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Effects of modified fly ash on mercury adsorption ability in an entrained-flow reactor

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HIGHLIGHTS

- Mercury concentration change rate was suggested for evaluating the adsorption rate.
- Combined Br^- with H^+, the adsorption ability of HBr-modified fly ash was obvious.
- Particle size was an important influential factor in fly ash adsorption.

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ABSTRACT

This study investigated the effectiveness of fly ash modified with halogenated material in absorbing mercury in an entrained-flow reactor. Two different types of fly ash from coal-fired power plants were treated with varying amounts of $CaCl_2$, $CaBr_2$ and HBr. The first derivative of the Hg removal concentration was explored to help quantify the effectiveness of adsorbents. Characterization studies of the fly ash using SEM and BET indicate that the surface structure of the modified fly ash was altered, and the specific surface area, average pore size and pore volume were all slightly increased. Compared to the unmodified fly ash, both the mercury adsorption efficiency and the mercury concentration change rate in the flue gas improved significantly. The fly ash oxidized by HBr showed the greatest adsorption ability among the three additives. The improvement in the characteristics of the modified fly ash was due to both physical and chemical adsorption. The study also showed that particle size of the fly ash is a significant factor in the removal of mercury from the flue gas. Under experimental conditions, the adsorption efficiencies for the two HBr-modified fly ash (A and B) were 2.4 and 6.7 times greater for >200 mesh than for 80–200 mesh.

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1. Introduction

Coal combustion for electrical production is one of the largest sources of global anthropogenic mercury emissions [1]. A suggested cost-effective strategy for mercury control involves selective manipulation of boiler control settings in combination with other control measures, such as sorbent injections [2]. Although activated carbon is regarded as an effective adsorption material [3,4] in reducing Hg emission in coal-fired flue gas, the mercury capture rate is low and there is tremendous potential for increasing efficiency, as well as, the development of economical non-carbon based sorbents [3–6]. Fly ash from coal-fired power plants can serve as a substitute for activated carbon based on it's abundance, low cost, and convenient location near power plants. The characterization of fly ash, including: microstructure (surface area and pore structure), unburned carbon content, and operational conditions on Hg adsorption have been widely investigated [5,7,8]. Existing research suggests that the addition of halogenated compounds significantly improves the adsorption efficiency of fly ash [7–9]. Modifying fly ash with $CuBr_2$ or $CuCl_2$ showed that both the halogens and Cu^{2+} could be used as an oxidizing agent to facilitate the conversion of elemental mercury (Hg^0) into oxidized mercury (Hg^{2+}) [10]. Cao et al. found that halogens on the surface of fly ash could promote Hg adsorption when HBr and fly ash were simultaneously injected into the flue gas [11].

In the context of industrial power plant technology, the injection of sorbents into the flue gas is currently the most feasible method for removing gaseous Hg. To date, most sorbents have been widely evaluated in lab-scale fixed-bed reactors [4,12]; however, these methods may not reflect the actual two-phase flow characteristics of fly ash and flue gas in a power plant. Therefore,

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adsorption characteristics should be explored under actual flow conditions. Wu et al. evaluated the Hg adsorption efficiency of different fly ash samples in a lab-scale flow bed [13]. Cao et al. studied the synergy of HBr and fly ash for removing Hg in a multiphase flow reactor in order to improve the Hg adsorption behaviors of fly ash and to reduce the adsorption efficiency gap between fly ash and activated carbon [11]. Additionally, their results showed that flue gas residence time was approximately 1.4 s in the reactor. The injection of HBr at a concentration of approximately 4 ppm could oxidize more than 90% of Hg^0 while simultaneously improving the mercury capture efficiency of the fly ash by almost 50%. It is generally accepted that the Hg adsorption efficiency of fly ash is closely related to its surface area. Scala et al. found that augmenting the area between gas and solid could improve the Hg removal efficiency in the flue gas by comparing the results in a fluidized bed reactor and an entrained-flow reactor [14]. Prior studies used qualitative adsorption efficiency to evaluate Hg capture ability in the sorbent injection process based upon experimental conditions and samples. An index characterizing the mercury adsorption rate of the material would be very beneficial [15]. If the adsorption index of a material was very low, the sorbent could not be effectively applied in actual flue gas conditions. However, there is currently no widely accepted adsorption rate index system available [16].

The main goal of this study was to explore the Hg adsorption ability of fly ash in turbulent gas–solid two-phase flow. The mercury concentration change rate was investigated in an entrained-flow reactor. Halogen compounds, such as $CaCl_2$, $CaBr_2$, and HBr, were used to modify the fly ash samples. The effects of chemical reagents and particle size on the mercury adsorption efficiency were investigated.

