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Mercury adsorption characteristics of HBr-modified fly ash in an entrained-flow reactor

Yongsheng Zhang^{1,*}, Lilin Zhao¹, Ruitao Guo¹, Na Song¹, Jiawei Wang¹, Yan Cao², William Orndorff², Wei-ping Pan¹

1. Key Laboratory of Condition Monitoring and Control for Power Plant Equipment, Ministry of Education, North China Electric Power University, Beijing 102206, China

2. Institute for Combustion Science and Environmental Technology, Western Kentucky University, Bowling Green, KY 42101, USA

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ABSTRACT

In this study, the mercury adsorption characteristics of HBr-modified fly ash in an entrained-flow reactor were investigated through thermal decomposition methods. The results show that the mercury adsorption performance of the HBr-modified fly ash was enhanced significantly. The mercury species adsorbed by unmodified fly ash were HgCl_2 , HgS and HgO . The mercury adsorbed by HBr-modified fly ash, in the entrained-flow reactor, existed in two forms, HgBr_2 and HgO , and the HBr was the dominant factor promoting oxidation of elemental mercury in the entrained-flow reactor. In the current study, the concentration of HgBr_2 and HgO in ash from the fine ash vessel was 4.6 times greater than for ash from the coarse ash vessel. The fine ash had better mercury adsorption performance than coarse ash, which is most likely due to the higher specific surface area and longer residence time.

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Introduction

Mercury and its associated compounds are highly toxic and bioaccumulative, causing great harm to humans and the ecosystem (Macrae et al., 2006). Coal-fired power plants are the largest source of anthropogenic mercury emissions, and widespread usage of effective mercury control measures is imperative (Zhang et al., 2013). Engineered solutions, such as the injection of powdered activated carbon (PAC) sorbent into the flue, were proposed to help reduce mercury in the flue gas (Romero et al., 2006); however, PACs are very expensive and the cost is expected to rise (Hower et al., 2010). Fly ash from coal-fired power plants has been studied as a substitute for PACs due to its abundance and low cost. Studies showed that halogens can facilitate the oxidization of elemental mercury,

and thus promote the adsorption of mercury by the fly ash (Xu et al., 2013; Cao et al., 2009; Zheng et al., 2012). Cao et al. (2007) found that in a comparison of halogen-modified fly ashes, HBr has better adsorption performance compared to HCl.

In sorbent evaluation facilities, the entrained-flow reactor more accurately reflects the injection process and two-phase flow characteristics of the flue gas and fly ash, and hence, more accurately simulates the power plant flue gas adsorption process, as compared to the fixed bed reactor (Zhang et al., 2014). The experimental study in this work was carried out in a lab-scale entrained-flow reactor to better understand the mercury adsorption characteristics of HBr-modified fly ash.

Hower et al. (2010) suggested that the development of efficient mercury capture technology was limited by an understanding of the mechanism of mercury oxidation and subsequent

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

adsorption by fly ash. X-ray absorption spectroscopy (XAS) and X-ray photoelectric spectroscopy (XPS) are techniques that have been employed to determine information about speciation and binding of mercury on sorbents (Li et al., 2012, 2014). Li et al. (2012) used XAFS to determine the species of mercury compounds adsorbed by CuCl_2 - and HCl -modified activated carbon. Their findings suggested HgCl_2 and HgS as the dominant species. In Hutson et al.'s study, the mercury species adsorbed by brominated activated carbon were mainly in the form of HgBr_2 and HgSO_4 (Hutson et al., 2007). On the other hand, because the thermal decomposition temperature of different mercury species is different, mercury species can be identified by a method utilizing a temperature-programmed thermal decomposition setup, as described in the literature. In Rallo et al.'s study, HgS was the most probable Hg species in gypsums from power station A, whereas the main compound was halogenated Hg compounds in gypsums from power station B (Rallo et al., 2010). Temperature-programmed thermal decomposition is a method that is cheap and allows easy identification of the main mercury species as well as quantitative determination of the mercury compounds present in the fly ash. The mercury compounds in the fly ash were identified by this method in this study, and the oxidation and adsorption processes in the entrained-flow reactor were proposed indirectly.

