

THE ROLE OF UNBURNED CARBON CONCENTRATES FROM FLY ASHES IN THE OXIDATION AND RETENTION OF MERCURY

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Abstract

During the combustion of coal in power plants Hg is released from the coal into the environment. Several technologies are under developed to reduce these emissions, but the need to implement new control systems will depend in part on the extent to which Hg can be captured in the fly ash. Previous studies have demonstrated that fly ashes may not only retain Hg species but also oxidize Hg⁰(g). This should be taken into consideration when developing technologies for Hg retention. The aim of this study is to acquire a better understanding of the interactions between Hg⁰(g) and fly ashes and to clarify the effect of unburned carbon and the flue gas composition upon the retention and oxidation mechanisms. A series of retention, oxidation and desorption experiments were carried out using lab-scale reactors. All the results obtained indicate that the interaction between Hg and fly ash is mainly chemical since the retention of Hg involves oxidation. Moreover, if the oxidation takes place in gas phase, condensation of oxidized mercury occurs. Carbonaceous matter is involved in most of the retention and oxidation mechanisms between Hg and fly ash. The carbon concentrates with the highest Hg retention capacity produce the highest Hg oxidation. The gas mixtures containing O₂ + CO₂ + SO₂ + H₂O were observed to increase Hg retention in the carbon concentrates from fly ashes. However, the presence of HCl in the mixtures may increase or decrease Hg capture. Heterogeneous oxidation was only significant in the fly ash fractions enriched in unburned carbon.

Keywords: mercury; fly ash; retention, oxidation

1. Introduction

The reduction of Hg emissions from coal combustion is a global objective with which the scientific community is becoming increasingly involved. According to the latest estimates on global Hg emissions, coal combustion power plants are responsible for nearly half of man-made Hg emissions, and are the largest industrial source of Hg entering the atmosphere [1-2]. Hg can remain airborne for up to one year making this not just a local problem but also one of global impact. This has led a number of national governments to introduce legislation aimed at enforcing tighter control over Hg emissions [3-4].

Hg in coal-fired power plants can be classified into three mainly forms: elemental mercury ($\text{Hg}^0(\text{g})$), oxidized mercury ($\text{Hg}^{2+}(\text{g})$) and particulate-associated mercury (Hg^{P}). Because the different modes of occurrence of Hg involve different physical and chemical properties it is necessary to analyze the Hg speciation in the flue gas. Hg^{2+} is soluble and has a tendency to associate with particulate matter. Consequently, emissions of gaseous oxidized Hg can be efficiently controlled by air pollution control devices, such as, electrostatic precipitators (ESP), fabric filters (FF) or flue gas desulphurization systems (FGD). In contrast, Hg^0 is extremely volatile and insoluble and is the species that is most likely to reach the stack [5].

Several full-, pilot-, and bench-scale studies have revealed that fly ashes can both adsorb and oxidize Hg in coal combustion flue gases [6-14]. A number of investigations have attempted to correlate Hg retention and oxidation with the content and characteristics of unburned carbon in raw fly ashes [15-17] and have found that, in general, Hg capture increases in fly ashes with a high carbon content [18]. However, the precise mechanisms by which the unburned carbon present in fly ash interacts with Hg species in gas phase are not yet well understood. This is partly due to the heterogeneous characteristics of the fly ashes and their generally low carbon content. When evaluating the role of carbon particles and the

influence of gas composition, the interactions between the gas species and the surface of the activated carbons should be taken into account [19-20]. In combustion atmospheres, it has been observed that chlorine and sulfur species may be absorbed onto the surface of activated carbons and that these species may modify the surface and influence Hg retention [21]. Bench-scale experiments by Yan et al. [22] have revealed that Hg^0 can be oxidized by Cl_2 to varying degrees depending on the concentrations of SO_2 , NO_x , CO present and the characteristics of the fly ash. However other studies have shown that it is the combination of fly ash + NO_2 + HCl + SO_2 that gives rise to the highest levels of Hg oxidation [13]. The influence of chlorine and fly ash particles on oxidation is borne out by several studies [5, 23] while the role of unburned carbon as the main component responsible for the enhancement of Hg oxidation and capture has also been confirmed [24]. Niksa et al. [25] have even proposed a possible mechanism whereby Hg oxidation may be catalyzed by unburned carbon.

