An Experimental Study on Oxidized Mercury Adsorption by Bromide Blended Coal Combustion Fly Ash

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ABSTRACT

The application of forced mercury oxidation technology would lead to an increase of Hg²⁺ concentration in the flue gas. Although Hg²⁺ can be easily removed in the WFGD, the mercury re-emission in the WFGD can decrease the total removal of mercury from coal-fired power plants. Hence, it is necessary to control Hg²⁺ concentration in the devices before the WFGD. Fly ash adsorbent is considered as a potential alternative for commercial activated carbon adsorbent. However, the adsorption efficiency of the original fly ash is low. Modification procedure is needed to enhance the adsorption performance. In this study, the adsorption of Hg²⁺ by brominated fly ash was studied. The fly ash was collected from the full-scale power plant utilizing bromide-blended coal combustion technology. The brominated fly ash exhibited excellent performance for Hg²⁺ removal. The flue gas component HBr and SO₂ could improve adsorbent's performance, while HCl would hinder its adsorption process. Also, it was demonstrated by Hg-TPD experiments that the adsorbed Hg²⁺ mainly existed on the fly ash surface in the form of HgBr₂. In summary, the brominated fly ash has a broad application prospect for mercury control.

KEYWORDS

Mercury; fly ash; bromide; adsorbents; flue gas

1 Introduction

Due to high volatility and biological toxicity, mercury (Hg) has been received increasing attention in recent years [1]. Coal-fired power plants emitted millions of tons of mercury each year. There are main three forms of mercury in the flue gas, elemental mercury (Hg⁰), oxidized mercury (Hg²⁺), and particulate mercury (Hgₚ) [2,3]. By existing air pollutant control devices (APCDs), partial mercury could be captured. Wherein, Hg⁰ is the trickiest form to be removed by existing APCDs due to its stable physical and chemical properties. Improving the oxidation rate of Hg⁰ is crucial to mercury control.

Bromide-blended coal combustion technology has proven to improve the oxidation rate of Hg⁰ significantly [4,5]. Vosteen et al. [6] research found that the oxidation rate could reach 90% when bromide was added into coal. Although Hg²⁺ is easily water-soluble, the mercury re-emission is not
negligible contributed to the reducing substances in the desulfurization slurry. It was reported that the mercury re-emission rate could reach 88% in some power plants [7]. Our previous studies [8,9] also demonstrated that the transformation from Hg2+ to Hg0 occurred in the aqueous phase. Therefore, it is necessary to remove Hg2+ as much as possible before the wet flue gas desulfurization systems (WFGD). Activated carbon (AC) injection technology is already commercially available in the United States, which was considered as one of the most mature mercury removal technologies [10,11]. It exhibited a good performance on Hg0 removal. However, the cost of commercial activated carbon is high, which hinders its large-scale utilization. As a by-product of coal-fired power plants, fly ash adsorbent is considered as a potential alternative to AC [12,13]. However, the Hg removal efficiency of the original fly ash is poor due to its undeveloped pore structure and low content of unburned carbon. So it has to be modified before its application. It was reported that the mercury removal efficiency could be improved by attaching active materials (such as halogens and sulfur) on fly ash surface [14–16]. Many researchers [17–19] have investigated the catalytic oxidation removal of elemental mercury in flue gas by brominated fly ash. But little attention was paid to the Hg2+ adsorption performance of fly ash.

Even though, the adsorption efficiency of Hg2+ by fly ash still needs more investigation. The Hg2+ adsorption performance of brominated fly ash produced from bromide-blended coal combustion technology is worth being studied. Hence, the Hg2+ adsorption performance of brominated fly ash adsorbents was studied in this paper. We collected different fly ash samples from the coal-fired power plant utilizing bromide-blended coal combustion technology. Meanwhile, Hg2+ adsorption experiments were carried out in the laboratory. Hg2+ adsorption efficiencies were compared to select the optimal fly ash modification strategy. Also, Hg-TPD experiments were also conducted in order to characterize the bonding nature of Hg2+ on fly ash surface. Finally, the possibility of utilizing the brominated fly ash to remove Hg2+ was verified in this research.