1. Experiment

1.1. Sample preparation

Except for the mercury standards preparation, the fly ash in this study was only dried in an oven at 40°C for 12 hr, without being heated to high temperatures. Dried fly ash from a coal-fired power plant was modified with HBr using the impregnation method. This method involves mixing 100 mL of 1% (W/W) HBr solution with 10 g of fly ash. The mixture was placed in a rotary agitator for 12 hr, dried at 115°C for 12 hr, and then ground with a mortar and pestle. Because high feed rates of modified fly ash can produce significant mercury removal efficiencies (Zhang et al., 2014), and since relatively low injection rates (on the order of 0.5 g/hr) of the modified fly

ash were desired in order to approximate a 2–4 lb/MACF rate (2–4 pounds of adsorbent dispersed per million actual cubic feet of contact volume), it was necessary to dilute the modified fly ash with unmodified ash in the mass ratio of 1:49 (the fly ash is referred to as 1:49 mixed fly ash in this paper).

1.2. Set-up and procedure

A custom built lab-scale entrained-flow reactor was used to evaluate the mercury adsorption ability of the fly ash. The platform consists primarily of a flue gas generator, a reactor, and a mercury monitoring system (Fig. 1); more detailed information is provided in a previous publication (Zhang et al., 2014). Air enriched with elemental mercury was used as the simulated flue gas at a flow rate of 50 L/min and mercury content of $10\text{ }\mu\text{g}/\text{m}^3$. The feed rate of the fly ash mixture was 0.5 g/min. The temperature of the entrained-flow reactor was maintained at 150°C to simulate the air preheater outlet temperature of a power plant. A continuous mercury emission system (Sir Galahad, PSA, UK) monitored the mercury content in the flue gas exiting the system, with data points provided every 5 min. After each experimental run the fly ash was collected and the reactor was cleaned. The majority of the fly ash was collected at the bottom of the reactor from the coarse ash vessel; however a small quantity of fine ash was trapped and collected at the bottom of the cyclone separator in the fine ash vessel.

The collected fly ash was analyzed for mercury using a unique equipment setup. First, a representative fly ash sample (approximately 10 mg) was placed into a temperature-programmed furnace. The sample was heated from 50 to 650°C with a heating rate of $10^\circ\text{C}/\text{min}$. Air flowed through the system at a rate of 100 mL/min, forcing the desorbed mercury into a constant-temperature furnace held at 800°C . At this temperature, it is assumed that all of the different mercury compounds are converted into elemental mercury. Finally the gases flowed through a mercury analyzer (RA-915+, Ohio Lumex, Russia) to provide real-time mercury data. The mercury spectrum produced by the analyzer was combined with the temperature program of the furnace, hence producing the mercury compound decomposition profile.

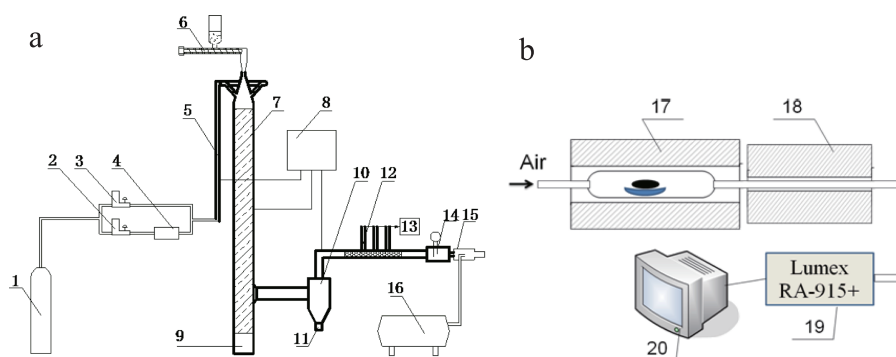


Fig. 1 – Experimental set-up of (a) entrained-flow reactor evaluation platform (Zhang et al., 2014) and (b) unit of mercury species thermal decomposition. (1) Gas cylinder; (2) mass flowmeter 1 (MFC1); (3) MFC2; (4) mercury vapor generator; (5) preheater; (6) screw feeder; (7) simulated flue; (8) temperature controller; (9) coarse ash vessel; (10) cyclone; (11) fine ash vessel; (12) filter; (13) CEM analyzer; (14) venturi flow meter; (15) ejector; (16) compressor; (17) temperature-programmed furnace; (18) constant temperature furnace; (19) Lumex RA-915+; (20) computer.

