Properties of Semi-dry Flue Gas Desulfurization Ash and Used for Phosphorus Removal

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Abstract: The composition of Semi-dry Flue Gas Desulfurization ash was as follows: CaSO₃·0.5H₂O and Ca(OH)₂. Most of the particle size was about 8 µm; particles were irregular and small, while the other part was rough and globular. CaSO₃ strongly oxidized at about 466 ℃ and Ca(OH)₂ decomposed at ~ 662 ℃. The maximum amount of phosphorus removal in Semi-dry Flue Gas Desulfurization ash was 79.898 mg/g.

1. Introduction

Buring coal to generate energy releases SO₂ caused acid rain and accelerated soil acidification. In order to reduce the impact of SO₂, many efforts have been made over the past years. Flue gas desulfurization technologies were usually classified as either wet or dry methods[1-2]. The semi-dry FGD process used lime as sorbent was the most used FGD technology in powder and thermal industry.[3] There were 43 million tons FGD gypsum produced in 2010 (China Association Environment Protection industry)[4]. T Zaremba[5] reported the semi-dry adsorption process offered many advantages such as no waste water, straightforward operation, no or little reheating, low space requirements and lower investment, however the product had a complicated composition with higher content of CaSO₃, which affected the comprehensive utilization of flue gas desulfurization ash. The dry and semi-dry flue gas desulfurization were rich in a large number of active substances and activated substances, consists of CaSO₃, CaSO₄, CaCO₃, CaF₂ and fly ash, which had great potential application value in the field of building materials. Liming Chen al. reported that it was safe to grow plants in soil treated with CaSO₃ if the application was made at least three days to several weeks before planting[6]. The CaSO₃ could rapidly oxidize to gypsum in oxygenated environments[7]. Gypsum could improve the physical and chemical properties of soils and mitigating subsoil acidity and Al toxicity[8].

The FGD contained a large amount of hydroxyl ions, which could be used as heavy metal ions removal agent, such as Cu(II), Fe(III), Pb(II), Cd(II). Yubo Yan al.[8] reported that the FGD gypsum generated from coal-fired power plants to adsorptively removed Pb(II) and Cd(II) from wastewater. The kinetic analysis displayed that the adsorption processes both followed the pseudo-second order model well, and the FGD gypsum provided a higher
sorption rate for Pb(Ⅱ). The maximum adsorption capacities of Pb(Ⅱ) and Cd(Ⅱ) were respectively calculated as 161.3 and 32.57 mg/g[9], which could compete with some other synthesized adsorbents. Phosphorus was a key factor of eutrophication and it could affect the people's production and life[10-11]. Research on an efficient method for removal phosphorus was meaningful to improve the economic and social benefit. MTG Viana [12] modified the solar coral powder as adsorbent and the amount of phosphorus removal was 9.597 mg/g. C Han[13] took the slag as adsorbent and the amount of phosphorus removal was reached 89.9 mg/g. The Semi-dry contained a large number of Ca(OH)₂ and CaCO₃, all of which had good precipitation ability for phosphorus. It was a new attempt to use Semi-dry FGD for the phosphorus removal. The utility model not only reduced the waste and protected the environment, but also facilitated the reutilization of waste materials.

2. Properties of Semi-dry Flue Gas Desulfurization Ash

2.1 Properties of Semi-dry FGD ash. A variety of analytical methods were used to obtain semi-dry FGD composition and properties. The chemical composition and content of the substance were determined by ARL-9800 X-ray fluorescence spectrometer (XRF). X-ray diffraction (XRD) patterns were recorded by the Rigaku SmartLab (made in Japan) with the powdered samples less than 30 μm, with Cu Kα radiation in the diffracton angle (2θ) range of 10-90° at a sweep rate of 10°/min⁻¹ (λ=0.154 nm, Voltage=40 KV, I=20 mA). The morphology of Semi-dry FGD before and after reaction was observed by scanning electronic microscope (JSM-6390A 15KV) and the size parameter was measured by Laser particle sizer (Mastersizer 2000) though wet measurement. The differential thermal and thermogravimetric analysis was carried out by means of a DTG-60H type derivatograph within the range of temperatures 20-1000°C under air atmosphere.