2 Materials and Methods

2.1 Preparation of Samples

All the fly ash samples were collected from coal-fired power plant which utilized bromide-blended coal combustion technology. The bromide mass proportion in coal corresponding to the fly ash was 0, 25, 75, 130 ppm, respectively. The collected fly ash was dried and then screened, and the 80~200 mesh particles were selected as samples. The samples were named as BCFA0, BCFA25, BCFA75, and BCFA130. Here, BC represents calcium bromide which was used to be blended with coal. FA denotes represents for fly ash. The numbers (0, 25, 75 and 130) refer to the bromide proportion blended with coal.

2.2 Hg2+ Adsorption Experiments

The Hg2+ adsorption experimental apparatus (see Fig. 1) consists of four parts: a gas generator, a reaction unit, a test unit, and exhaust gas treatment system. The gaseous HgCl2 was generated by the 3315 module of the Hg-CEMS system (Tekran, America). The concentration of HgCl2 at the export of the 3315 module was 10.88 μg/m3. The HBr, HCl, and SO2 gases were controlled by the mass flowmeters. The HgCl2 and other gases were mixed with a gas mixer. The quartz reactor was placed inside a tubular furnace, and the adsorbents were fixed in the middle of the reactor with quartz cotton. The heating temperature was 110°C. The concentration of Hg2+ was detected by the 3320 and 2537 module of Hg-CEMS systems. Exhaust gas was purged by the exhaust gas treatment systems and then emitted into the atmosphere.

2.3 Temperature-Programmed Desorption (TPD) Experiment

The temperature-programmed desorption (TPD) experiment (see Fig. 2) was carried out in a fixed bed reactor to identify the binding form of adsorbed Hg2+ by fly ash adsorbent. 1 L/min high purity N2 controlled
by a mass flowmeter was used as the carrier gas. The gas produced by TPD was detected by the 3320 and 2537 module of Hg-CEMS systems. The temperature range was controlled between 40°C–60°C, and the heating rate was set as 8 °C/min. Before the experiment, 100 mg adsorbed fly ash adsorbents were weighed and placed in the middle of the reactor. The exhaust gas was purged into the atmosphere swept by high purity N₂.

Figure 1: Schematic of Hg²⁺ adsorption experiments

Figure 2: Schematic of mercury TPD experiments

3 Results and Discussion

3.1 Effects of Bromide Proportion in Coal on Hg²⁺ Adsorption by Fly Ash

In order to investigate the effects of bromide proportion on Hg²⁺ adsorption efficiency, fly ash adsorbents produced by bromide-blended coal combustion were utilized to adsorb oxidized mercury. The Hg²⁺ adsorption experiment was conducted at 110°C. The concentration of Hg²⁺ at the reactor inlet was 10.88 µg/m³. The space velocity is 4123.8 h⁻¹. It can be seen from Fig. 3a that the initial Hg²⁺ removal efficiency of BCFA0 is around 17.79%, which is the lowest among all the fly ash absorbents. With the increase of bromide concentration in coal, the adsorption efficiency of fly ash is enhanced gradually. Moreover, the breakthrough time of fly ash adsorbents became longer. It was implied that bromine could promote the Hg²⁺ adsorption capacity of fly ash. However, the difference in the initial Hg²⁺ removal
efficiency between BCFA75 and BCFA130 is not obvious, which means the Hg$^{2+}$ adsorption capacity could not be improved significantly with high bromide concentration. Previous study [4] has shown that bromide in coal was transformed into HBr largely in the flue gas. A large amount of HBr could be adsorbed by the active sites on the fly ash surface. The bromine sites have an ability to capture Hg$^{2+}$, which is the reason why brominated fly ash could adsorb Hg$^{2+}$. When the bromide proportion in coal increased, the bromine adsorption sites in fly ash also increased. Hence, Hg$^{2+}$ adsorption efficiency was improved. However, the adsorption efficiency of BCFA75 and BCFA130 were very close to each other. In other words, the increase of Br content did not continue to improve the adsorption efficiency of fly ash. According to the study of Niksa [20], the bromine could bind to the adsorption site on unburned carbon which could adsorb Hg$^{2+}$. It might be that the number of bromine adsorption sites on the two adsorbents is similar, so the adsorption efficiency of BCFA75 and BCFA130 were similar.

