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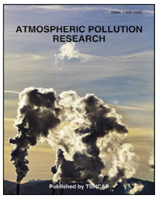

Original article

A model for performance of sulfite oxidation of ammonia-based flue gas desulfurization system

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ABSTRACT

A mathematical model was developed to simulate the oxidation of total sulfite in the holding tank of ammonia-based flue gas desulfurization (FGD) system. The model could provide predictions of the oxidation ratio of total sulfite at different operating condition such as pH, concentration of total sulfur, air flow and residence time. The calculation results of an ammonia-based FGD system for 2 × 150 MW boilers by this model were compared to that of corresponding measured values. The comparison results show that the simulated oxidation ratio of total sulfite agrees well with the measured data. The difference between calculated values and measured data is below 4.2%. This model appears to be beneficial for optimizing design and operation of total sulfite oxidation of an ammonia-based FGD system.

1. Introduction

Sulfur dioxide (SO_2) is a main atmospheric pollutant from combustion of fossil fuel, which has been a major environmental concern because of its hazardous effects on human health and ecosystems (Zhong et al., 2008; Sun et al., 2010; Valle-Zermeño et al., 2014). Accordingly, the flue gas should be treated before being discharging into atmosphere. Among various flue gas desulfurization technologies, the ammonia-based desulfurization process is attractive as it results in an efficient removal of SO_2 and the production of valuable ammonium sulfate without generating any other polluting by-products (He et al., 2003; Gao et al., 2010; Jia et al., 2013). In the ammonia-based desulfurization system, SO_2 is absorbed in a wet scrubber and the most common wet scrubber is the countercurrent spray scrubber on the bottom of which a holding tank for sulfite oxidation (Pisu et al., 2004). Due to the thermal instability of ammonium sulfite, oxidation of ammonium sulfite into ammonium sulfate efficiently and economically is crucial to enhance the commercial competitive power for ammonia-based desulfurization technique (Zhou et al., 2000; Long et al., 2006; Wang and Zhao, 2008).

The oxidation of ammonium sulfite has been received much attention in the recent decades (Zhou et al., 2000; Long et al., 2006; Wang and Zhao, 2008; Mishra and Srivastava, 1975; Neelakantan and Gehlawat, 1980; Ahamd et al., 1987; Gǔrkan et al., 1992; Bengtsson and Bjerle, 1975; Linek and Vacek, 1981). However, most of these previous investigations did not take the changes of ionic strength in the process of adjusting the pH and the oxidation of ammonium bisulfite into account. Moreover, in these previous investigations, the pH of solution (Zhou:5.0–8.0, Ahamd:7.6–8.5, Gǔrkan:7.0–8.0, etc.) was significantly different from that in ammonia-based wet flue gas desulfurization (FGD) plants (Zhou et al., 2000; Ahamd et al., 1987; Gǔrkan et al., 1992). Accordingly, a systematic study of the kinetics of oxidation of total sulfite ($SO_2(aq)$, $(NH_4)_2SO_3$ and NH_4HSO_3) was conducted under operating conditions relevant to ammonia-based wet FGD plants in our previous investigation. The rate expression for the oxidation of total sulfite, including the operating parameters SO_3^{2-} concentration, SO_4^{2-} concentration, pH, temperature and air flow, had also been developed (Jia et al., 2010). In the ammonia-based desulfurization system, the total sulfite is oxidized in the holding tank by bubbling air. The oxidation ratio of total sulfite is mainly depended on operating parameters pH, concentration of total sulfur, air flow and residence time, etc. Usually, the oxidation of total sulfite is performed empirically in ammonia-based desulfurization plants,

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which could result in a waste of energy and cost (Wang and Zhao, 2008). However, there is no theoretical model reported in the literature is available for the performance of total sulfite oxidation in ammonia-based desulfurization system. On the basis of our previous investigation, the present work was undertaken to develop a mathematical model to simulate the process of oxidation of total sulfite in the holding tank.

2. Mathematical model

2.1. Assumptions

In the holding tank, the total sulfite is oxidized by bubbling air, thus allowing the formation of a by-product ammonium sulfate. The physical and chemical process in the holding tank include some complex factors such as the distribution of sulfite concentration, bubble size distribution and heat exchange, etc. It is difficult to describe all the processes in the holding tank by mathematical model. Therefore, some assumptions were made as below (Zhong et al., 2008):

a. The slurry in the holding tank is considered to be totally mixed and the concentration of total sulfite is well-distributed.
b. The chemical equilibrium and ionic equilibrium in the holding tank are considered to be an instantaneous process.
c. The pH value is a constant in the process of oxidation of total sulfite.
d. Both bubble diameters and the temperature in the holding tank are evenly distributed.

