

Study on mechanism of mercury oxidation by fly ash from coal combustion

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Received July 5, 2009; accepted July 28, 2009

To understand the interaction of fly ash and mercury, systematic experiments on mercury oxidation in single flue gas composition are conducted on a fixed bed reactor system, the desorption rate and speciation of mercury are valued. The results indicate that fly ash itself can significantly promote elemental mercury oxidation. A classification of fly ash activated sites is developed according to the speciation of mercury during adsorption-desorption tests, the reaction mechanism of mercury oxidation by fly ash is proposed. Acid gas can promote mercury oxidation and improve the stability of oxidation product. Lattice oxygen is an important oxidant of mercury oxidation.

mercury, fly ash, oxidation, adsorption-desorption, flue gas

Citation: Zhao Y C, Zhang J Y, Liu J, et al. Study on mechanism of mercury oxidation by fly ash from coal combustion. Chinese Sci Bull, 2010, 55: 163–167, doi: 10.1007/s11434-009-0567-7

Study on emission and control of mercury is one of the hot issues recently [1–10]. The partition and interaction of mercury and flue gas, as well as fly ash particles during coal combustion have significant influence on its distribution, emission and control [1]. The characters of fly ash and interaction with flue gas have an important impact on mercury heterogeneous oxidation [2]. The heterogeneous interaction of fly ash-flue gas-mercury is complex because of the complexity of flue gas compositions and fly ash components. Previous studies investigated the effect of acid gas including Cl₂, HCl, SO_x, NO_x, etc. on mercury catalytic removal [2–5], but less concerned about other components such as O₂, CO₂, and H₂O, which were generally considered to have little effect or no effect on Hg⁰ oxidation [3]. Besides, the report about intrinsic properties of fly ash on mercury oxidation is rare. Considering the characteristic of fly ash, the contained unburned carbon and activated inorganic components are the key factors of mercury adsorption and oxidation [6–9].

However, the interaction of fly ash and mercury is still not clear until now. Presto et al. suggest that there are two types of activated sites on the surface of sorbent for mercury: One is stable activated site with higher binding energy between mercury and sorbent, mainly used to capture mercury; the other is catalytic activated sites that can also capture mercury, but its binding energy is low and mercury is easy to re-release from the sorbent, this type of activated sites is just for catalytic oxidation of Hg⁰ [11]. This concept explains the difference between adsorption activated site and oxidation activated site, however, this classification is not comprehensive. To understand the detailed interaction mechanism of mercury and fly ash, systematic mercury adsorption-desorption experiments are carried out on a fixed bed reaction system, the interaction between fly ash and mercury with common flue gas components is discussed, and the distribution of mercury species during adsorption-desorption process is investigated, which provide the basis for clarifying the mechanism of mercury oxidation by fly ash.

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1 Experimental section

The experimental device used for the mercury capture experiments at the laboratory scale consisted of a glass reactor fitted with an internal tube and external tube, and heated by a furnace (Figure 1). The mercury permeation tube was put into a U-tube inside the constant temperature water tank to generate gaseous mercury. The gaseous mercury was carried by nitrogen and then mixed with air before passing the sorbent bed. The flow was 0.5–1 L/min. The sorbent was composed by 0.5 g fly ash mixed with 1.5 g sand, and then was put into the internal tube. The height of the sorbent bed was about 3 mm, and the temperature was 120°C. A continuous emission monitor (UT3000) was used to measure mercury concentration at the outlet of the reactor, and the Ontario Hydro impinger was used to analyze mercury speciation, the waste gas was adsorbed by chemical solutions. Fly ash samples were collected from electrostatic precipitator ash bucket of power plant which burns typical bituminous coal in Spain (SPA). Duplicate tests were conducted in different atmospheres and conditions to get the average value.

2 Results and discussions

2.1 Homogeneous oxidation in different atmospheres

The fly ash-flue gas-mercury gas solid reactions are complex. To exclude the effects of flue gas compositions, know the detailed mechanism of mercury oxidation by fly ash, the systematic homogeneous oxidation of mercury in different flue gas compositions was conducted, the results are shown in Figure 2. There is no obvious homogeneous oxidation for Hg^0 at 120°C in different atmospheres, even with 33 ppm HCl. Widmer investigated the influence of HCl on Hg^0

oxidation, and they found that high mercury oxidation rate only obtained at high temperature and high HCl concentration [12]. Laudal et al. suggested that Cl_2 was the main oxidant of Hg^0 in low temperature flue gas [3]. Therefore, there is no homogeneous oxidation of mercury under all kinds of atmospheres in this experimental system.