Deconvolution software Peakfit V4.2 was utilized to analyze spectra with overlapping peaks. The thermal decomposition profiles of mercury substances in the fly ash were obtained from the mercury species thermal decomposition unit, and were the superposition of spectra of all mercury compounds in the fly ash. Using Peakfit software, the peaks of mercury compounds could be separated one by one. Comparing these peaks with the thermal decomposition profiles of standard mercury species, the species and concentrations of the mercury compounds were identified. The software deconvolutes the spectrum based on temperature, area of the peaks, and derivatives. Thus, different mercury species curves were obtained. Then, the mercury compounds in the fly ash were distinguished by comparison with standard mercury species.

1.3. Thermal desorption profile of standard mercury species

Different bonding forces acting on the mercury species during decomposition can significantly alter the decomposition profile. In Lopez-Anton et al.'s study (Lopez-Anton et al., 2011), the peak thermal decomposition temperature of each mercury species shifted more than 20°C when mixed with fly ash and silica powder. In this experiment, fly ash was chosen as a base material for the standards in order to more accurately represent the thermal decomposition characteristics of mercury species within the fly ash matrix. Mercury fly ash standards were prepared by calcining raw fly ash for 1 hr at 650°C in a muffle furnace to ensure the complete volatilization of mercury. For water-soluble HgBr_2 and HgCl_2 , 100 μL of 400 ppm aqueous mercury solution was added dropwise onto 10 g of the calcined fly ash. The water-insoluble mercury compounds of HgS , HgO and HgSO_4 were also added to deionized water respectively, and after sufficient shaking, emulsions with the same concentrations were obtained, then these were added dropwise onto the calcined fly ash. Five different standards, one each for HgBr_2 , HgCl_2 , HgS , HgO , and HgSO_4 , were produced. The mercury fly ash standards were then put into the thermal decomposition experimental unit and the standard thermal decomposition profile for each mercury species was obtained (Fig. 2). In Fig. 2, the profile of HgBr_2 was close to that of HgCl_2 and it was difficult to distinguish them from each other. In order to obtain a more accurate analysis and distinguish HgBr_2 from HgCl_2 , the concentration of Cl and Br of the fly ash samples was measured by ion chromatography (ICS-1100, DIONEX, USA). If the thermal decomposition profile of samples is similar to that of HgBr_2 and HgCl_2 , the components and contents of HgBr_2 or HgCl_2 can be distinguished according to the concentrations of Cl and Br.

2. Results and discussion

2.1. Effect of HBr modification on the mercury compounds on the surface of fly ash

Fig. 3a shows the thermal decomposition profile for mercury compounds in the fly ash (modified with HBr and unmodified) before injection into the entrained-flow reactor. It was readily observed that there was a very significant difference in the thermal decomposition characteristics of mercury compounds

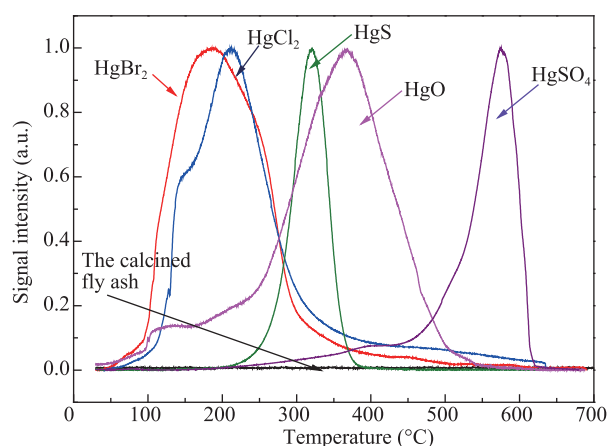


Fig. 2 – Thermal decomposition profiles of standard mercury species.

between the unmodified and HBr-modified fly ash. The mercury concentrations were 780 and 492 ng/g, respectively, for the fly ash before and after modification. This finding illustrates that HBr modification significantly reduced the original mercury content in the fly ash. Fig. 3b shows the thermal decomposition characteristics of the fly ash used in the entrained-flow reactor (fly ash modified with HBr and unmodified at a ratio of 1:49). Comparing the unmodified fly ash in Fig. 3a with the mixed fly ash used for mercury adsorption experiments, as shown in Fig. 3b, indicates that there was no significant difference between the two ashes. This is mainly due to the fact that HBr-modified fly ash was only 2% of the mixture.

