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Full Length Article

Study on the mercury captured by mechanochemical and bromide surface modification of coal fly ash

Yongsheng Zhang [a,*], Zhensen Zhang [a], Zhao Liu [a], Pauline Norris [b], Wei-ping Pan [a,b]

[a] Key Laboratory of Condition Monitoring and Control for Power Plant Equipment, Ministry of Education, North China Electric Power University, Beijing 102206, China
[b] Institute for Combustion Science and Environmental Technology, Western Kentucky University, Bowling Green, KY 42101, USA

HIGHLIGHTS

- Mercury adsorption was improved by coupled mechanochemical and bromide modification method.
- Mercury capture increased with increased grinding time initially and then stabilized.
- Improvements in mercury capture performance are due to both physical and chemical factors.
- More grinding produces smaller particles and exposes more unburned carbon.

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ABSTRACT

Power plant coal fly ash was modified for mercury adsorption. The fly ash was subjected to mechanochemical ball milling and bromide compounds were added. The results show that mercury capture capacity increased with increasing grinding time, up to 50 min. Grinding over 50 min did not lead to further improvements. Results from the mercury adsorption test show that the mechanochemical processing technique coupled with the addition of bromide compounds improves mercury adsorption performance for fly ash. Both physical and chemical factors contribute to the improvements in capture performance. Increasing the grinding time produced smaller particles with higher surface area. As a result, more unburned carbon was exposed, which resulted in better mercury adsorption. Thermal gravimetric analysis of modified fly ash shows combustion peak temperatures shift towards lower temperatures with increased grinding time. This result indicates that mechanical treatment increased the thermal activity of fly ash. As a result of this study, the first on-line modified fly ash unit was installed on site at a 300 MW coal fired power plant in China.

1. Introduction

Elemental mercury is widely recognized as an environmental hazard [1,2]. Currently, many coal-fired power plants use activated carbon injection as the primary method for mercury removal [3]. Using fly ash in place of activated carbon is an attractive alternative given the cost advantages and the benefits of reusing a waste product. However, mercury adsorption performance for fly ash is relatively poor in comparison to activated carbon [4]. Studies have shown that the mercury adsorption performance can be improved through physical and chemical modification of fly ash. Several techniques for modification of fly ash are available [5]. Chemical modification via the addition of halogens, especially bromide, can significantly increase the mercury adsorption capacity of fly ash [6]. Isometric impregnation and ion exchange can be used to modify fly ash with halogens, however, these techniques are difficult to implement in a large scale industrial setting. The mechanochemical technique, on the other hand, could be applied at a large-scale relatively easily by using large machinery.

Recently, some scholars have used mechanochemical methods to refine raw materials. Stellacci et al. [7] used modified fly ash in the stabilization/solidification treatment of hazardous waste and contaminated soil. The adsorption capacity of coal-derived fly ash was enhanced by mechanochemical activation with a high energy mono-planetary ball mill. Fly ash with high carbon content was mechanochemically activated for 4 h in a nitrogen atmosphere. This material had more favorable adsorption isotherms, improved specific adsorption capacity and faster adsorption rates than powdered activated carbon. Palaniandy et al. [8] reported that ground particles exhibit particle size decreases with increasing grinding time. Crystallite size and lattice strain had little effect

* Corresponding author.
E-mail address: yszhang@ncepu.edu.cn (Y. Zhang).

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on the particles if the grinding time was too short or if the particle size was above submicron range. Silica ground in the oscillating mill had undergone mechanochemical effects although the particle size was not in the submicron range [9,10]. There has been some previous research into mercury adsorption using mechanochemical modified fly ash.

Mechanochemical modification processes often require a long grinding period, sometimes even exceeding 20 h [11]. By itself, this modification technique requires a great deal of energy and is too inconvenient for engineering applications. Therefore, this paper proposes combining mechanochemical and bromide modified methods to improve the mercury adsorption performance. Details on the modification process are provided and the mercury adsorption characteristics of fly ash are investigated and discussed.

2. Experimental

2.1 Fly ash characteristics

The major factors affecting mercury removal efficiency are composition of the fly ash, unburned carbon content, reactivity, and surface area [12]. For this study, the fly ash sample was collected at the outlet of the ESP from a Chinese pulverized coal boiler utilizing bituminous coal.