2.2. Model

In the spray scrubber, the flue gas flow upwards and contact slurry drops sprayed from nozzles counter currently to remove the SO_2, according to the following reactions:

$$2NH_3 + SO_2 + H_2O \rightleftharpoons (NH_4)_2SO_3 \tag{1}$$

$$(NH_4)_2SO_3 + SO_2 + H_2O \rightleftharpoons 2NH_4HSO_3 \tag{2}$$

$$NH_4HSO_3 + NH_3 \rightleftharpoons (NH_4)_2SO_3 \tag{3}$$

The slurry drops fall down to the holding tank after absorbing SO_2 in the spray zone. Then the total sulfite formed in the slurry is oxidized to sulfate by bubbling air in the holding tank. Corresponding oxidation reactions are as follows:

$$(NH_4)_2SO_3 + 1/2O_2 \rightarrow (NH_4)_2SO_4 \tag{4}$$

$$NH_4HSO_3 + 1/2O_2 \rightarrow NH_4HSO_4 \tag{5}$$

The diagrammatic sketch of the holding tank is shown in Fig. 1. In order to keep the solution density within a certain range, parts of the slurry in the holding tank is discharged to produce ammonium sulfate. Most of the slurry in the holding tank is injected into spray zone again by recirculation pumps.

The steady-state slurry flow balance equation of the holding tank could be expressed as follows:

$$Q_{in} = Q_{out} + Q_{re} \tag{6}$$

The flow of slurry discharged to produce ammonium sulfate is determined by Eq. (7):

$$Q_{out}(C_{S^{4+}} + C_{S^{6+}}) = M_{SO_2} \tag{7}$$

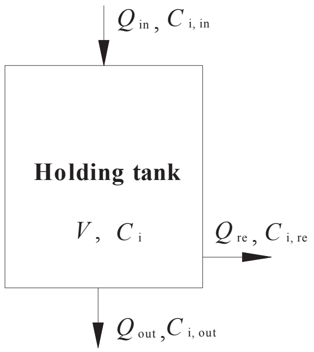

Fig. 1. Diagrammatic sketch of the holding tank.

The integral mass balance on number of moles of ions in holding tank can be expressed as Eq. (8):

$$\frac{dC_i}{dt} = (N_i + r_{react})/V \tag{8}$$

Where:

$$N_i = Q_{in}C_{i,in} - Q_{re}C_{i,re} - Q_{out}C_{i,out} \tag{9}$$

The generation rate of ions in Eq. (8) is achieved by Eq. (10):

$$r_{react} = r_{(IV)}V \tag{10}$$

Accordingly, the cumulative rate of sulfite and sulfate in the holding tank can be determined separately as Eqs.11 and 12:

$$\frac{d\left(C_{SO_3^{2-}} + C_{HSO_3^-} + C_{H_2SO_3}\right)}{dt} = \left(N_{SO_3^{2-}} + N_{HSO_3^-} + N_{H_2SO_3} - r_{(IV)}V\right)\Big/V \tag{11}$$

$$\frac{dC_{SO_4^{2-}}}{dt} = \left(N_{SO_4^{2-}} + r_{(IV)}V\right)\Big/V \tag{12}$$

The oxidation rate of total sulfite $r_{(IV)}$ is defined by Jia et al. (2010):

$$r_{(IV)} = C^*_{O_2}\Bigg/\left(\frac{1}{k_La} + \frac{1}{k_0\exp\left(\frac{-2.8\times10^4}{RT}\right)}\cdot\frac{1}{10^{-0.39pH-1.14}}\cdot\frac{1}{C_{SO_3^{2-}}^{-0.5}}\cdot\frac{1}{-4C_{SO_4^{2-}}+9}\right) \tag{13}$$

The interfacial concentration of oxygen could be calculated by Eq. (14) (Thomas et al., 2003; Ueyama and Hatanka, 1982; Zhu, 2012):

$$C^*_{O_2} = Hp^*_{O_2} \tag{14}$$

In Eq. (14), the solubility coefficient of O_2 in solution H is determined as Eq. (15):

$$\log\left(\frac{H^0}{H}\right) = h_1I_1 + h_2I_2 + \cdots + h_iI_i + \cdots \tag{15}$$

Where:

$$h_i = h^+ + h^- + h_G \tag{16}$$