INFLUENCE OF IRON SPECIES PRESENT IN FLY ASHES ON MERCURY RETENTION AND OXIDATION

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Abstract

The aim of this study was to assess the effect of iron species present in fly ashes produced from coal combustion on mercury retention and oxidation. To achieve this objective the work was divided into two parts. In the first part the relationship between the mercury and iron content in fly ashes of different origin and characteristics was evaluated. In the second, a series of fractions enriched in iron oxides were separated from the fly ashes to determine the effect of increasing iron content on mercury retention and oxidation. Special attention was paid to the influence of iron on mercury behavior in enriched carbon particles in fly ashes. From the results obtained it can be inferred that, in the range of fly ashes studied, iron species do not affect the retention of mercury and do not play any role in heterogeneous mercury oxidation.

Keywords: mercury; fly ash; iron; oxidation

1. Introduction

The control of mercury in coal-fired power plants is a worldwide objective [1]. Mercury speciation is an important parameter that affects the mercury removal efficiency of various pollution abatement technologies. Fly ash can catalyze the oxidation of elemental mercury and can absorb elemental mercury [2]. For this reason, it is essential to have a good understanding of the nature of mercury-fly ash interactions and mercury oxidation in fly ashes during the coal combustion process.

Several studies have focused on the influence of iron species present in fly ashes on mercury oxidation. It has been reported that hematite ($\alpha\text{-Fe}_2\text{O}_3$) is one of the catalytically active compounds and that the iron content of fly ash could be used to predict relative catalytic activity among fly ashes [3-5]. Ghorishi [3] evaluated the major mineral constituents of coal fly ashes and found that copper and iron oxides exhibited significant catalytic activity toward the surface-mediated oxidation of elemental mercury. Experimental studies [4-5] in simulated flue gas (N_2 , O_2 , and CO_2 with varying concentrations of HCl , NO , NO_2 , SO_2 and H_2O) in the presence of several model fly ashes composed of mixtures of alumina, silica, ferric oxide, cupric oxide and calcium oxide indicated that the catalytic effects of these species depend on the composition of the flue gas. Tests on actual fly ashes showed that the catalytic activity of their components is more complex than suggested by the results from the model mixtures [6]. Dunham et al. [2] observed that the oxidation of elemental mercury increased with the increase in the amount of magnetite, indicating that an iron oxide with a spinel-type structure may play a role in mercury oxidation in fly ashes. However, in the same study, a high-carbon subbituminous ash which contained no magnetite also showed considerable mercury oxidation. In fact, the injection of $\alpha\text{-Fe}_2\text{O}_3$ into coal combustion flue gases produced from burning subbituminous and lignitic coals did not

catalyze any heterogeneous elemental mercury oxidation reactions [7]. Galbreath et al. [8] suggested that Al_2O_3 and/or TiO_2 present in fly ashes may act as catalysts for mercury oxidation. A series of studies [9-11] in which fly ash was fractionated into magnetic (iron-rich) and nonmagnetic (aluminosilicate-rich) fractions showed that there were no substantial differences in the amount of oxidized mercury produced in these two cases. When NO_2 and HCl were added to the baseline blend, the amount of oxidized mercury was roughly four times higher in the nonmagnetic phase than in the magnetic one.

It follows from this that the role of iron in the catalytic oxidation of mercury in fly ashes is still unclear. The aim of this study is to clarify the influence of iron species present in fly ashes on mercury retention and oxidation and the possible catalytic effect of iron on several fly ash fractions containing magnetic materials and unburned carbon particles of different contents and characteristics.

2. Experimental Section

Five fly ash samples (CTP, CTA, CTSR, CTL and CTE) of different origin and characteristics were used in this study. CTP was taken from a fluidised bed combustion plant (FBC) that burns mixtures of coal and coal wastes. The other four were obtained from pulverized coal combustion (PCC) power plants in which high rank (CTA), bituminous (CTSR, CTL) and subbituminous coals (CTE) are burned. Enriched unburned carbon (EC) fractions from each fly ash (CTA-EC, CTSR-EC, CTL-EC and CTE-EC) were obtained by size fractionation by means of dry and wet sieving. In the case of CTP only the raw sample was employed because unburned particles were homogeneously distributed among all the sizes.

Three of the samples impoverished in unburned particles and obtained by size fractionation were subsequently separated into magnetic (CTL-M, CTE-M, CTSR-M) and nonmagnetic (CTL-NM, CTE-NM, CTSR-NM) fractions. A high intensity magnetic field separator (Master Magnets) operating in a water medium was used for CTL and CTSR and a high intensity magnetic induced roll (Capco) working in dry mode was employed for the CTE.

The unburned carbon particle content in each fraction was estimated as loss of ignition (LOI) and was determined by combustion of the organic matter at 815°C. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was used to determine the iron content. The crystalline species in the fly ash samples were identified and estimated by X-ray diffraction (XRD). The mercury content was determined using an Automatic Mercury Analyser (AMA).

