Effect of calcium formate as an additive on desulfurization in power plants

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ARTICLE INFO

Article history:
Received 29 November 2016
Revised 7 June 2017
Accepted 16 June 2017
Available online 28 June 2017

Keywords:
Calcium formate
Desulfurization
Lime-gypsum process
Additive
Power plant

ABSTRACT

SO₂ in flue gas needs to be eliminated to alleviate air pollution. As the quality of coal decreases and environmental standard requirements become more stringent, the high-efficiency desulfurization of flue gas faces more and more challenges. As an economical and environmentally friendly solution, the effect of calcium formate as an additive on desulfurization efficiency in the wet flue gas desulfurization (WFGD) process was studied for the first time. Improvement of the desulfurization efficiency was achieved with limited change in pH after calcium formate was added into the reactor, and it was found to work better than other additives tested. The positive effects were further verified in a power plant, which showed that adding calcium formate could promote the dissolution of calcium carbonate, accelerate the growth of gypsum crystals and improve the efficiency of desulfurization. Thus, calcium formate was proved to be an effective additive and can potentially be used to reduce the amount of limestone slurry required, as well as the energy consumption and operating costs in industrial desulfurization.

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Introduction

With the increasingly rapid development of the global economy, air pollution has become more and more serious due to the increase of annual energy consumption worldwide in recent years. Especially in developing countries, air pollution has increased along with urbanization and industrialization (Kan et al., 2009; Leung, 2015; Wang et al., 2016; Zheng et al., 2011). In recent years, serious smog pollution in China – a weather phenomenon featuring a high concentration of fine particles in the air, which leads to visibility loss (less than 10,000 m at a relative humidity (RH) lower than 90%) – has greatly hindered people’s outdoor activities and also poses severe potential harm to human health (Kampa and Castanas, 2008; Shen, 2015; Tan et al., 2009; Zhuang et al., 2014).

Clean energy and renewable energy can alleviate energy shortages and pollution, but renewable energy resources such as solar, wind and biomass energy are still under exploration and have not yet been put into large-scale use, while fossil fuels like petroleum, natural gas and coal are still the main energy sources (Forsberg, 2009; Simons, 2005). In the power plants of China, coal is widely used due to its relatively low price and abundant reserves (Hadjipaschalis et al., 2009). However, sulfur compounds in coal will inevitably generate a large amount of pollutants during combustion. One of the main types of air pollutants is sulfur oxides (SOₓ), which are generated when sulfur compounds react with oxygen. In

