Investigation on the relationship between the fine particle emission and crystallization characteristics of gypsum during wet flue gas desulfurization process

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ABSTRACT

The relationship between the fine particles emitted after desulfurization and gypsum crystals in the desulfurization slurry was investigated, and the crystallization characteristics varying with the operation parameters and compositions of the desulfurization slurry were discussed. The results showed that the fine particles generated during the desulfurization process were closely related to the crystal characteristics in the desulfurization slurry by comparison of their morphology and elements. With the higher proportion of fine crystals in the desulfurization slurry, the number concentration of fine particles after desulfurization was increased and their particle sizes were smaller, indicating that the optimization of gypsum crystallization was beneficial for the reduction of the fine particle emission. The lower pH value and an optimal temperature of the desulfurization slurry were beneficial to restrain the generation of fine crystals in the desulfurization slurry. In addition, the higher concentrations of the Fe³⁺ ions and the F⁻ ions in the desulfurization slurry both promoted the generation of fine crystals with corresponding change of the morphology and the effect of the Fe³⁺ ions was more obvious. With the application of the desulfurization synergist additive, it was beneficial for the inhibition of fine crystals while the thinner crystals were generated.

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Introduction

In an attempt to control SO₂ emission, various flue gas desulfurization processes are adopted in the coal-fired power plants, and the limestone-gypsum wet flue gas desulfurization (WFGD) is one of the most widely used technology due to a high SO₂ removal efficiency, whereas the problem of fine particle emission is addressed, which leads to the reduced visibility of the flue gas and the haze formation (Yang et al., 2011; Baccini et al., 2011; Tao et al., 2014).

During the desulfurization process, the particles were partly eliminated from the flue gas via the desulfurization slurry scrubbing while the fine particle concentration might be increased after desulfurization. For instance, the spot measurements (Nielsen et al., 2002) on the limestone-gypsum desulfurization process was made and found that the particle removal efficiency was 50%–80%, while the submicron particle concentration was increased by 20%–100%. For the particle emissions from coal-fired power plants (Wang et al., 2008a,b; Zhou et al., 2013), similar results were illustrated that the concentrations of coarse particles were reduced while the fine particles were increased after desulfurization, indicating the formation of fine particles during the desulfurization process. Besides, the current investigations

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preliminarily revealed that particles of the unreacted CaCO₃ and CaSO₃·2H₂O were found after desulfurization (Meij and Winkel, 2004; Bao et al., 2009; Yan et al., 2011; Saarnio et al., 2014). Therefore, in order to reduce the formation of fine particles during the desulfurization process, investigations were required to clarify the relationship between the fine particles emitted after desulfurization and the crystals in the desulfurization slurry, as well as the crystallization characteristics of gypsum in the desulfurization slurry. During the limestone-gypsum desulfurization process, the nucleation and the growth of gypsum crystals were determined by various parameters. Baebier et al. (2009) analyzed the gypsum crystallization and the crystal growth kinetics via the chemical neutralization with the limestone and the industrial effluent containing sulfuric acid. In addition, the effects of the temperature and the metal ions on the gypsum crystallization were investigated via the reaction between the calcium chloride solution and the sulfate solution (Hamdona and Hadad, 2007; Gao et al., 2008; Peng et al., 2010; Xu et al., 2010; Thomas and George, 2013), which had obvious difference with the actual desulfurization process. Brian et al. (Hansen and Kiil, 2012) studied the particle size distribution and morphology of gypsum crystals formed in a pilot-scale experimental setup, while the investigations were aimed at the gypsum dewatering properties. Furthermore, in order to achieve a higher SO₂ removal efficiency, desulfurization synergist was added into the desulfurization slurry to promote the SO₂ mass transfer and the limestone dissolution (Kikkawa et al., 2003; Nimmo et al., 2005; Wang et al., 2008a,b; Peng et al., 2011, 2015). However, the effect of desulfurization synergist on the gypsum crystallization was barely investigated. Therefore, the relationship between the fine particles emitted after desulfurization and the gypsum crystals in the desulfurization slurry was required further verified and there was a lack of information on the crystallization characteristics of gypsum during the desulfurization process.

