas have little influence on the sulfur fixation efficiency. When the SO$_2$ concentration drops from 2.5% to 1.0%, the sulfur fixation efficiency only decreases by 0.5%. The particle size of sulfur fixation agent decreased from 0.85 ~ 2 mm to 0.425 ~ 0.6 mm, and the sulfur fixation rate increased significantly. After further decrease, the change of the sulfur fixation rate slowed down. The temperature inside the furnace and the ratio of calcium to sulfur have a great influence on the rate of sulfur fixation. When the temperature inside the furnace exceeds 900 ℃ and the ratio of calcium to sulfur exceeds 2.0, the change of the efficiency of sulfur fixation is significantly reduced. In conclusion, the optimal parameters were 900 ℃, 1.5% SO$_2$ concentration, 1.5 Ca/S ratio, 25% water content and 0.6-0.85mm particle size.

![Figure 3. Factors affecting the rate of sulfur fixation.](image-url)
3.4. Optimum additive

Desulfurization additive has the function of surface activity and catalytic oxidation, which can promote the direct reaction of $\text{SO}_2$, accelerate the dissolution of $\text{CaCO}_3$, promote the rapid oxidation of $\text{CaSO}_3$ into $\text{CaSO}_4$, strengthen the precipitation of $\text{CaSO}_4$, increase the activity of desulfurizer, and improve the sulfur fixation rate [10]. The relationship between addition ratio and sulfur fixation rate is shown in Figure 4.

As can be seen in Figure 4, the effect of adding iron oxide is the most significant. When the addition ratio of iron oxide and acetic acid is increased, the sulfur fixation rate increases linearly. When the addition ratio of sodium carbonate is at 4%, the sulfur fixation rate is the largest. Figure 5 shows the comparison of the sulfur fixation effect between the sludge-based desulfurizer with iron oxide, sodium carbonate, and acetic acid at the optimal ratio and the pure calcium oxide and the sludge-based desulfurizer without additives.

**Figure 4.** Effect of additive types and addition ratio on sulfur fixation rate.

**Figure 5.** Comparison of sulfur fixation rates of different desulfurizers.
Figure 5 shows that the sulfur fixation rate of the sludge-based desulfurizer with additives is higher than that of the sludge-based desulfurizer without additives. Iron oxide is the best additive for the sludge-based desulfurizer, and 6% is the best proportion of iron oxide. The lowest sulfur fixation rate is pure calcium oxide, only 49.96%.

4. Conclusion
The optimum preparation conditions of sludge-based desulfurizer were 0.425~0.6mm particle size, 30% water content and 6% iron oxide addition ratio. The optimum condition of sulfur fixation in furnace was 900°C, SO$_2$ concentration 1%, Ca/S=2.0. The sulfur fixation rate reached 61.86%, which was 23.8% higher than that of pure calcium oxide.

Compared with pure calcium oxide, the porosity and specific surface area of the sludge-based desulfurizer were increased by 0.68 and 5.3 times, respectively. The more contact with SO$_2$, the less diffusion resistance of SO$_2$ gas in the pores of the sulfur fixation agent, making the effect of sulfur fixation in the furnace of the sludge-based desulfurizer better than that of pure calcium oxide.

According to range analysis, the order of influence of various factors on sulfur fixation efficiency is as follows: temperature in the furnace> the ratio of calcium to sulfur> desulfurizer particle size>the concentration of SO$_2$> the moisture content.

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