3.2 Effects of Temperature on Hg$^{2+}$ Adsorption by Fly Ash

Temperature is a significant factor that could affect the adsorption efficiency of absorbents. The BCFA75 was chosen to investigate the effects of temperature. The adsorption temperature range was selected from 110°C to 180°C. It can be seen from Fig. 4a that the initial Hg$^{2+}$ removal efficiency declined with the increase of temperature. Obviously, the adsorption capacity was also greatly reduced (Fig. 4b). Both physical adsorption and chemical adsorption occurred in the Hg$^{2+}$ adsorption process. The Hg$^{2+}$ compounds were firstly adsorbed on the fly ash surface by physical adsorption, and then they were bound to functional groups. On the one hand, the physical adsorption process is due to the intermolecular Van der Waals force. Because of the increased thermal motion of molecules, Van der Waals force was weakened under higher temperature. On the other hand, chemical bonds formed by chemical adsorption could be broken with the increase of the temperature. Therefore, the Hg$^{2+}$ adsorption efficiency of BCFA75 decreased. In addition, the breakthrough time also shortened from the 1200 s to 900 s, which indicated that high temperature would hamper the Hg$^{2+}$ adsorption.

3.3 Effects of Space Velocity on Hg$^{2+}$ Adsorption by Fly Ash

BCFA130 was chosen to determine the effects of space velocity in this section. The experiment was conducted at 110°C. The space velocities were set as 16497.0 h$^{-1}$, 8247.6 h$^{-1}$, and 4123.8 h$^{-1}$, respectively. It can be observed from Fig. 5 that the initial adsorption efficiency and the breakthrough time decreased with the increase of space velocity, which indicated that low space velocity could improve the removal of Hg$^{2+}$. It is due to lower space velocity corresponds to more amounts of adsorbents. Higher doses of adsorbents could certainly absorb more Hg$^{2+}$.

![Figure 3](image-url)
3.4 Effects of Flue Gas Compositions on Hg$^{2+}$ Adsorption by Fly Ash

The HBr, HCl and other components in realistic flue gas could also affect the adsorption performance of fly ash adsorbents. The simulated gas was used to conduct adsorption experiments. The experimental conditions were summarized in Tab. 1.

![Figure 4](image1.png)  
**Figure 4:** (a) Effects of temperature on the Hg$^{2+}$ adsorption efficiency. (b) Hg$^{2+}$ adsorption amount of adsorbents

![Figure 5](image2.png)  
**Figure 5:** Effects of space velocity on the Hg$^{2+}$ adsorption

| Adsorbent | BCFA130 |
|-----------|---------|
| Temperature | 110°C |
| Space velocity | 4123.8 h$^{-1}$ |
| HBr | 0, 10 ppm, 18 ppm |
| HCl | 0, 30 ppm, 60 ppm, |
| SO$_2$ | 0, 400 ppm, 800 ppm |

**Table 1:** Experimental conditions
3.4.1 Effects of HBr

As described in the previous section, HBr has unignorable influences on Hg$^{2+}$ adsorption. Yang et al. [4] found that the concentration of HBr in flue gas could not exceed 18 ppm no matter how much bromide was added in the coal combustion process. Accordingly, the HBr concentration of 0, 10, 18 ppm was chosen in our adsorption experiments. The results were depicted in Fig. 6. It can be seen that the adsorption efficiency decreased by 20% when HBr was added. As previously mentioned, HBr could bind to the adsorption sites of fly ash, which affected the adsorption process of Hg$^{2+}$. The competitive adsorption of HBr with Hg$^{2+}$ reduced Hg$^{2+}$ removal efficiency. We can also see that the BCFA130 adsorbents were broken through after 1200 s in the absence of HBr. However, the BCFA130 adsorbents showed stable adsorption capacity in the presence of HBr. This was because HBr could supplement the brominated active sites on the fly ash surface, which enabled the BCFA130 adsorbents to adsorb Hg$^{2+}$ continuously. It was indicated that we could make full use of the adsorption sites of fly ash in the flue gas contained HBr.