In this study, an experimental system was set up to simulate the limestone-gypsum WFGD process, and the investigations on the relationship between the fine particles emitted after desulfurization and the crystals in the desulfurization slurry were carried out. In addition, the effects of the operation parameters and desulfurization slurry compositions on gypsum crystallization characteristics were also discussed.

1. Experimental details
1.1. Experimental

The investigations were carried out with an experimental system, which is outlined in Fig. 1. The simulated flue gas with volume flux up to 15 Nm³/hr was heated to be 120°C before entering the spray scrubber, in which the flue gas and the desulfurization slurry maintained a countercurrent. The three-level scrubber with a demister at the top was made up of the polycarbonate pipes and plates with excellent heat resistance. The diameter and the height of the scrubber were 72 and 2500 mm, respectively. Gypsum from a coal-fired power plant was used to prepare the desulfurization slurry, whose temperature was maintained by means of the electric-heated thermostat water bath during the desulfurization process and limestone slurry was added into the desulfurization slurry to ensure constant pH value.

1.2. Measurement

The laser particle size analyzer (9300ST, Bettersize Instruments Ltd., China) was used for the measurement of size distribution of particles with the sizes ranging from 0.1 to 1000 μm. The concentration and size distribution of particles with the sizes ranging from 0.023 to 9.314 μm were measured in real time by means of an electrical low pressure impactor (ELPI, Dekati Ltd., Finland). The sample gas stream was withdrawn from the main gas stream and routed through a cyclone to a dilutor before it went into the ELPI, which had 13 stages (12 channels). The cyclone separated the particles with the aerodynamic diameters larger than 9.314 μm and the dilutor diluted the gas with the particle-free dry air (150°C, dilution ratio 8.18:1). In addition, the aerosol mass spectrometry (AMS, Aerodyne, USA) was used to measure the size distribution of the particle components with the sizes ranging from 0.04 to 1.0 μm. Particles emitted after desulfurization were collected by the aluminum film on the impact plate of the PM2.5/10 impactor (Dekati Ltd., Finland). Then the morphology and element analysis were carried out using a Zeiss Ultra Plus scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) detector system. Besides, the SO₂ concentration in the flue gas was measured by flue gas analyzer (J2KN Pro, Ecom Ltd. Germany). Liquid droplets after desulfurization were collected by the droplet catcher (Duohatu Ltd., China) designed by the national standard.
2. Results and discussion

2.1. Morphology and elements of fine particles after desulfurization and crystals in the desulfurization slurry

The experiments were conducted at inlet SO2 concentration to be 2857 mg/m³ and a liquid–gas ratio to be 15 L/m³. Fig. 2 illustrates the size distribution of fine particle components measured by AMS, indicating that the fine particles generated during the desulfurization process were mainly sulfate and their sizes were primarily in the submicron range with a peak value at 0.2 μm. In an attempt to clarify the relationship between the fine particles generated during the desulfurization process and the crystals in the desulfurization slurry, the morphology and elements of them were analyzed with results shown in Figs. 3 and 4. As can be seen from Fig. 3a, crystals in the desulfurization slurry were mainly in the shapes of clithemiform and prismatic. The clithemiform crystals displayed regular cuboid with a length of 50–100 μm and a thickness around 10 μm, while the prismatic crystals were vimeineous with a width less than 10 μm. Besides, some irregular crystals with the sizes ranging from 1 to 20 μm were scattered onto them. By comparison, the morphology of fine particles after desulfurization (Fig. 4a), was analogous to those in the desulfurization slurry while their sizes were mainly in the submicron range and the prismatic particles were turned into the major components. The diameters of particles with prismatic shape were less than 0.5 μm whereas those with clithemiform shape were larger ranging from 0.2 μm to 1 μm with the widths less than 0.1 μm. Moreover, as indicated in Fig. 3b, the main elements of the crystals were O, Ca, S, C, whose proportions were 52.11%, 19.06%, 15.28% and 7.45%, respectively. The EDS analysis of fine particles after desulfurization was also carried out, as illustrated in Fig. 4b. By contrast, the proportions were turned into 46.66%, 13.27%, 18.20% and 7.4%, respectively, indicating that the mass ratio of Ca and S was decreased from 1.25 to 0.73, as well as the contents of C and O, which might be attributed to the reactions between SO2 and CaCO3 during the desulfurization process, leading to the higher proportion of sulfate in the particles. In addition, according to the desulfurization process, the sprayed droplets of desulfurization slurry containing crystals would partly escape from the capture of the demister with the flue gas, resulting in the emission of fine particles after desulfurization. Therefore, it could be attributed to the lower particle removal efficiency of the demister. Meanwhile, as can be seen from Fig. 6b, c, with the higher proportion of fine crystals in the desulfurization slurry, the fine particle number concentration was increased from 1.18 × 10⁷ to 1.25 × 10⁷ cm⁻³ and the peak value of the fine particle size distribution was shifted to the smaller end, indicating that more smaller particles were emitted out of the desulfurization scrubber. As the concentration and the size distribution of fine particles in the entrained droplets were related to those in the desulfurization slurry, the fine particle concentration in the droplets out of the scrubber was correspondingly increased with higher proportion of fine crystals in the desulfurization slurry. As a consequence, more fine particles were emitted after desulfurization when the desulfurization slurry with higher fine crystal proportion was used.