The experimental device employed to retain mercury consists of a glass reactor containing the fly ash bed which is heated to 120°C. Elemental mercury in gas phase obtained from a permeation tube was passed through the sorbent bed in an O₂+N₂ stream of 0.5 L min⁻¹. The O₂ concentration of the atmosphere was 12.6 % v/v. The mercury concentration in gas phase was 120 µg m⁻³. The duration of the mercury retention experiments varies depending on the type of fly ash but in general it is the time needed for the samples to reach their maximum retention capacity ($C_{out}/C_{in}=1$). A continuous mercury emission analyzer (VM 3000) was used to monitor the mercury that was not retained during the sorption experiments. The total amount of mercury retained was determined by analysing the fly ashes post-retention by means of AMA equipment.

3. Results and discussion

The influence of iron content on mercury capture was evaluated using two approaches: i) comparing the mercury and iron concentrations in the fly ashes and

fractions enriched in carbon particles of different characteristics and ii) evaluating the influence of the iron content on mercury retention capacity at 120°C in these fly ashes in a laboratory scale device. The possible relationships between mercury and iron in both cases were considered by comparing the mercury content with total iron content (Figure 1). The iron species identified in the fly ashes by XRD were magnetite (Fe_3O_4) and hematite ($\alpha\text{-Fe}_2\text{O}_3$). The concentration of total crystalline material for magnetite ranged from 3.2% (CTL) to 16% (CTA) and for hematite from 2.2% (CTP) to 5.8% (CTE), whereas the total iron content ranged from 3 to 7%. The mercury concentration in the raw fly ash samples ranged from 0.04 $\mu\text{g g}^{-1}$ to 1.8 $\mu\text{g g}^{-1}$ in increasing order: CTE<CTA<CTL<CTP<CTSR.

No correlation between the mercury captured by the fly ashes taken directly from the coal combustion processes and the total iron content was found (Figure 1a). Neither did the fly ashes used as sorbents in a fixed bed for the capture of elemental mercury in gas phase show any such correlation (Figure 1b). A remarkable case is that of CTE because, in spite of having the highest iron content (7.3 %), it shows the lowest mercury retention capacity (1.1 $\mu\text{g g}^{-1}$) (Figure 1b). What is more, when the magnetite and hematite contents were compared with the amount of mercury captured, the lack of correlation was confirmed.

Several studies have emphasized the important role of unburned carbon particles present in fly ashes on the sorption of mercury [12]. Because this theory is held by a number of authors, we paid special attention to the effect of iron on mercury retention in carbon particles present in fly ashes. The relationship between mercury capture and iron content in fly ashes enriched in unburned carbon particles is presented in Figure 1c-d. Figure 1c shows the mercury content versus the iron content in carbon particles separated from the fly ashes taken directly from the power station. Figure 1-d shows the

same relationship for the fly ashes used as sorbents in laboratory scale experiments. The mercury content in the enriched carbon fly ashes (CTA-EC, CTSR-EC, CTL-EC, CTE-EC) ranges from $0.10 \mu\text{g g}^{-1}$ (CTE-EC) to $4.9 \mu\text{g g}^{-1}$ (CTSR-EC). No correlations between the mercury content and iron content were observed in these fly ashes (Figure 1c), nor when they were used as sorbents of mercury at laboratory scale (Figure 1d). For instance, the iron content in CTL-EC was 0.59% and the mercury retained at 120°C was $20 \mu\text{g g}^{-1}$, whereas in CTE-EC which had a higher iron content (5.9%) mercury retention was much lower ($8.5 \mu\text{g g}^{-1}$).

In order to confirm the effect of the iron species on mercury retention, an additional study was performed to evaluate the behavior of fly ash fractions enriched in iron oxides and impoverished fractions (magnetic and non magnetic fractions). XRD analysis of the magnetic fly ash fractions (CTL-M, CTE-M, CTSR-M) show a clear enrichment in iron oxides relative to the quartz and silicate phases. Predictably, the nonmagnetic fractions (CTL-NM, CTE-NM, CTSR-NM) contained more quartz and silicates than iron oxides. Figure 2 shows the diffractogram for the magnetic and nonmagnetic fractions of CTE. ICP-OES analysis of the magnetic fly ash fractions indicated variations in iron content, ranging from 6% to 33% (Table 1). No improvement in mercury retention capacity was observed in any of the magnetic fly ash fractions (Table 1). The mercury retention in CTL-M and CTSR-M was even slightly lower than in CTL-NM and CTSR-NM, respectively. These slight differences seem to be due more to carbon content (%LOI) than to iron content (Table 1).