Unburned carbon, halogens content and major inorganic components of the unmodified fly ash are summarized in Table 1. For the original fly ash selected in this paper, the surface composition included elements such as calcium (Ca), silicon (Si), aluminum (Al), and iron (Fe). Obviously, the content of SiO_2 and Al_2O_3 in fly ash is about 81%, which indicate that the activity is high. Although the unburned carbon, Cl and Br is beneficial to promote the mercury adsorption of fly ash, the concentration of unburned carbon, Cl and Br in the fly ash selected in this study may be relatively low. Therefore, this study results show that the original fly ash is not very good for mercury adsorption.

2.2 Apparatus and methods

Mercury absorption experiments using raw and modified fly ash were conducted in a fixed-bed adsorption apparatus, shown in Fig. 1. Fly ash sorbent was loaded into the fixed-bed reactor via a valve and rotameter. The gas flow rate into the fixed-bed was held at 6 L·min^{-1} and the exhaust gas generated by the process was discharged through the activated carbon barrel to the outside atmosphere. CEM fixed-bed experiments were designed to determine the mercury adsorption capacity of fly ash samples. The system consisted of an Hg^0 permeation source—PSA Cavkit, fixed-bed reactor, and a PSA mercury analyzer (Sir Galahad). This system measured the Hg^0 concentration every 5 min. The Hg^0 permeation source was designed to generate Hg^0 vapor at a desired concentration. The inorganic compositions (Ca, Fe, Al, and Si) of fly ash samples were analyzed by a Leeman Teledyne PRODIGY ICP-AES. Particle size distribution was carried out using a JEOL JSM540-LV scanning electron microscope (SEM). The thermal stability of fly ash samples were conducted by TAI SDT Q600 with Thermostar MS system. A Dionex ICS-1100 IC instrument was used to quantify the bromine content in the solutions [13].

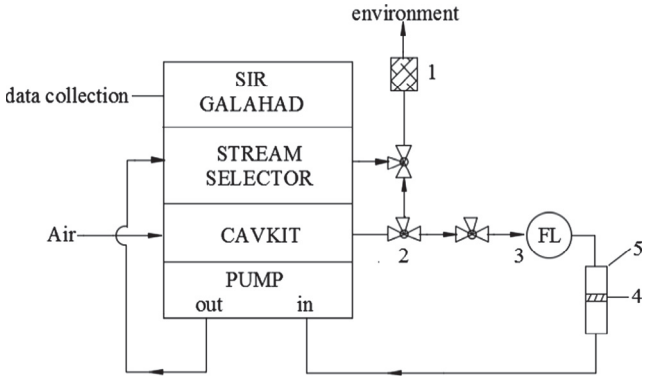

Fig. 1. Fixed-bed adsorption experimental system.

2.3 Modification of fly ash

Parameters such as bromide modifier type and length of grinding time were varied in this experiment. Different modifiers included sodium bromide, ammonium bromide, potassium bromide and calcium bromide. Different grinding times were 0 min (i.e. unground), 10 min, 30 min, 50 min and 4 h. Experimental parameters are provided in Table 2. The fly ash modification process is summarized as follows:

(1) Ten grams of original fly ash was collected and passed through an 80 mesh sieve.
(2) Five ml of deionized water was mixed with 0.1 grams of bromide solid until completely dissolved.
(3) The fly ash and bromide solution mixture was stirred with a glass rod and dried at 115 °C for 6 h.
(4) The fly ash was ground for 0 min, 10 min, 30 min, 50 min or 4 h and then used in the adsorption experiment.

2.4 Evaluation of adsorption performance

In a fixed-bed dynamic adsorption process, the fly ash mercury adsorption rate (dq_t/dt ng·mg^{-1}·min^{-1}), mercury removal efficiency (η %) and cumulative adsorption amount (q_t ng·mg^{-1}) can be estimated by the breakthrough curve at a certain time t (min), which can be regarded as the average of the entire bed [14–16].

The formula:

$$\frac{dq_t}{dt} = \frac{C_{in} - C_{out}}{m} Q \quad (1)$$

$$q_t = \int_0^t \frac{C_{in} - C_{out}}{m} Q dt \quad (2)$$

$$\eta = \left(1 - \frac{C_{out}}{C_{in}}\right) \times 100\% \quad (3)$$

wherein, C_{in} and C_{out} are, respectively, the inlet and outlet Hg^0 concentrations of fixed-bed reactor, μg·m^{-3}; Q is the gas flow inlet rate, L·min^{-1}, and m is the fly ash adsorbent loadings, mg.

Table 1
Unburned carbon, halogens, and major inorganic components of unmodified fly ash (%).

Sample	C	CaO	Fe_2O_3	Al_2O_3	SiO_2	Cl	Br
Unmodified fly ash	5.9	2.8	2.6	31.0	50.1	0.03	0.005