2.2 Heterogeneous oxidation of mercury by fly ash

Mercury oxidation tests by SPA fly ash in three typical atmospheres (N_2 , Air, and HCl) were conducted and lasted for 20 h. As shown in Figure 3, fly ash promoted Hg^0 oxidation during the capture process of mercury. The Hg^0 oxidation rate of SPA fly ash ranges from 3.1% to 18.6% in three atmospheres. HCl is the most important factor of Hg^0 oxidation, however, the influence of O_2 should not be ignored. Hall et al. found O_2 promoted Hg^0 oxidation in their early study [13]. It is worth to mention that SPA fly ash also showed a certain degree of Hg^0 oxidation in the N_2 atmosphere.

To validate the oxidation of Hg^0 by fly ash, the fly ashes after adsorbing mercury in these three atmospheres were used to conduct desorption tests. Desorption tests were carried out in an inert atmosphere lasted for 3 h, and the temperature was set as 180°C. The desorption amount of mercury from these three fly ashes ranges from 15% to 25% (Figure 4), which is less than that from activated carbon sorbent [14], this indicates that mercury on fly ash has relatively good stability. Comparing these fly ashes got in different atmospheres, the desorption rate from fly ash in N_2 is similar to that in Air, and both of them are more than that from fly ash in HCl, which illustrates that the interaction between fly ash and mercury is more stable with the occurrence of HCl.

The desorption mercury species vary from fly ashes in

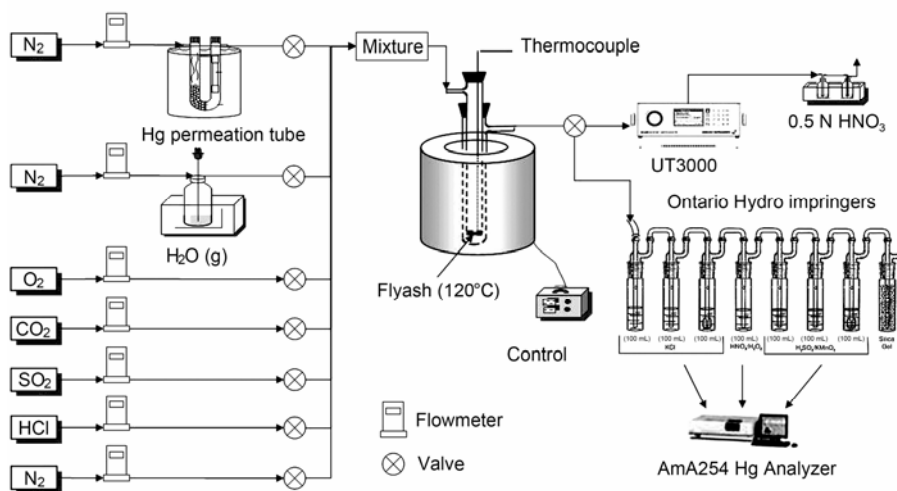


Figure 1 Schematic diagram of mercury adsorption fixed bed system.

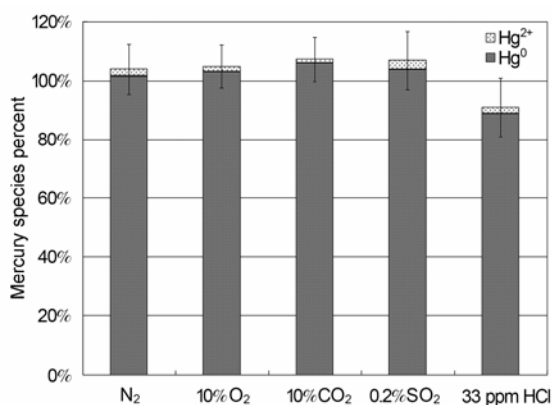


Figure 2 Homogeneous oxidation of mercury in different atmospheres.