Using the standard profiles of Fig. 2 and the Peakfit software, Fig. 4a reveals the different mercury compounds found in the dried fly ash of Fig. 3a. The first peak in Fig. 3a represents HgCl_2 because there is 4.10 ppm Cl in the unmodified fly ash and no Br present. Therefore, the dominant species in the raw dried fly ash are HgCl_2 and HgS with a corresponding mercury content of 537 and 243 ng/g, respectively. During the combustion process in a power plant, when temperatures exceed 800°C, it is assumed that all species of mercury in the coal are converted to the element. Elemental mercury can rapidly react with HCl, Cl_2 , or Cl^- and generate HgCl_2 in the flue gas (Schager, 1990; Hall et al., 1991). At the same time, elemental mercury can also react with sulfur-containing gas, generating HgS . As the temperature decreases in the flue, the HgCl_2 and HgS will be adsorbed by the fly ash (Wu et al., 2006). Thus, here the dominant species in the raw fly ash are HgCl_2 and HgS . The deconvoluted profiles of Fig. 4b suggest that the main mercury species present in the HBr-modified fly ash sample are HgBr_2 , HgS and HgO , with a corresponding mercury content of 157.88, 251.85 and 82.27 ng/g, respectively. The halogen concentration of fly ash samples was measured by ion chromatography; it was found that 9278.73 ppm elemental Br adhered to the HBr-modified fly ash and Cl could be detected. These results illustrate that the first peak of the mercury compound thermal decomposition profile of modified fly ash represents HgBr_2 rather than HgCl_2 . In fact, if the fly ash contains Cl originally, Cl may be dissolved in water during the process of modification, and then be evaporated into the air with water

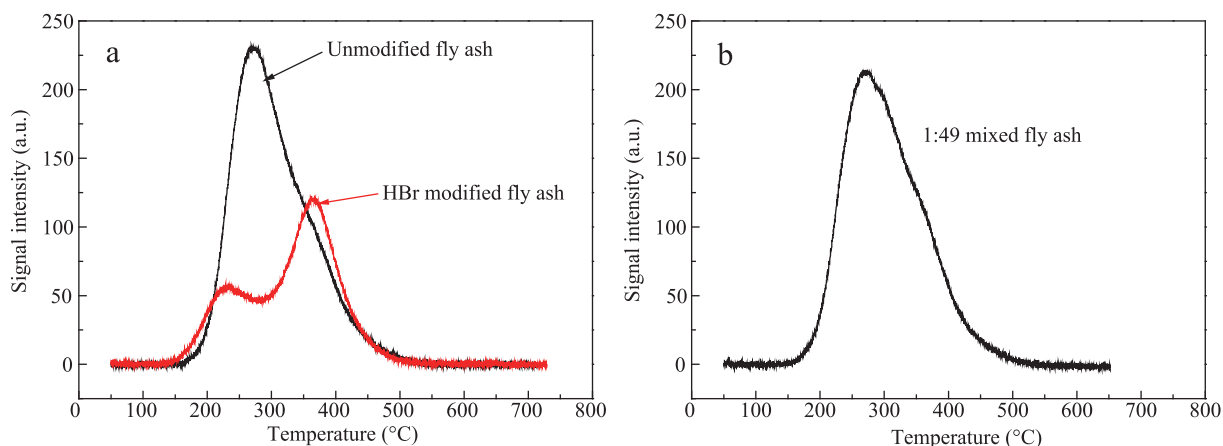


Fig. 3 – Thermal decomposition characteristics of mercury compounds of unmodified and HBr-modified (a) and 1:49 mixed (b) fly ash before injection.

during the drying process, and thus it cannot be retained on the surface of the fly ash.