http://dx.doi.org/10.1016/j.jes.2017.06.023
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China, the pollution caused by emission of SO₂ is one of the main barriers to the efficient use of coal (Guan et al., 2003). In practice, power plants are the main sources of SO₂, which is a major cause of acid rain around the world (Lu et al., 2010; Mohanty et al., 2009; Ohara et al., 2007; Shen et al., 1991; Zhao et al., 2008). Therefore, to alleviate air pollution, flue gas needs to be desulfurized before emission. Many kinds of desulfurization technologies such as the wet process, dry process, semi-dry process, biological method and electronic method have been applied to solve the problem (Hansen and Kiil, 2012; Lin et al., 2015; Mo et al., 2007; Wang et al., 2013; Zhang et al., 2006). Among them, wet desulfurization technology is used most widely on account of its highly operational stability, high efficiency and long experience. Limestone/lime is widely applied in the wet flue gas desulfurization (FGD) process due to its relatively low price (Heidel et al., 2014; Ren et al., 2010). However, with the increased stringency of environmental standards and the gradual decrease of coal quality (Ito and Rob van Veen, 2006; Liu et al., 2005; Lin et al., 2011; Mortaheb et al., 2012; Tewalt et al., 2005), the desulfurization apparatus for coal gas is confronted with more and more challenges. An economical solution is to use additives which can effectively improve the desulfurization efficiency. According to Ren et al. (2010), a good additive in the limestone/lime FGD process can reduce the dissolution resistance of the absorbent and improve the desulfurization efficiency (Heidel et al., 2014). Therefore, to alleviate air pollution, flue gas needs to be desulfurized before emission. Many kinds of desulfurization technologies such as the wet process, dry process, semi-dry process, biological method and electronic method have been applied to solve the problem (Hansen and Kiil, 2012; Lin et al., 2015; Mo et al., 2007; Wang et al., 2013; Zhang et al., 2006). Among them, wet desulfurization technology is used most widely on account of its highly operational stability, high efficiency and long experience. Limestone/lime is widely applied in the wet flue gas desulfurization (FGD) process due to its relatively low price (Heidel et al., 2014; Ren et al., 2010). However, with the increased stringency of environmental standards and the gradual decrease of coal quality (Ito and Rob van Veen, 2006; Liu et al., 2005; Lin et al., 2011; Mortaheb et al., 2012; Tewalt et al., 2005), the desulfurization apparatus for coal gas is confronted with more and more challenges. An economical solution is to use additives which can effectively increase the mass transfer coefficient of the liquid phase and the pH buffer capacity between the gas–liquid interface, thus improving desulfurization efficiency (Heidel et al., 2014). According to Ren et al. (2010), a good additive in the limestone/lime FGD process can improve the absorbent reactivity, reduce the dissolution resistance of the absorbent or diffusion resistance of SO₂ and keep the pH value of the desulfurization slurry more stable. Desulfurization additives can be classified into organic additives or inorganic ones according to their different mechanisms. The organic additives mainly include acids such as benzoic acid, adipic acid, formic acid, acetic acid and citric acid, which have a buffering effect (Dong et al., 2004a; Kong et al., 2001; Wu et al., 2003); the inorganic additives are mainly sodium salts, ammonium salts and magnesium compounds (Dong et al., 2004b; Sun et al., 2001, 2002a, 2002b, 2002c). The organic additives are widely used in power plants due to their ability to buffer the pH and improve the growth of gypsum crystals, which can thus significantly increase desulfurization efficiency. However, formic acid and acetic acid are liquid phase additives with a relatively high volatility at room temperature, for which the transportation costs have greatly increased, while the solid phase additives such as benzoic acid and adipic acid are very expensive, and their limited pH buffer capacity can significantly affect the pH value in a desulfurization system and even lead to the pH getting out of control. Furthermore, the production and usage of organic acids generate a large amount of effluents that pollute the surrounding soil and water. Also, some of these additives have the side-effect of irritating the skin, mucosa, and eyes, etc. In addition, if the organic additives carried out with gypsum in the desulfurization system are not handled in time and with care, they may cause water and soil pollution that harm many kinds of plants and even animals that eat the contaminated plants. Calcium formate, which is widely used with livestock, the chemical industry, environmental protection and construction, is a common additive for feed, chemicals, construction and tanneries (Antipov and Aleshin, 2002; Blinova et al., 2005; Chernoplekov, 2001). It is not only easier to transport as a solid phase than formic acid, but also cheaper than adipic acid. To the best of our knowledge, calcium formate has not been used as a desulfurization additive so far, though many other kinds of calcium compounds such as calcium chloride and calcium nitrate have been studied (Jørgensen et al., 1986). Thus, the potential for using calcium formate as a desulfurization additive in power plants is worthy of investigation.

In this work, the effect of calcium formate as an additive on desulfurization was investigated in a stirred tank. The limestone requirement and pH value of the lime-gypsum slurry were determined after different amounts of calcium formate were added. In addition, the mechanism for the desulfurization efficiency improvement with calcium formate was investigated in depth and the results were verified in an industrial power plant.

1. Materials and methods

1.1. Materials

Sulfur dioxide (SO₂, high purity, purity of 99.999%) was purchased from Tianjin Liufang Industrial Gases Co., Ltd., Tianjin, China; Calcium carbonate, adipic acid, citric acid and formic acid (AR, ≥99.0%) were purchased from Tianjin Guang Fu Fine Chemical Research Institute, Tianjin, China; Calcium formate (AR, ≥99.0%) for the laboratory tests was purchased from Real & Lead Chemical Co., Ltd., Tianjin, China. The calcium formate (mass fraction purity ≥98.0%) for the industrial scale test was purchased from Zibo Ruibao Chemical Co., Ltd., Shandong, China, and used as an additive in the power plant. They were all used without further treatment.