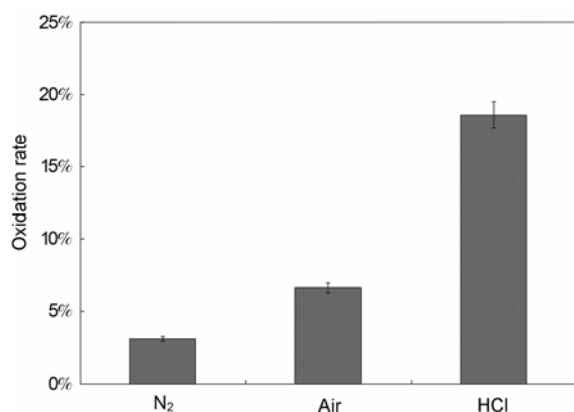


Figure 3 Mercury oxidation by fresh SPA fly ash in different atmospheres.

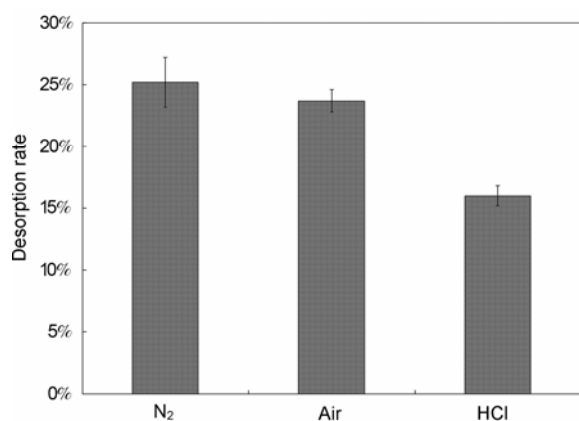


Figure 4 Desorption rates of fly ashes in N₂ (180°C).

three atmospheres. Almost all of the mercury released from the fly ash in Air and HCl are Hg²⁺, while mercury released from the fly ash in N₂ contains about 50% Hg⁰ and Hg²⁺ (Figure 5). Although the Hg²⁺ concentration in flue gas after passing the sorbent is not so high in N₂, the released Hg²⁺ during desorption of this fly ash occupied about 7% of the total mercury in the inlet, which validates that fly ash itself can oxidize Hg⁰, even in N₂.

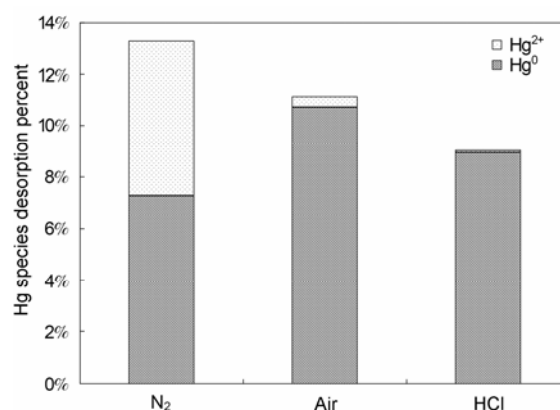


Figure 5 Percent of desorption mercury species in different atmospheres (180°C).

2.3 Interaction mechanism of fly ash and mercury

The oxidation of mercury happened simultaneously with the capture of mercury by fly ash. To understand the detailed interaction mechanism of mercury and fly ash, mercury species generated during adsorption-desorption process were classified as follows:

(i) Hg²⁺ in adsorption process: similar to the Hg²⁺ from the oxidation by catalytic activated sites proposed by Presto et al.^[15]. This kind of activated sites is called low binding energy catalytic oxidation active sites—FA①;

(ii) Hg²⁺ released during desorption process: the active sites that generate this Hg²⁺ can oxidize Hg⁰, and the binding energy is higher. So this type of active sites is called catalytic oxidation active sites—FA②;

(iii) Hg⁰ released during desorption process: the active site combined with this Hg⁰ only adsorbed Hg⁰, no catalytic oxidation happened on this site. So this type of active sites is called adsorption active sites—FA③;

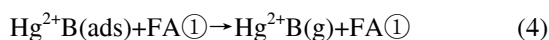
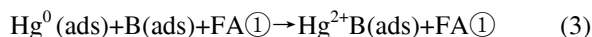
(iv) Residual mercury in fly ash after desorption: this kind of active sites is similar to the high binding energy active sites described by Presto et al., which can be called high binding energy adsorption active sites—FA④.

Distribution of mercury species during adsorption-desorption process in different atmospheres is listed in Table 1. The contents of mercury species vary in different atmospheres, and the total Hg²⁺ in flue gas during adsorption-desorption process in three atmospheres is N₂, 10.3%; Air, 16.8%; and HCl, 27.5%, respectively.