In order to gain a better understanding of the relationship between flue gas composition, fly ashes and Hg retention and oxidation and to clarify the role of carbon particles in Hg behavior, this paper assesses the results of a lab-scale evaluation carried out at the lowest temperatures of the particle control devices (electrostatic precipitators and backhouses). Although some gaseous species like bromine are able to interact with Hg^0 [26] we have focused on the gaseous species that are commonly found in high concentrations in the capture particle systems of a coal combustion power plant. Two carbon particle concentrates were obtained from fly ashes of different origin and their Hg retention capacity and oxidation was evaluated in a series of gas mixtures. Desorption experiments were conducted to identify the Hg species retained in the fly ashes and assess their stability. In the light of the results obtained the fundamental mechanisms responsible for Hg retention and oxidation are discussed.

2. Experimental Section

Two fly ashes, denoted as CTL-O and CTE-O, obtained from pulverized coal combustion power plants were selected to carry out these studies. Whereas CTL-O came from the burning of bituminous coals, CTE-O was obtained from coal blends that are mainly made up of subbituminous coals. Moreover two fractions of these fly ashes enriched in unburned carbon particles (CTL-EC and CTE-EC) were used as part of the study. The fractions were obtained by subjecting the raw fly ashes to wet sieving. CTL-EC is the fly ash fraction of particle size higher than 100 μm and CTE-EC is formed by fly ash particles higher than 200 μm .

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. The oxygen content was determined by microanalysis using a LECO analyser (VTF-900) and chlorine concentration by means of oxidative high pressure digestion combined with ion chromatography. Atomic absorption spectrometry (AAS) was used to determine the elemental composition. The Brunauer-Emmett-Teller (BET) surface area was measured by volumetric adsorption of nitrogen at 77 K.

Thermodynamic equilibrium models using HSC-Chemistry 6.1 software were employed to theoretically predict the Hg compounds formed in the atmospheres tested.

The experimental device employed to retain Hg in the fly ashes at laboratory scale is shown in Figure 1. The fly ash bed was placed inside a glass reactor and was heated to 120°C. The sorbent bed was prepared by mixing 0.5 g of fly ash with 2 g of sand. Elemental mercury in gas phase obtained from a permeation tube was passed through the sorbent bed at 0.5 L min^{-1} . The Hg concentration in gas phase was 120 $\mu\text{g m}^{-3}$. The atmospheres tested consisted of one of the compounds O₂, CO₂, SO₂, H₂O or HCl in N₂ or any combination of them in identical proportions. It was assumed that by the time they reached the control particle

devices DeNOx would already have taken place. The duration of the Hg retention experiments varied depending on the type of fly ash but in general it was the time needed for the samples to reach their maximum retention capacity. A continuous mercury emission analyzer (VM 3000) was employed to monitor the Hg that was not retained during the sorption experiments. The total amount of Hg retained was determined by analysing the fly ashes post-retention using an AMA apparatus.

The oxidation of Hg was evaluated in an experimental device identical to the one used for mercury retention. However, first the Hg analyzer was replaced by a system of impingers known as the Ontario-Hydro Method (Figure 1). The Ontario-Hydro method is based on collecting Hg in different solutions capable of quantitatively and selectively retaining Hg⁰ and Hg²⁺. The error of the method, expressed as relative standard deviation, is <11% for Hg concentrations higher than 3 mg m⁻³, and <34% for Hg concentrations lower than 3 mg m⁻³ (ASTM D 6784-02).

3. Results and discussion

The results of the work are discussed on the basis of i) the retention of Hg in the raw fly ashes (CTL-O and CTE-O) and enriched unburned carbon fractions (CTL-EC and CTE-EC), ii) the homogeneous and heterogeneous oxidation of Hg and iii) the desorption of Hg species retained in the fly ashes.

3.1. Hg retention

CTL-O was found to have approximately twice the unburned carbon content (LOI: 5.6%) than that of CTE-O (LOI: 2.0%). When these fly ashes were concentrated in carbon, the fractions obtained, CTL-EC and CTE-EC, showed LOI values from 6 to 9 times higher, 35 and 18%, respectively. As a consequence, the surface area also increased in the enriched

carbon fractions (CTL-O: $4.1 \text{ m}^2 \text{ g}^{-1}$; CTL-EC: $24 \text{ m}^2 \text{ g}^{-1}$; CTE-O: $1.9 \text{ m}^2 \text{ g}^{-1}$; CTE-EC: $13 \text{ m}^2 \text{ g}^{-1}$).