The results presented above confirm that the iron species present in fly ashes do not have any capacity as mercury sorbents. The results also suggest that the iron species do not have any catalytic activity to improve the mercury retention in other components of the fly ashes. However, equally important as understanding the role of iron species in

mercury retention is the need to ascertain their role in mercury oxidation, since oxidized mercury can be more easily removed from gases than elemental mercury. To evaluate mercury oxidation from the data of the laboratory retention experiments, we used the mercury adsorption curves. Figure 3 shows an example of these curves for magnetic and nonmagnetic fly ash fractions. Because the continuous mercury analyzer employed in this study is only able to detect elemental mercury, if the sample curves reach the background line ($C_{out}/C_{in}=1$), this not only means that the samples have arrived at their maximum retention capacity but also that the mercury species in gas phase leaving the sorbent bed is elemental mercury and not oxidised mercury. As can be seen in Figure 3 the mercury retention curves are similar for both the nonmagnetic and the magnetic fractions. This proves that the iron oxides present in these fly ashes do not catalyse the oxidation of mercury.

An additional aim of this study was to evaluate the possible beneficial effect of a high iron-oxide content on the carbonaceous matter present in fly ashes. Retention experiments were performed on fly ash fractions enriched in iron oxides mixed with fly ash fractions enriched in unburned carbon. Figure 4 compares the mercury adsorption curves for CTL-EC and the mixture of CTL fractions enriched in carbon and iron content (CTL-ECM). It can be observed that the mercury retention for CTL-ECM (2.6% Fe) is similar to that in CTL-EC (0.6% Fe) (Figure 4). The background line ($C_{out}/C_{in}=1$) was reached in both cases, confirming that the presence of a high content in iron oxides does not influence the mercury retention capacity of carbon particles present in fly ashes. Moreover, no mercury oxidation was observed.

In summary, no correlation between mercury capture and the iron content of fly ashes was found either in the raw fly ashes or in the fractions enriched in carbon particles. Even when high iron-oxide concentrations were mixed with the carbon

material, mercury retention capacity was not improved. Although it has been reported that iron oxides may be an active component of fly ashes able to catalyze mercury oxidation, the results of this study suggest that iron species do not play any role in heterogeneous mercury oxidation.

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References

- [1] United Nations Environment Programme. Process Optimization Guidance Document for Reducing Mercury Emissions from Coal Combustion in Power Plants, Chemical Branch, DTIE, Geneva, Switzerland, Draft report, July 2010.
- [2] Dunham GE, DeWall RA, Senior CL. Fixed-bed studies of the interactions between mercury and coal combustion fly ash. *Fuel Process Technol* 2003;82:197-213.
- [3] Ghorishi SB. Fundamentals of mercury speciation and control in coal-fired boilers. EPA-600/R-98-014, February 1998.
- [4] Ghorishi SB, Lee CW, Kilgroe JD. Mercury speciation in combustion systems: studies with simulated flue gases and model fly ashes. *Proceedings of the Air & Waste Management Association 92nd Annual Meeting and Exhibition*, St. Louis, MO, June 20-24, 1999.

- [5] Ghorishi SB, Lee CW, Kilgroe JD. Speciation of mercury in the presence of coal and waste combustion fly ashes. Proceedings of the Air & Waste Management Association 93rd Annual Meeting and Exhibition, Salt Lake City, UT, June 19-22, 2000.
- [6] Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL et al. Status review of mercury control options for coal-fired power plants. Fuel Process Technol 2003;82:89-165.
- [7] Galbreath KC, Zygarlicke CJ, Tibbetts JE, Schulz RL, Dunham GE. Effects of NO_x, α -Fe₂O₃, γ -Fe₂O₃ and HCl on mercury transformations in a 7-kW coal combustion system. Fuel Process Technol 2004;86:429-48.
- [8] Galbreath KC, Zygarlicke CJ. Mercury transformations in coal combustion flue gas. Fuel Process Technol 2000;65-66:289-310.
- [9] Norton GA, Yang H, Brown RC, Laudal DL, Dunham GE, Erjavec J et al. Effects of fly ash on mercury oxidation during post combustion conditions. Final Report DOE Award No. DE-FG26-98FT40111 September 1, 1998 through November 30, 2001.
- [10] Norton GA, Yang H, Brown RC, Laudal DL, Dunham GE, Erjavec J et al. Role of fly ash on mercury chemistry in simulated flue gas streams. Proceedings of the Air & Waste Management Association 94th Annual Meeting and Exhibition, Orlando, FL, June 24-28, 2001.
- [11] Norton GA, Yang H, Brown RC, Laudal DL, Dunham GE, Erjavec J. Heterogeneous oxidation of mercury in simulated post combustion conditions. Fuel 2003;82:107-16.
- [12] Hower JC, Senior CL, Suuberg EM, Hurt RH, Wilcox JL, Olson ES. Mercury capture by native fly ash carbons in coal-fired power plants. Prog Energy Combust Sci 2010;36:510-29.

Figure captions

Figure 1. Mercury retention versus iron content in (a) raw fly ashes, (b) fly ashes post-retention at 120°C, (c) fly ashes enriched in unburned carbon particles (FA-EC) and (d) FA-EC post sorption at 120°C

Figure 2. XRD profiles of magnetic and nonmagnetic CTE fractions

Figure 3. Mercury adsorption curves in magnetic and nonmagnetic fly ash fractions

Figure 4. Mercury adsorption curves in enriched unburned carbon (EC) and a mixture of magnetic enriched and unburned carbon fractions (ECM)