Fig. 4c shows the change of composition and concentration of mercury for unmodified and HBr-modified fly ash. Comparing these two, it can be found that HBr modification had a negligible effect on the HgS content, but HgCl₂ disappeared, and two new mercury species, HgBr₂ and HgO, were produced. These changes most likely are due to the following reasons: during the modification process, the original fly ash was placed into HBr solution and mixed. The water-soluble HgCl₂ present in the fly ash was extracted with the HBr solution. It can be found that the concentration of Br[−] in the solution was far higher compared to Cl[−] from ion chromatography test results, so the reversible reaction ($\text{HgBr}_2 + 2 \text{Cl}^- \leftrightarrow \text{HgCl}_2 + 2 \text{Br}^-$) will be shifted toward HgBr₂ generation. The contact opportunity between Hg²⁺ and Br[−] was relatively large, based on the concentration of Br[−] in the solution. Thus HgBr₂ was generated by Hg²⁺ and Br[−] and bound with the fly ash in the subsequent drying process. At the same time, a small amount of Hg²⁺ combined with O₂ in the air, or possibly was oxidized in solution, to form HgO. HgBr₂ begins to decompose before 115°C (Rumayor et al., 2013), therefore a fraction of HgBr₂ combined with the fly ash and decomposed in the drying process. HgS is not soluble, therefore HgS remains with the HBr modified ash at its original concentration.

2.2. Adsorption characteristics in the entrained-flow reactor

In order to evaluate the removal characteristics of fly ash toward Hg in the flue gas, the following definition of mercury adsorption efficiency was employed (Wu et al., 2008).

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

where, $C_{\text{in}}(\mu\text{g}/\text{m}^3)$ is the mercury concentration in the flue gas before the sorbent injection, that is, at the inlet of the reactor, and $C_{\text{min}}(\mu\text{g}/\text{m}^3)$ is the lowest stable Hg concentration after sorbent injection.

Fig. 5 shows the mercury adsorption capability of 1:49 mixed fly ash and unmodified fly ash in the entrained-flow reactor. The fly ash injection began at 0 min, and the exit concentration of Hg in the flue gas started to decrease and reached a stable concentration (C_{min}). After the fly ash feeder was shut down and the injection stopped, the mercury concentration started to increase slowly. This phenomenon was due to some of the fly ash adhering to the inner wall of the entrained-flow reactor. The fly ash on the sides of the reactor slowed the rise in mercury content in the flue gas to pre-injection levels. As shown in Fig. 5, the mercury adsorption efficiency of unmodified fly ash was 11%. When 1:49 mixed fly ash was injected into the reactor, the Hg concentration in the flue gas sharply declined, and the

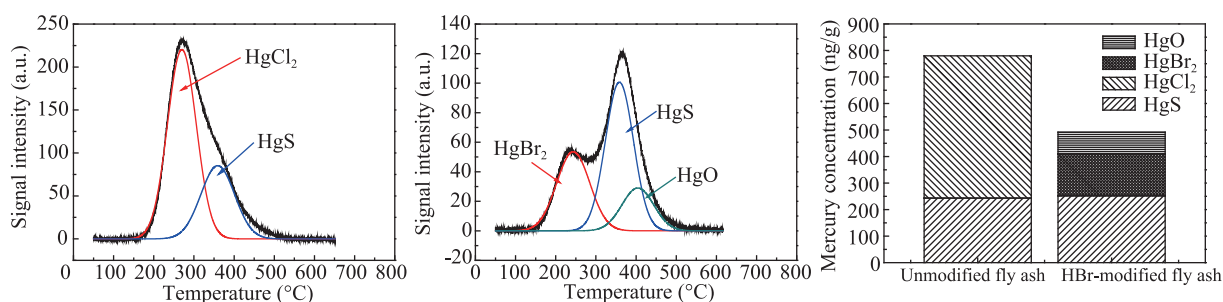


Fig. 4 – Mercury species on the surface of unmodified and HBr-modified fly ash. (a) Deconvoluted thermogram for unmodified fly ash; (b) deconvoluted thermogram for HBr-modified fly ash; (c) speciation and concentration of mercury compounds for unmodified and HBr-modified fly ash.