The Hg retention capacities in all the gas mixtures tested in this study are shown in Table 1. As was expected, different amounts of Hg were captured depending on the gaseous species. However and as already noted in a previous work by the authors [27] no relation was found between fly ash inorganic components and Hg retention (Table 2).

Hg retention was similar in the N_2 , CO_2 and O_2 atmospheres for all the fly ashes. SO_2 and $\text{H}_2\text{O}(\text{g})$ only produced a decrease in Hg retention in the CTE-EC fly ash, whereas HCl was always accompanied by an increase in Hg capture. With different gas mixtures different behaviours were observed (Table 1). In general, regardless of the atmosphere used in the retention experiments, the amount of Hg retained in descending order was CTL-EC > CTE-EC > CTL-O > CTE-O. Therefore, as already reported in several studies [15-16, 18], a higher unburned carbon content favours the retention of Hg. In fact, the fly ash with twice the amount of unburned carbon content (CTL) shows twice the Hg retention capacity in most of the atmospheres studied. However, this proportion is not exactly maintained in the carbon concentrates (CTL-EC and CTE-EC) in the atmospheres of SO_2 , HCl, water vapour and $\text{O}_2 + \text{CO}_2 + \text{SO}_2$ (Table 1). It is inferred, therefore, that certain characteristics of the fly ashes themselves may cause different interactions between the gases and carbon particulates in the presence of certain gases.

3.1.1. Influence of sulfur dioxide and water vapour

As already mentioned SO_2 and $\text{H}_2\text{O}(\text{g})$ only modified Hg retention in the CTE-EC fly ash. The fall in Hg retention capacity observed may have been due to competition between SO_2 or $\text{H}_2\text{O}(\text{g})$ and Hg^0 for the bond sites of the fly ash. Both carbon concentrates (CTL-EC and CTE-EC) should have a similar effect on Hg retention. However, with these two gases

this is not the case. In order to find an explanation for this different behaviour of CTL-EC and CTE-EC in the SO₂ atmosphere, a flow of 0.2% SO₂ at 0.5 L min⁻¹ was passed through the fly ash concentrates during 15 hours before being subjected to a Hg retention experiment in a N₂ atmosphere (Treated SO₂ experiment). As can be seen in Figure 2, Hg retention in CTE-EC was lower not only in the SO₂ atmosphere compared to the N₂ atmosphere but also when the fly ash had been treated with SO₂. The reduction after treatment with SO₂ was greater in CTE-EC (72% reduction against 44% in CTL-EC) suggesting that more SO₂ had accumulated on the surface of this fly ash. This may be due to the fact that CTE-EC has higher oxygen concentration (2.4%) than CTL-EC (1.3%), which has been demonstrated that is related to be the ability to absorb SO₂ [28], so that molecules of SO₂ may be blocking the bond surface sites of this fly ash causing a reduction in Hg retention.

From a study of the adsorption isotherms of water vapor at 298 K (Figure 3) it can be seen that, in an N₂ atmosphere, the amount of water that CTL-EC and CTE-EC are able to adsorb is different. The amount of water that a material is able to adsorb is related to the concentration of hydrophilic groups (e.g. oxygen) it contains. CTE-EC has a higher concentration of oxygen groups than CTL-EC. Therefore, the higher amount of water adsorbed on the surface of CTE-EC (Figure 3) may make it more difficult to bind Hg, with a consequent reduction in Hg retention capacity (Table 1).

3.1.2. Influence of hydrogen chloride

Hg retention in a HCl atmosphere was higher than in N₂ for all the fly ashes tested (Table 1) and even in CTL-EC and CTE-EC saturation of the sorbent under this gas atmosphere was not attained. This could be due to HCl binding onto the surface of the fly ash as it does onto activated carbons [29], favouring Hg retention. To confirm this hypothesis the ashes with the lowest and highest Hg retention capacities, CTE-O and CTL-EC, were first treated with HCl gas at 0.5 L min⁻¹ during 15 hours and then, the samples were used as