1.2. Desulfurization efficiency measurement

The experiment aiming to study the effect of calcium formate as additive on desulfurization was conducted in a 60 mm diameter × 1000 mm tall packed tower (as shown in Fig. 1) at 50°C. The experiment was conducted under the following conditions: the flue gas flow rate was 15 m³/hr with SO₂ concentration of 2200 mg/m³ in air, the liquid–gas ratio was

![Fig. 1 – Absorptive desulfurization apparatus.](link)
3.0 L/m³, the gypsum slurry contained 1 wt.% CaCO₃, and the initial pH of the slurry was 5.0. The lime-gypsum slurry with different concentrations of calcium formate was added in a pulp tank, then was pumped to the top of the tower and distributed to increase the interfacial area of mass transfer; the pH values of the slurry were recorded by a PHS-3C pH meter (PHS-3C, Shanghai INESA Scientific Instrument Co., Ltd., China). The SO₂ concentrations of inlet and outlet gases were analyzed on-line by a Testo 350 flue gas analyzer (Testo 350, Testo Instruments International Trading Co., Ltd., China). The desulfurization efficiency (De.) was calculated by the following equation:

$$\text{De.}(\%) = \frac{c(SO_2)_{\text{in}} - c(SO_2)_{\text{out}}}{c(SO_2)_{\text{in}}}$$

where \(c\) is the mass concentration of SO₂ in gas, mg/m³.

1.3. Power plant verification

The conditions of the industrial desulfurization process in a power plant are much more complicated than that in a laboratory. To check whether the results in a power plant were in accordance with the results in the laboratory, the desulfurization efficiency of the lime-gypsum slurry with calcium formate additive was evaluated in a system including two circular sections (as shown in Fig. 2). The first one mainly pretreats flue gas and oxidizes calcium sulfite to gypsum at pH value of 4.5–5.2, temperature of 50–60°C; the second one mainly removes SO₂ from flue gas to the desired purity at pH value of 5.8–6.4, temperature of 50–60°C. The experiment was conducted at a limestone slurry spray flow rate of 14.1 m³/hr, flue gas flow rate of \(1.0 \times 10^6\) m³/hr (under standard conditions), circulating liquid–gas ratio of 20 L/m³ and various concentrations of calcium formate.

2. Results and discussion

2.1. Effect of calcium formate concentrations on desulfurization efficiency

The desulfurization efficiency at different calcium formate concentrations is presented in Fig. 3. The results indicated that the desulfurization efficiency was improved by adding calcium formate, and the efficiency was further enhanced by increasing the concentration of calcium formate. After calcium formate was added into the slurry, the Ca²⁺ concentration in the liquid phase was increased, which accelerated the formation of CaSO₄. In addition, the acidity of the liquid phase was increased, which promoted the dissolution of CaCO₃ in the slurry. As reported by Ma et al. (Heikal, 2004; Ma et al.,

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Fig. 2 – Double cycle wet desulfurization process. AFT: absorber feed tank.

Fig. 3 – Desulfurization efficiency at different calcium formate concentrations. t: time; De.: desulfurization efficiency.
2013; Singh and Abha, 1983), calcium formate acted as an accelerator for the hydration of calcium salts and could promote the formation of CaSO₄, accelerate the growth of gypsum crystals and then facilitate their separation from the slurry. So, adding calcium formate enhanced the reactivity of the limestone slurry absorbent and then improved the utilization rate of the absorbent.

2.2. Effect of calcium formate concentrations on pH value of lime-gypsum slurry

The pH value affects many aspects of the operation of a desulfurization system. On one hand, a relatively high pH value contributes to the dissolution of SO₂ so that the dissolution rate of SO₂ at pH 6 is about 5–10 times as high as that at pH 4; on the other hand, a relatively low pH value is helpful for limestone dissolution. In practice, the appropriate pH value in the absorption liquid in desulfurization tower is between 4 and 6, which also leads to high oxygenation efficiency for SO₃²⁻.

The pH value of the lime-gypsum slurry at different calcium formate concentrations is shown in Fig. 4. It was clear that the pH value of the lime-gypsum slurry showed a slight decline, and the decline trend became more evident with increasing calcium formate concentration. This was because calcium formate could accelerate the migration of SO₂ from gas to liquid. This migration speed increased with increasing concentrations of calcium formate in the slurry, resulting in the increase of the SO₂ concentration in the liquid phase. The decline of pH can be attributed to the increasing SO₂ concentration in the liquid phase. On the other hand, the limited decline in pH was because calcium formate could facilitate the absorption of SO₂ in the liquid film and kept the concentration of SO₂ in the liquid phase relatively stable, which made the pH value in the system controllable. Moreover, the decline of pH helped to accelerate the oxidation from CaSO₃ to CaSO₄ and the dissolution of CaCO₃. As reported by Zhou (2005), sulfite in the slurry was oxidized very fast at pH 4.5–5.0, in accord with the improvement of desulfurization efficiency.