![Figure 6: Effects of HBr concentration on Hg$^{2+}$ adsorption efficiency](image)

3.4.2 Effects of HCl

There was a large amount of HCl in the actual flue gas. The concentration of 0, 30, 60 ppm HCl was selected to investigate the HCl effects. From Fig. 7, we can see that the Hg$^{2+}$ removal efficiency declined from 58.6% to 47.0% when HCl was added. Moreover, the breakthrough time also decreased. It was inferred that HCl preempted the adsorption sites on the fly ash, which led to the decrease of Hg$^{2+}$ adsorption process. In contrast to HBr, the addition of HCl did not improve the adsorptive performance. It was because most of Hg$^{2+}$ existed in the flue gas in the form of HgCl$_2$. The chlorinated sites on the fly ash surface could not adsorb the HgCl$_2$. Therefore, the critical problem is the solution to the adverse effects of HgCl$_2$ on fly ash adsorbents.

3.4.3 Effects of SO$_2$

A large amount of SO$_2$ was added in the experiments to observe its effects on the fly ash adsorbent. It can be seen from Fig. 8 that the adsorbents were not broken through during the experiment in the presence of SO$_2$. But the initial Hg$^{2+}$ adsorption efficiency was dropped. Previous research [21] has shown that the SO$_2$ molecules are easily adsorbed inside the microporous structure on the surface of the adsorbent because of their strong polarity. The adsorbed SO$_2$ could react with O$_2$ and H$_2$O to form sulfur-containing groups, which have a strong adsorption capacity to Hg$^{2+}$ [22, 23]. Therefore, SO$_2$ can improve the adsorption performance of fly ash adsorbents. Due to the competitive adsorption process, the
adsorption efficiency of Hg\(^{2+}\) was reduced in the concentration of 800 ppm SO\(_2\) compared with 400 ppm. It was shown that the fly ash adsorbents are a promising candidate for being used in the equipment the upstream of the WFGD system.

![Figure 7: Effects of HCl concentration on Hg\(^{2+}\) adsorption efficiency](image)

![Figure 8: Effects of SO\(_2\) concentration on the Hg\(^{2+}\) adsorption efficiency](image)

3.5 Hg-TPD Experiments

In order to investigate the binding form of Hg\(^{2+}\) with fly ash adsorbents, the Hg-TPD experiments were conducted on the BCFA130 adsorbents, which were broken through. It can be seen from Fig. 9 that the maximum precipitation peak was located at 260°C. It was proved that the precipitation peak at 260°C corresponds to HgBr\(_2\) [22]. The mechanisms of the Hg\(^{2+}\) adsorption process are as follows [20]:

\[
\text{HBr}(g) + \text{StSA}(s) \rightarrow \text{StBr(ad)} \quad (1)
\]

\[
\text{Hg}^{2+}(g) \rightarrow \text{Hg}^{2+}(\text{ad}) \quad (2)
\]

\[
\text{StBr(ad)} + \text{Hg}^{2+}(\text{ad}) \rightarrow \text{StHgBr}_2(\text{ad}) \quad (3)
\]
4 Conclusions

The Hg\(^{2+}\) adsorption performance of brominated fly ash adsorbents was investigated in this paper. The effects of various parameters on Hg\(^{2+}\) adsorption efficiency were explored systematically by Hg\(^{2+}\) adsorption experiments. The main conclusions of this research are as follows. (1) Moderate bromide proportion in coal, lower temperature, and smaller space velocity could enhance the Hg\(^{2+}\) adsorption efficiency. In the realistic coal-fired power plants, the performance of brominated fly ash adsorbents can be greatly improved under suitable working conditions. (2) The HBr and SO\(_2\) can extend the breakthrough time of brominated fly ash adsorbents. The HCl would hinder adsorbents’ adsorption efficiency. The HBr, SO\(_2\), and HCl will compete with Hg\(^{2+}\) for adsorption sites on brominated fly ash surface. (3) The Hg\(^{2+}\) adsorption process mainly takes place by chemical adsorption. The adsorbed mercury mainly exists on the fly ash surface in the form of HgBr\(_2\).

As a by-product of the bromide-blended coal combustion technology, the brominated fly ash adsorbent is easily available, economical and efficient.

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