2.2. Relationship between size distributions of crystals in the desulfurization slurry and the fine particle emission

The desulfurization slurries from two different power plants were used to investigate the relationship between size distributions of crystals in the desulfurization slurry and the fine particle emission with the experimental system. The crystal size distributions in the desulfurization slurries, as demonstrated in Fig. 5, reflected a significant difference and smaller crystals were generated in the power plant 2. The proportion of fine crystals in the desulfurization slurry from the power plant 2 was 4.8%, almost 65% higher than that of the ones from the power plant 1, which was 2.9%. As a consequence, the corresponding median diameters of the crystals were 26.85 and 38.22 μm, respectively. With the experimental system, the fine particle emissions after desulfurization with different desulfurization slurries were measured by ELPI as shown in Fig. 6. The experiments were conducted at the SO2 concentration to be 1800 ± 20 mg/m³. The solid content percentages of the entrained droplets after desulfurization and the desulfurization slurry were measured with results in Fig. 6a, which ranged from 30% to 40%. The value was obviously higher with the desulfurization slurry from the power plant 2, indicating that droplets of more particles were emitted out of the desulfurization scrubber with smaller crystals in the desulfurization slurry, which could be attributed to the lower particle removal efficiency of the demister. Meanwhile, as can be seen from Fig. 6b, c, with the higher proportion of fine crystals in the desulfurization slurry, the fine particle number concentration was increased from 1.18 × 10⁷ to 1.25 × 10⁷ cm⁻³ and the peak value of the fine particle size distribution was shifted to the smaller end, indicating that more smaller particles were emitted out of the desulfurization scrubber. As the concentration and the size distribution of fine particles in the entrained droplets were related to those in the desulfurization slurry, the fine particle concentration in the droplets out of the scrubber was correspondingly increased with higher proportion of fine crystals in the desulfurization slurry. As a consequence, more fine particles were emitted after desulfurization when the desulfurization slurry with higher fine crystal proportion was used. Therefore, it was feasible to reduce the fine particle emission via the optimization of gypsum crystallization to inhibit the generation of fine crystals in the desulfurization slurry.

