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

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A B S T R A C T

SO_2 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.

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 (SO_x), which are generated when sulfur compounds react with oxygen. In

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China, the pollution caused by emission of SO_x 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 SO_x, 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 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 Heidel et al. (2014) and 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 SO_2, 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 (Jorgensen 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 (SO_2, 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 m^3/hr with SO_2 concentration of 2200 mg/m^3 in air, the liquid–gas ratio was

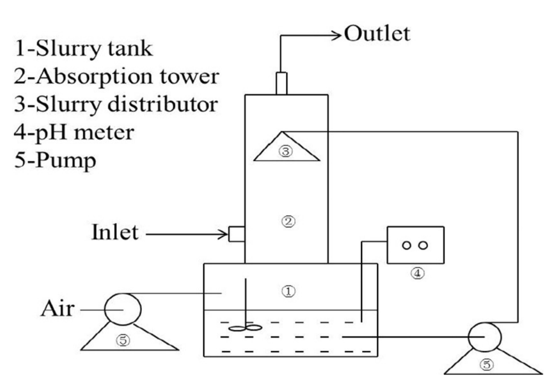

Fig. 1 – Absorptive desulfurization apparatus.

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