Fig. 1 was the X-ray diffraction diagram of semi-dry FGD and Table 1 was the chemical compositions of it. It consisted of Ca(OH)₂, CaCO₃, CaSO₃·0.5H₂O, CaSO₄. The main chemical composition of semi-dry FGD were CaO and SO₃. The sum of both was over seventy percent. Fig. 3 showed that the size distribution ranged from 1 to 30 μm. Most of the particles size were about 8 μm and it contained small amounts of larger particles. Table 2 was specific parameters of each particle diameter.

| Table 1 Chemical compositions of semi-dry FGD ash w% |
| SiO₂ | Al₂O₃ | Fe₂O₃ | CaO       | MgO       | SO₃       | LOI       |
|------|------|------|-----------|-----------|-----------|-----------|
| 0.465| 0.207| 0.985| 48.77     | 1.05      | 21.65     | 20.96     |

| Table 2 Size parameter of Semi-dry FGD |
| Parameter        | Semi-dry FGD ash | Obscuration (%) | Uniformity Span | Dispersant |
|------------------|------------------|-----------------|-----------------|------------|
| D₁₀/μm           | 3.038            | 15.05           | 2.41            | 9.465      | Water     |
| D[4,3]/μm        | 8.796            |                 |                 |            |           |
| D[3,2]/μm        | 1.864            |                 |                 |            |           |
| D₅₀*/μm          | 0.955            |                 |                 |            |           |
| D₅₈*/μm          | 1.445            |                 |                 |            |           |
| D₇₅*/μm          | 7.586            |                 |                 |            |           |
| D₈₄*/μm          | 17.378           |                 |                 |            |           |
| D₉₀*/μm          | 30.200           |                 |                 |            |           |
Fig. 3 was the TG-DTA of the semi-dry FGD. There were three endothermic peaks (351°C, 414°C, 662°C) and one exothermic peak (466°C) in the DTA curve. The endothermic peaks at 351 and 414 degrees centigrade were accompanied by obvious mass loss due to the loss of adsorbed water and the CaSO₃·0.5H₂O lost its crystalline water. The DTA curve showed a sharp exothermic peak at 466 °C and it was accompanied by an apparent in mass increase due to the CaSO₃ was oxidized. The DTA curve appeared an endothermic peak at 662 °C, and there was obvious mass loss due to the decomposition of Ca(OH)₂ in the sample.
2.2 Removal of phosphorus by Semi-dry FGD. The precipitation of calcium and phosphorus was carried out in two steps. The first was the generation of Amorphous Calcium Phosphate (ACP), then the hydroxyapatite (HAP) crystallization.

ACP: \[ 3\text{Ca}^{2+}2\text{PO}_4^{3-}+x\text{H}_2\text{O} \rightarrow \text{Ca}_3(\text{PO}_4)_2\cdot x\text{H}_2\text{O} \]

\[ \text{Ca}_3(\text{PO}_4)_2\cdot x\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+}2\text{PO}_4^{3-}+x\text{H}_2\text{O} \]

HAP: \[ \text{Ca}_3(\text{PO}_4)_2\cdot x\text{H}_2\text{O}+2\text{Ca}^{2+}+\text{PO}_4^{3-}+\text{OH}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH}+x\text{H}_2\text{O} \]

Phosphorus concentration in wastewater was determined with molybdenum blue spectrophotometer method; Potassium dihydrogen phosphate (KDP) was used to simulate the phosphorus-containing wastewater, the initial phosphorus concentration 50 mg/L and the volume was 80 mL. All experiments were performed in 100 mL glass beakers and set the single variable (initial pH; add quantity; temperature; time). The linear regression equation was Y = 1.95488X + 0.00859, the R-Square = 0.9999. Absorbance was measured by using 752 UV-Vis spectrophotometer. Fig. 5 was the curve of phosphorus concentration-absorbance. Phosphorus concentration was obtained by the curve of Phosphorus concentration-absorbance.

\[ \text{P Elimination} = \frac{C_0-C_1}{C_0} \]  \hspace{1cm} (1)

Where \( C_1 \) represented the phosphorus concentration of wastewater solution and \( C_0 \) represented the initial concentration.

