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JES JOURNAL OF ENVIRONMENTAL SCIENCES

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

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ARTICLE INFO

Article history:
Received 28 June 2016
Revised 8 August 2016
Accepted 19 August 2016
Available online 4 October 2016

Keywords:
Wet flue gas desulfurization
Fine particle
Gypsum crystallization
Emission

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 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.

Introduction

In an attempt to control SO_2 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 SO_2 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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http://dx.doi.org/10.1016/j.jes.2016.08.020

preliminarily revealed that particles of the unreacted $CaCO_3$ and $CaSO_4{\cdot}2H_2O$ 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 SO_2 removal efficiency, desulfurization synergist was added into the desulfurization slurry to promote the SO_2 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 Nm^3/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

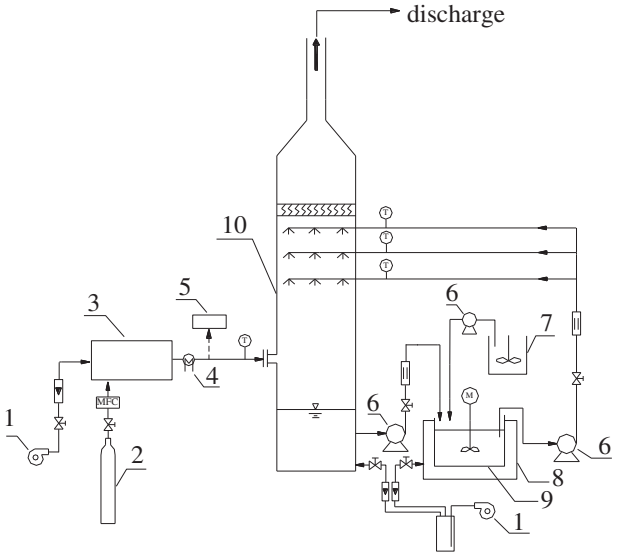

Fig. 1 – Schematic diagram of experimental system. (1) air blower; (2) SO_2; (3) mixer; (4) heater; (5) gas analyzer; (6) pump; (7) limestone slurry tank; (8) electric-hearted thermostatic water bath; (9) crystallization tank; (10) spray tower.

desulfurization slurry, whose temperature was maintained by means of the electric-heated thermostatic 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 $PM_{2.5/10}$ 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 SO_2 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.