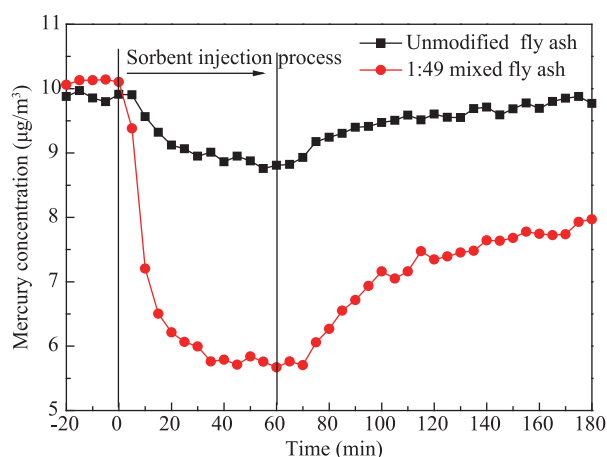


Fig. 5 – Mercury adsorption characteristics for 1:49 mixed fly ash and unmodified fly ash.

mercury adsorption efficiency increased to 44%, which is 4 times that of unmodified fly ash. The above results showed that the mercury adsorption efficiency was improved significantly even though only 2% HBr-modified fly ash was added. In our previous studies, in which the adsorption ability of the modified fly ash in the entrained-flow reactor was studied, results showed that the mercury adsorption was due mainly to chemical adsorption (Zhang et al., 2014).

2.3. Mercury compounds adsorbed on the HBr-modified fly ash

In this section of the experiment, the injected fly ash was the fly ash before mercury adsorption, which was sampled from the screw feeder, and the adsorbed fly ash was collected from the coarse ash vessel of the entrained-flow reactor, after mercury adsorption. Fig. 6 shows the thermal decomposition profiles of mercury substances in the fly ash before and after the mercury adsorption. It can be found that the mercury compounds in the injection fly ash started to decompose slightly below 200°C and were almost completely decomposed at 500°C. The mercury compounds in the unexposed unmodified fly ash after the mercury adsorption started to decompose slightly below 180°C and were almost completely decomposed at 500°C. After the 1:49 mixed fly ash was exposed, the mercury compounds started to decompose around 150°C and were almost completely decomposed at 500°C. As previously mentioned, the temperature of the entrained-flow reactor was maintained at 150°C, and some of the mercury species decompose below this temperature. This suggests that the HBr-modified fly ash began to oxidize and adsorb the mercury as soon as it was injected into the entrained-flow reactor.

In Fig. 5, it can be found that the unmodified fly ash has a small amount of adsorption ability toward the elemental mercury in the entrained-flow reactor mercury adsorption experiments. First, the mercury adsorption characteristics of modified fly ash were studied. Based on Fig. 6, after subtracting the mercury curve of the injected fly ash from that of the unmodified fly ash after adsorption in the entrained-flow reactor, the mercury curve of the unmodified fly ash that was adsorbed in the reactor was obtained. Comparing the data with the thermal

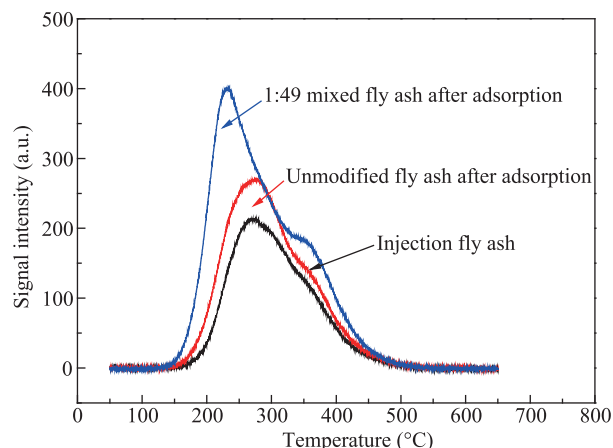


Fig. 6 – Thermal decomposition profiles of mercury compounds of fly ash samples.

desorption profiles of standard mercury species, the species and concentrations of the mercury compounds were identified. Fig. 7a shows the mercury species and concentration adsorbed by the unmodified fly ash in the entrained-flow reactor. The first peak in Fig. 7a represents HgCl_2 because the concentration of Cl was 4.10 ppm and Br could not be detected in the unmodified fly ash. Therefore, according to Fig. 2, mercury compounds adsorbed by unmodified fly ash were in the form of HgCl_2 , HgS and HgO , for which the mercury concentrations were 129.8, 61.9 and 44.3 ng/g, respectively.