2.3. Effects of the operation parameters and compositions of the desulfurization slurry on the crystallization characteristics

Based on the relationship between the fine particles emitted after desulfurization and the gypsum crystals in the desulfurization slurry, distinct correlation was verified, thus it was essential to further investigate the crystallization characteristics of gypsum crystals in the desulfurization slurry. During the desulfurization process, the gypsum was formed via the combination of SO4²⁻ ions and Ca²⁺ ions according to Reaction (1). When the desulfurization slurry was supersaturated, as expressed mathematically by Eq. (2), the solid crystals...
of gypsum were nucleated and grown, which were greatly influenced by the operation parameters and compositions of the desulfurization slurry in the slurry during the desulfurization process.

\[
\text{CaCO}_3 + \text{SO}_2 + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2
\]  

(1)

\[
S = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} \cdot a_{\text{H}_2\text{O}}^2}{K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}}
\]  

(2)

where \( S \) is the saturation ratio, and \( a \) and \( K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} \) are activity and solubility product of gypsum, respectively.

2.3.1. pH value of the desulfurization slurry

The pH value of the desulfurization slurry was an important parameter during the desulfurization process, which generally ranged from 5.5 to 6.5. Accordingly, the crystal size distributions in the desulfurization slurry were investigated with the experimental system when the pH values were controlled at 5.5 ± 0.1 and 6.5 ± 0.1, respectively. The results are demonstrated in Fig. 7. With a higher pH value, the limestone solubility was restricted, resulting in the lower \( \text{Ca}^{2+} \) concentration in the desulfurization slurry. However, it was beneficial for the \( \text{SO}_2 \) absorption due to the enhanced gas–liquid mass transfer which had greater impact on the ion concentrations. After the forced oxidation in the crystallization tank, the \( \text{Ca}^{2+} \) and \( \text{SO}_4^{2-} \) concentrations were increased correspondingly, resulting in a higher degree of supersaturation. As a consequence, when the pH value was increased, the nucleation was promoted and more fine crystals were generated, leading to the decrease of the overall particle size.

2.3.2. Desulfurization slurry temperature

The particle size distributions in the desulfurization slurry were investigated at various temperatures which were controlled by means of the thermostatic water bath with results demonstrated in Fig. 8. The temperatures were set at 35°C, 45°C and 52°C, respectively. They all revealed bimodal distributions whose peaks occurred at the sizes of 1 and 30 \( \mu \text{m} \). With the increase of the temperature, the particle median diameter depicted an increase from 17.44 to 25.13 \( \mu \text{m} \) and a following decrease turned into 19.93 \( \mu \text{m} \), which was contrary to the cumulative content of fine particles to be 11.23%, 5.34% and 9.57%, respectively, indicating that there was an optimal temperature for the crystal growth. With the increase of the desulfurization slurry temperature, the viscosity and the surface tension of the desulfurization slurry was decreased, which were beneficial for the ion diffusion, leading to the increase of the \( \text{CaSO}_4 \) solubility. Accordingly, the lower supersaturation degree was achieved, and it depressed the nucleation and increased the growth rate. Conversely, when the temperature exceeded a critical temperature, the reverse effect occurred and the high degree of supersaturation led to the higher nucleation rate and lower crystal growth rate. In addition, the impact between the
crystals was enhanced via the increase of the temperature, which gave rise to the crystal breakage. Correspondingly, the decrease of particle size distribution in the desulfurization slurry was addressed.

2.3.3. Compositions in the desulfurization slurry
With the fly ash and desulfurization mineral into the WFGD system, different metal ions, and halogens were accumulated in the desulfurization slurry. In addition, in order for higher SO₂ removal efficiency, the desulfurization synergist was used during the desulfurization process. Their presence not only influenced agglomeration or dispersion behavior but predominantly altered the nucleation, size distribution and morphology. Correspondingly, the effects of desulfurization slurry compositions on the particle size distributions and morphologies were investigated as Fe³⁺ ions, F⁻ ions and desulfurization synergist called TL-02 were added into the desulfurization slurry, respectively.

The particle size distributions in the desulfurization slurry with different additives at different ratios compared with the baseline (without impurity) were demonstrated in Fig. 9, which all showed the crystals in the absence of additives provided the
largest median diameters. As can be seen in Fig. 9a, the crystals shifted to a uniform distribution in the presence of Fe$^{3+}$, and an obvious increase of submicron particle percentage was observed when the Fe$^{3+}$ concentration was at 0.02 mol·L$^{-1}$.