![Figure 5 The curve of phosphorus concentration-absorbance](image)

3. Results and discussions

Fig. 2 was the XRD of the reaction product. The reaction product was \( \text{Ca}_4(\text{PO}_4)_2\text{OH} \). Although the side effect consumed \( \text{Ca}^{2+} \), the resulting \( \text{CaCO}_3 \) could be used as a weight agent to aid precipitation. L Montastruc [14] reported that the reaction pKs was 58.33 at 25°C.

Main reaction: \[ 5\text{Ca}^{2+}+7\text{OH}^-+3\text{HPO}_4^{2-} \rightarrow \text{Ca}_4(\text{PO}_4)_2\text{OH}_4+3\text{H}_2\text{O} \]

Side reaction: \[ 5\text{Ca}^{2+}+\text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \]

According to Fig. 8, the amount of Semi-dry FGD was 0.05 g and the pH was 6. When the reaction time was 12 h, the phosphorus concentration was 0.099 mg/L. The optimum phosphorus removal time was 12 h. The P Elimination was 79.898 mg/g. According to Fig. 7, temperature had little effect on phosphorus removal efficiency. The P Elimination ranged from 79.479-79.898 mg/g when the pH was 6 and temperature was 45°C. Fig. 8 showed that the pH and Semi-dry FGD addition on phosphorus had great influence on the efficiency of phosphorus removal. When the pH was 2, the amount of phosphorus removal ranged from
The range of phosphorus removal was 70.458-79.898 m/g when initial pH ranged from 2-10. The optimum phosphorus removal pH was 6. Excessive acid and alkali were not conductive to the efficient removal of phosphorus.

Figure 6 The time of phosphorus removal

Figure 7 The temperature of phosphorus removal

Figure 8 The concentration of phosphorus removal

Fig.9-Fig.10 was the scanning electron microscopy (SEM) photos of Semi-dry FGD. Some
particles were irregular and small, while the other part was rough globular. There were many holes in it. This was due to the formation of the Semi-dry FGD difficult to produced liquid phase when the gas-solid reaction happened at the high temperature. Although it could produce obvious diffusion of solid phase, it would not form strong densification, which would make its surface structure loose and porous. Fig. 11-Fig. 13 was the scanning electron microscopy (SEM) photos of phosphorus removal product. The particles were loosely spherical and larger pores. There were many small protrusions are formed on the surface of the particles.

Figure 9 SEM of Semi-dry FGD ash
Figure 10 SEM of Semi-dry FGD ash

Figure 11 SEM of Semi-dry FGD ash
Figure 12 SEM of P removal product

Figure 13 SEM of P removal product
4. Summary

Semi-dry FGD consists of Ca(OH)\(_2\), CaCO\(_3\), CaSO\(_3\)·0.5H\(_2\)O, CaSO\(_4\) and the main chemical content was CaO and SO\(_3\). The particles size were about 8 \(\mu\)m and particles were irregularly spherical, the surface was and the structure was loose. CaSO\(_3\) was strongly oxidized about 466 \(^\circ\)C and Ca(OH)\(_2\) was decomposed at about 662 \(^\circ\)C. The optimum phosphorus removal time was 12 h and the pH was 2. Temperature had little influence on phosphorus removal efficiency and the main influenced factors of phosphorus removal efficiency were initial pH, Semi-dry FGD addition. The maximum amount of phosphorus removal was 79.898 mg/g.

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