Because the 1:49 mixed fly ash is a mixture of unmodified fly ash and HBr-modified fly ash, here the curve of unmodified fly ash after mercury adsorption was subtracted from the curve of 1:49 mixed fly ash after mercury adsorption, so that the adsorption characteristics of the 2% modified fly ash in the 1:49 mixed fly ash could be more easily observed. Using this method, Fig. 7b reveals the mercury speciation and concentration adsorbed on the HBr modified fly ash in the entrained-flow reactor. Those results show that the mercury species adsorbed in the entrained-flow reactor by the HBr-modified fly ash were mainly in the form of HgBr_2 and HgO , in which the mercury concentrations were 363.8 and 105.9 ng/g, respectively. In these experiments, the mercury adsorbed by 1 g unmodified fly ash in the entrained-flow reactor was 236 ng, while the mercury adsorbed by 1 g HBr mixed fly ash, in which the modified fly ash accounted for only 2%, was 469.7 ng. This indicated that the mercury adsorption performance of fly ash after modification had been improved significantly.

When HCl is present in the flue gas, the chloride reaction is the dominant oxidation reaction mechanism for mercury (Zhao et al., 2010; Li et al., 2013). Bromine and chlorine are congener elements, and it can be deduced that elemental mercury is mainly oxidized by HBr, and thus generates HgBr_2 in the entrained-flow reactor. In addition, Hall et al. (1995) found that O_2 promotes oxidation of elemental mercury in the flue gas. Thus, in the entrained-flow reactor, the elemental mercury in the flue gas was adsorbed to active sites on the surface of fly ash, and then generated HgBr_2 and HgO through oxidation by HBr and O_2 and subsequently adhered to the fly ash. Based on the analysis of mercury species in the modified fly ash before

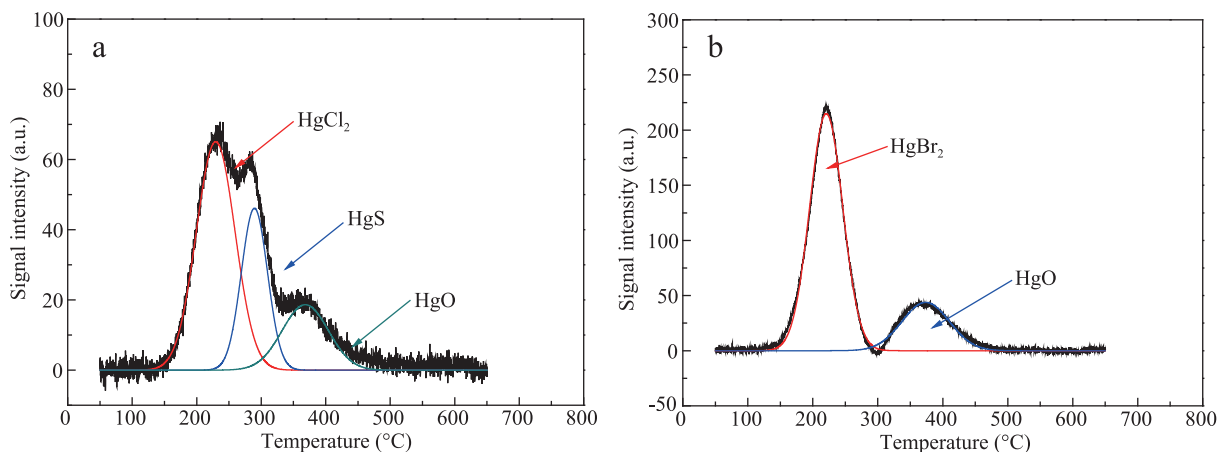


Fig. 7 – Mercury species adsorbed in the entrained-flow reactor on unmodified (a) and HBr-modified (b) fly ash.

and after the adsorption, and the oxidation and adsorption mechanism taking place between the elemental mercury and HBr-modified fly ash in the entrained-flow reactor, it is possible that the reaction simultaneously followed the Langmuir–Hinshelwood mechanism and the Eley–Rideal mechanism (Presto and Granite, 2006). In this study, the elemental mercury in the flue gas was oxidized primarily by HBr, since the concentration of HgBr₂ is more than two times that of HgO. Thus, it is concluded that HBr was the dominant factor promoting the oxidation of elemental mercury in the entrained-flow reactor.