Meanwhile, the results showed in Fig. 9b depicted an obvious shift to the smaller end with the increase of F$^{-}$ concentrations. By comparison, the inhibiting effect of F$^{-}$ ions on the fine crystal generations was much weaker. In addition, the desulfurization synergist was used in the experiments, which improved the CaCO$_3$ solubility and promoted the SO$_2$ absorption, leading to the increase of SO$_2$ removal efficiency from 90.1% to 92.5%. The particle size distribution, as demonstrated in Fig. 9c, had an overall decrease. The median diameter decreased to be 20.17 μm after adding the desulfurization synergist, while the cumulative content was decreased to be 1.09% from 5.06%, indicating that the formation of fine crystal nucleus and the crystal growth both were inhibited.

The structural characteristics for products were studied with the corresponding results in Fig. 10. According to Fig. 10a, crystals in the desulfurization slurry without any additives were mainly prismatic with a length of up to 20 μm–50 μm and a width of 5 μm–15 μm, while fine crystals located at their rough surfaces, which might be attributed to heterogeneous chemical reactions between gaseous phase and liquid phase during the flue gas desulfurization process. By comparison with the initial particles in the desulfurization, the particle morphology with additives showed significant distinctions. Fig. 10b illustrates the crystal morphology with Fe$^{3+}$ additive which clearly revealed similar prismatic particles with smaller size and numerous particles with size ranging from 2 to 5 μm were generated. Due to the presence of Fe$^{3+}$, the saturability of CaSO$_4$ was decreased correspondingly with the lower activity coefficient. Meanwhile, the accumulation of metal ions on the crystal surface led to the increase of the liquid–solid surface tension, resulting in
the decrease of the crystal growth rate. As a consequence, the gypsum crystallization was retarded, especially for the long axis direction. As can be seen in Fig. 10c, thinner crystals were generated in the presence of the $F^-$ ions and lots of fine crystals occurred on their surfaces. As the complex compounds were formed via the reactions between the $F^-$ ions and the $Al^{3+}$ ions from the limestone, the limestone dissolution was inhibited when they were absorbed onto the particles, leading to the formation of smaller crystals. Fig. 10d illustrates the particle morphology with desulfurization synergist additive and it depicted tabular crystals with smooth surfaces which might be caused by the influence of the surface active agent in the desulfurization synergist, resulting in the decreased crystal nucleation rate and the inhibition of the growth in the short axis direction.

In conclusion, the higher concentrations of the $Fe^{3+}$ ions and the $F^-$ ions in the desulfurization slurry both promoted the generation of fine crystals with corresponding change of the morphology and the effect of the $Fe^{3+}$ ions was more obvious. With the application of the desulfurization synergist additive, it was beneficial for the inhibition of fine crystals while the thinner crystals were generated. In an attempt to reduce the fine particle emission after desulfurization, the concentrations of different compositions in the desulfurization slurry were required control, especially for the $Fe^{3+}$ ions.

3. Conclusions

The relationship between the fine particle emission after desulfurization and the crystals in the desulfurization slurry was investigated, and the effects of the operation parameters and desulfurization slurry compositions on gypsum crystallization characteristics were also discussed. The conclusions were drawn from the results as follows.

(1) The fine particles generated during the desulfurization process were closely related to the crystal characteristics in the desulfurization slurry by comparison of their morphology and elements.

(2) With the higher proportion of fine crystals in the desulfurization slurry, the number concentration of fine particles after desulfurization was increased and smaller particles were generated, indicating that the optimization of gypsum crystallization was beneficial for the reduction of the fine particle emission.

(3) The lower pH value and an optimal temperature of the desulfurization slurry were beneficial to restrain the generation of fine crystals in the desulfurization slurry. In addition, the higher concentrations of the $Fe^{3+}$ ions and the $F^-$ ions in the desulfurization slurry both promoted the generation of fine crystals with corresponding change of the morphology and the effect of
the Fe$^{3+}$ ions was more obvious. With the application of the desulfurization synergist additive, it was beneficial for the inhibition of fine crystals while the thinner crystals were generated.

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