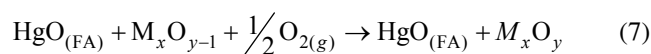
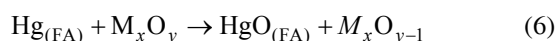
The content of type (I) mercury in HCl is the highest, which means the key point of Hg⁰ oxidation is the oxidant adsorbed on the surface of sorbent. This indicates that the interaction between low binding energy catalytic oxidation active sites FA① and mercury is according to Langmuir-Hinshelwood mechanism. Specific reactions are shown in the following eqs. (1)–(4). As the oxidant of Hg⁰, the adsorption capacity of HCl on FA① is the strongest, then follows O₂, while N₂ has no oxidation capacity. So the content of Hg²⁺ is the highest in HCl atmosphere.

Table 1 Mercury speciation during adsorption-desorption process in different atmospheres

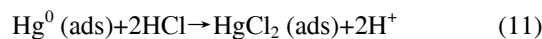
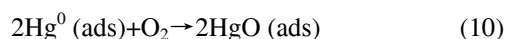
	Hg ²⁺ in adsorption process	Hg ²⁺ released during desorption process	Hg ⁰ released during desorption process	Residual mercury in fly ash after desorption
N ₂	3.0%	7.3%	6.0%	39.4%
Air	6.1%	10.7%	0.4%	36%
HCl	18.6%	8.9%	0.1%	47.4%



The contents of type (II) mercury in three atmospheres are similar. But it should be mentioned that a considerable amount of Hg²⁺ was generated in N₂ atmosphere, even N₂ is not the oxidant of mercury. This implies that the oxidant comes from fly ash itself, and fly ash components can oxidize Hg⁰ directly. This oxidation reaction is according to Mars-Maessen reaction mechanism. Oxygen atom in fly ash components was the same as the oxidant of mercury, when gaseous mercury passing the sorbent bed, it was captured by active site FA②, then oxidized by active oxygen atom to form Hg²⁺ (eq. (6)). Previous studies have indicated inorganic metal oxides in fly ash have significant mercury oxidation capacity [16,17]. And the sorbent itself can be oxidized with the occurrence of oxygen in flue gas (eq. (7)), then combines with HgO to form stable binary oxides (eq. (8)).



Type (III) mercury is only found in N₂ atmosphere, while there is almost no Hg⁰ released from fly ash in O₂ and HCl atmosphere. This implies that the adsorbed Hg⁰ was oxidized to Hg²⁺ in O₂ and HCl atmosphere, and the oxidation reaction followed Eley-Rideal mechanism (eqs. (9)) [15]. The adsorption active sites FA③ can also adsorb O₂ and HCl easily as oxidant, and then oxidize Hg⁰ which has been adsorbed following Langmuir-Hinshelwood mechanism. The adsorption active site FA③ is similar to low binding energy catalytic oxidation active site FA①, but has a higher binding energy with mercury.



Type (IV) mercury remained in fly ash has a high binding energy with FA④. It can be speculated that this mercury mainly occurs as Hg²⁺ in fly ash, even no direct evidence was found. The content of type (IV) mercury is higher in fly ash from HCl atmosphere than that from N₂ and air atmospheres, which implies that the interaction of fly ash, HCl, and mercury can be easily combined to form stable Hg²⁺. Comparing with the fly ash from air, the fly ash from N₂ has more residual mercury. This is because the oxidant in N₂ is lattice oxygen atom which has a higher binding energy with Hg than that of O₂—the oxidant in air.

3 Summary

The mercury oxidation rate by fly ash in three typical atmospheres (N₂, Air, HCl) ranges from 10.3% to 27.5%, and all of them are heterogeneous oxidation. The heterogeneous oxidation of mercury mainly includes adsorption oxidation and direct heterogeneous oxidation. The oxidant of adsorption oxidation can be flue gas composition or lattice oxygen atom. While the direct heterogeneous oxidation process is the reaction between the adsorbed mercury and flue gas component on fly ash surface. The active sites on fly ash surface can be classified into four types: low binding energy catalytic oxidation active sites, catalytic oxidation active sites, adsorption active sites, and high binding energy adsorption active sites. Three reaction mechanisms of fly ash and mercury are proposed, the lattice oxygen atom is an important oxidant for mercury, and the oxidation of mercury by fly ash itself is according to Mars-Maessen mechanism.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50906031, 50721005, 20877030), National Basic Research Program of China (Grant No. 2006CB200304) and China Postdoctoral Science Foundation Funded Project.

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