2.3. Comparison of calcium formate with other additives

The effects of different kinds of additives on desulfurization efficiency were studied at 1000 ppm of each additive, and the results are shown in Fig. 5. As shown in Fig. 5, the desulfurization efficiency of calcium formate was higher than that of formic and adipic acids, while it was lower than that of citric acid. Given that the price of calcium formate is lower than citric acid, it is reasonable to infer that using calcium formate as an additive is economical and has good potential to improve the desulfurization efficiency and reduce SOₓ emission in power plants.

2.4. Verification results in a power plant

The results showing the effect of calcium formate as an additive on the desulfurization efficiency of the wet lime-gypsum process in a power plant are shown in Figs. 6–8. Fig. 6 shows the effect of calcium formate concentration on desulfurization efficiency for different concentrations of SO₂. It was clear that for the SO₂ concentration of 2500 mg/m³, the average concentration of SO₂ in the outlet gas declined from 47.2 to 14.9 and 12.7 mg/m³, and the average desulfurization efficiency rose from 98.05% without calcium formate to 99.48% at calcium formate concentrations of 500 and 1000 ppm. At a SO₂ concentration of 3500 mg/m³, the average concentration of SO₂ in the outlet gas declined from 78.8 to 68.0 and 46.5 mg/m³, and the average desulfurization efficiency rose from 97.83% to 98.08% and 98.78% at calcium formate concentrations of 500 and 1000 ppm, respectively. Clearly, the addition of calcium formate significantly improved the desulfurization efficiency in the power plant. As reported by Liu and Xiao (2006), too much SO₂ in fuel gas could lead to obstruction and instability of the desulfurization system. Fig. 7 shows that the pH value in the absorption tower at different concentrations of calcium formate was almost the same as the pH value without addition of calcium formate, which demonstrated that the pH was still under control with the addition of calcium formate, and no negative influences were found in the system of the industrial power plant. In accordance with the results in Fig. 4, this can
further illustrate that even though the SO₂ concentration in the liquid phase was increased, the absorption tower in the desulfurization system had the ability for self-restoration by changing the dissolution rate of CaCO₃ and the separation rate of CaSO₄. Fig. 8 shows the amount of limestone required to obtain the same desulfurization efficiency at different concentrations of calcium formate along with the variation of the inlet concentration of SO₂. It was clear that the amount of calcium carbonate needed to obtain the same desulfurization efficiency was decreased with increasing concentrations of calcium formate. At the SO₂ inlet concentration of 3500 mg/m³, the limestone amount required was reduced by 4%–9%. Therefore, adding calcium formate can promote the dissolution of calcium carbonate and maintain a relatively high desulfurization efficiency at a low limestone amount. Since the amount of calcium carbonate slurry consumed in a power plant is directly related to the economic benefit, the addition of the calcium formate is beneficial for the power plant.

3. Conclusions

The effect of calcium formate as an additive on desulfurization efficiency improvement was investigated both at laboratory scale and at industrial scale. The results indicated that the addition of calcium formate in the lime-gypsum slurry could not only promote the dissolution of calcium carbonate, the formation of CaSO₄ and the growth of gypsum crystals, but also accelerate the migration velocity of SO₂ from gas phase to liquid phase and the absorption rate of SO₂ in the liquid film. As a result, a significant improvement in desulfurization efficiency was observed after calcium formate was added. The degree of increase was larger than 1% at the inlet gas SO₂ concentration of 2500 mg/m³ and nearly 1% at the inlet gas SO₂ concentration of 3500 mg/m³ in the power plant. The amount of limestone slurry needed to maintain the same desulfurization efficiency could be reduced. Thus, the energy consumption in a desulfurization system using calcium formate will be reduced significantly, as will the operating costs. All these findings demonstrated that calcium formate could be used as an additive to enhance the desulfurization efficiency in power plants.

Acknowledgments

This work was supported by the Hi-Tech Research and Development Program (863) of China (No. 2012AA06A113).
The authors are thankful to Beijing Guodian Longyuan Environmental Engineering Co., Ltd. (Chengde branch) for providing necessary help and facilities for testing the desulfurization efficiency of calcium formate in their power plant. Special thanks to Mr. Guangjie Lu and Dr. Jianhui Yang from Beijing Guodian Longyuan Environmental Engineering Co., Ltd. for participating in the on-site desulfurization efficiency test with us.

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