2. Experiment

2.1. Sample preparation

There are several different procedures for the adsorbent modification including: dry mixing method, precipitation method, impregnation method, and sol–gel method. Of these methods, the impregnation method is the logical choice for large-scale implementation in power plants due to it's simplicity and low cost. Cai et al. modified clays impregnated with KI and KBr. The hydroxyl groups removal efficiency of mercury was significantly enhanced [17]. De et al. modified bio-char impregnated with KCl, KBr, KI, NH_4I and NH_4Br, and the adsorption characteristics in different conditions were analyzed [18]. In this paper, the fly ash was modified using the impregnation method. Two samples of fly ash (A and B) were collected from China-based coal-fired power stations with capacities of 200 MW and 300 MW. $CaCl_2$, $CaBr_2$, and HBr were used to modify the fly ash in order to improve the Hg adsorption ability. Two different particle sizes (80–200 mesh and >200 mesh) were obtained through manual screening. 100 ml of a modifying agent, such as $CaCl_2$, $CaBr_2$, or HBr solution, was mixed with 10 g of the fly ash. The mixture was then placed in a rotary agitator for 12 h and subsequently dried at 115 °C for 12 h. A Micrometrics ASAP 2020 surface analyzer and JEOLJSM 5400-LV scanning electron microscopy (SEM) were used to determine the surface characteristics of the sorbents. Table 1 shows the results of different sorbents under BET analysis.

2.2. Set-up and procedure

A self-designed lab-scale entrained-flow reactor was used to evaluate Hg adsorption ability. The platform consisted primarily of a flue gas generator, an entrained-flow reactor and a flue gas detection device (Fig. 1). The flue gas was generated by using compressed air and an elemental mercury source (PSA CavKit). The entrained-flow reactor was made from stainless steel with an inner diameter of 55 mm and a height of 1.2 m. A screw feeder was used for sorbent metering on the top of the entrained-flow reactor. The feed rate was controlled by adjusting the voltage of a variable-speed motor. Also, a low volume supply of air was provided on top of the feeding system to ensure a constant fly ash feeding rate. In accordance with sedimentary separation mechanisms, the majority of larger fly ash particles in the flue gas fell into the coarse ash vessel from the bottom of the entrained-flow reactor. The smaller particles were collected in the fine ash vessel, located at the bottom of the cyclone separator. The remainder of the fly ash in the flue gas, which was only a small amount, was removed by a fine filter medium, allowing clean flue gas to be discharged into the atmosphere. Acontinuous mercury emission system (PSA Sir Galahad) monitored the Hg content in the flue gas and an Ohio Lumex RA-915$^+$ Hg instrument was used to measure the Hg content in the fly ash samples. The temperature of the Hg elemental generator was set to 40 °C. The flow rate of air through the elemental mercury generator was adjusted between 0 and 20 ml/min, and subsequently diluted with compressed air and then preheated. An electric temperature controller set was used to maintain the entrained-flow reactor at 150 ± 2 °C. The Hg concentration in the flue gas was controlled to approximately 10 ng/L. The residence time of the flue gas in the reactor was between 2 and 5 s, depending on the operational conditions. In order to balance the high-capture ability of the modified fly ash and reasonable operating conditions for the feeding system, background fly ash with low adsorption ability was initially used. In order to decrease the influence of previous experimental processes, the walls of the entrained-flow reactor were cleaned prior to each injection run.

2.3. Evaluation methodology

In order to evaluate the removal characteristics of fly ash for Hg in the flue gas, the following definition of Hg adsorption efficiency was employed [13].

$$\eta = \frac{C_{in} - C_{min}}{C_{in}} \times 100\% \quad (1)$$

where C_{in} is the Hg concentration in the flue gas before the sorbent injection, that is, at the inlet of the reactor (ng/L). C_{min} is the lowest stable Hg concentration after the sorbent injection (ng/L).

Fly ash absorbent characteristics are based on both adsorption efficiency and sorbent injection rate [19]. Generally, the Hg adsorption rate of fly ash refers to the reduction in Hg concentration per unit of time when the fly ash remains in the flue gas for a specified period. Based on the experimental gas flow rates used in this study, the residence time of fly ash was between 2 and 5 s. Theoretically, the Hg adsorption rate of fly ash can easily be obtained as soon as the CEM reaches a new stable value. However, in practice, fly ash particles undergo dispersion, mixing, adsorption and reaction within the entrained-flow reactor when the injection starts. Furthermore, portions of the fly ash injection adhere to the surface of the reactor wall and then continue to adsorb Hg from the flue gas. As a result, the Hg adsorption rate of fly ash is not readily obtainable during the test process.

It is generally accepted that thermogravimetric analysis (TGA) curves indicate sample weight loss characteristics. The derivative thermogravimetric analysis (DTG) curves obtained through TGA curve derivatives can be used to analyze the weight loss rate. In this study, flue gas mercury concentration varied from the initial stable value (C_{in}) to the final end stable value (C_{min}) during the fly ash injection stage, sharing similar characteristics to TGA experiments. The Hg concentration change rate is based on the

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