2.4. Mercury adsorption characteristics of fine ash

In this section of the experiment, the fine-particle fly ash collected in the fine ash vessel (As shown in Fig. 1a) was analyzed. The particle size of the fine ash was smaller than the fly ash collected in the coarse ash vessel (the particle sizes of the fine ash and the coarse particle fly ash were 200–400 and 80–200 mesh, respectively).

As shown in Fig. 8, the mercury species in the fine-particle fly ash were also mainly HgBr₂ and HgO, in which the mercury concentrations were 1365.9 and 812.6 ng/g, respectively. Both

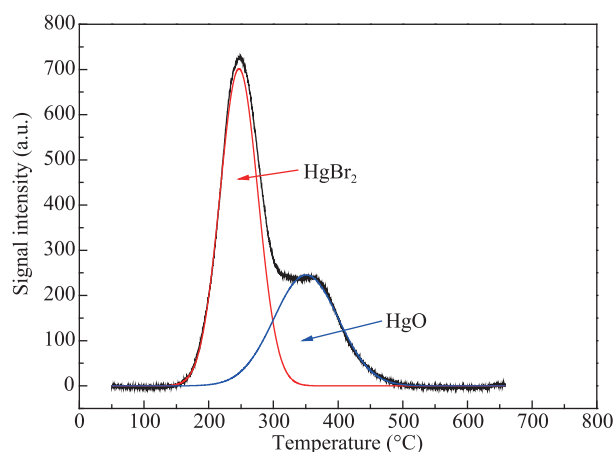


Fig. 8 – Mercury species adsorbed on fine ash in the entrained-flow reactor for the HBr-modified fly ash.

the mercury species in the coarse and fine fly ash consisted of HgBr₂ and HgO; however, the concentration of HgBr₂ and HgO in the fine ash was about 4.6 times greater than in the coarse ash. This may be due to the specific surface area of fine ash being larger than the coarse ash, so that the probability of the fly ash contacts with the mercury is higher, leading to more elemental mercury reacting on the fine ash surface than on the same weight of crude ash. On the other hand, for coarse ash with larger particle sizes, there are some micropores with larger volume, which are greater than the volume of the mercury atom. Thus the force of physical adsorption for mercury atoms by the Van der Waals force is weak. Under the unstable conditions, the mercury could easily be desorbed from the larger pores again. At the same time, the fine ash has a longer residence time in the entrained-flow reactor than coarse ash, resulting in a longer reaction time for elemental mercury. Contrasting Fig. 7b with Fig. 8, for the different particle size fly ash from the entrained-flow reactor, it can be found that the end temperature of HgBr₂ thermal desorption for fine ash is higher than that of crude ash. This may be due to the fact that the residence time of coarse fly ash in the entrained-flow reactor is shorter, so that the mercury adsorbed on the surface of fly ash could not enter the deep holes in the fly ash; thus thermal desorption took place relatively easily, and the mercury adsorbed on the surface of coarse fly ash desorbed at low temperature. However, the above explanation cannot explain why the adsorption onset temperature of HgO on the surface of fine fly ash was lowered about 50°C relative to coarse ash; more work will be necessary to address this issue in a future study.

3. Conclusions

In this study, the temperature-programmed thermal decomposition method was employed to study the adsorption mechanism of HBr-modified fly ash in a lab-scale entrained-flow reactor. The main conclusions are as follows:

- (1) Compared to the unmodified fly ash, the mercury adsorption efficiency improved significantly after modification with HBr.

- (2) For the unmodified fly ash, the main species of mercury were HgCl_2 and HgS , whereas for the HBr -modified fly ash, the main species of mercury were HgBr_2 , HgS and HgO .
- (3) The mercury species adsorbed by unmodified fly ash were HgCl_2 , HgS and HgO .
- (4) The mercury species adsorbed by HBr modified fly ash were HgBr_2 and HgO .
- (5) The fine ash had a better mercury adsorption performance than coarse ash, which is most likely due to the higher specific surface area and longer residence time. The major mercury species present were also HgBr_2 and HgO , and the concentrations of HgBr_2 and HgO in the fine ash were 3 times greater than in the coarse ash.

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