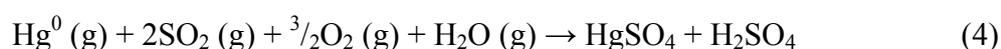
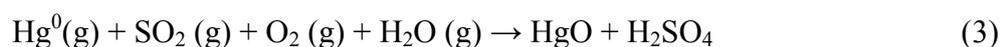
sorbents for Hg retention in a N₂ atmosphere (Treated HCl experiment). Contrary to what occurred in the SO₂ atmosphere (Figure 2), the amount of Hg retained was greater after treatment with HCl in both fly ashes than in the N₂ (Figure 4). Although the value was not as high as that obtained in the HCl atmosphere, both results suggest that HCl binds to the fly ash surface, favouring the retention of Hg. The chloride content was determined after HCl treatment and the concentration was higher (200 μg g⁻¹) than in the untreated fly ashes (20 – 60 μg g⁻¹). These results suggest that the mechanism of interaction between chlorine, Hg and the fly ash surface may be similar to that proposed by Gale et al. [24] i.e. that chlorinated-carbon sites form on the surface of the fly ash facilitating the capture of Hg⁰.

3.1.3. Gaseous mixtures

The first mixture studied was that made up of 10% O₂ + 16% CO₂ + 0.2% SO₂ in N₂. In this atmosphere Hg retention was similar to retention in simple gases for all the fly ashes with a slightly higher capture being observed in CTL-EC (Table 1). It is worth emphasizing that the inhibitor effect of SO₂ on Hg retention previously observed for CTE-EC disappears when SO₂, O₂ and CO₂ are together (Table 1). Therefore, new Hg compounds may form which can more easily be retained in fly ash especially when there is a high amount of carbon particles. As we have already pointed out, in most cases, the differences in Hg retention capacities between the atmospheres studied are only noticeable in the enriched carbon fractions of the fly ashes (Table 1). Theoretical thermodynamic studies carried out with the aid of the HSC Chemistry software show that the most probable Hg compound to form in this gaseous atmosphere is HgSO₄, although HgO is also possible. The possible reactions between Hg⁰ and these gases at 120°C would then be:



When the gas mixture made up of 10% O₂ + 16% CO₂ + 0.2% SO₂ + 3% H₂O in N₂ was tested, it was observed that the addition of water produces a significant increase in Hg retention in carbon concentrates. In fact, even after 67 hours of experimentation, saturation was not reached (Table 1). Therefore new reactions apart from (1-2) must have taken place between Hg and these gases which did not occur in the case of the simple gases in N₂. The fact that an increase in Hg retention capacity is only observed in CTL-EC and CTE-EC indicates again that these reactions take place on the surface of the carbon particles catalysing the reactions between Hg and the gaseous species. Moreover, the unburned carbon particles provide the necessary surface for retaining Hg. According to theoretical thermodynamic calculations the Hg compound to form at 120°C in this atmosphere with H₂O(g) are again HgSO₄ and/or HgO. The possible reactions that may then be:



It is known that the formation of HgO and HgSO₄ is thermodynamically more favourable in the presence of water vapour which may explain the increase in Hg retention.

In the atmosphere containing 10%O₂ + 16%CO₂ + 0.2%SO₂ + 3%H₂O + 50ppm HCl, Hg retention capacity is the highest in the raw fly ashes, with the exception of HCl atmosphere (Table 1). Interestingly, Hg retention in the enriched carbon fractions was lower in the gas mixture with HCl than in the same atmosphere without HCl (Table 1). As previously pointed out, SO₂ may have accumulated on the surface of the fly ashes and compete with HCl for the bond sites, thus displacing Hg from the surface [20]. This would explain the lower Hg retention observed for CTL-EC and CTE-EC. Several reactions between Hg and the gaseous compounds may take place in this gaseous mixture. According to thermodynamic calculations, HgCl₂ would be the most probable Hg compound to form in the

experimental conditions applied. It may then be partially displaced from the fly ash surface by SO_2 or another compound formed in the gas mixture, such as SO_3 or H_2SO_4 .

3.2. Hg oxidation

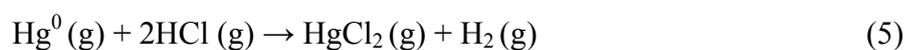
To evaluate the extent of Hg oxidation the Hg adsorption curves were used. The continuous Hg analyzer (VM 3000) has the capacity to detect Hg^0 . Consequently, if the curves reach the background line ($C_{\text{out}}/C_{\text{in}}=1$), this is not only because maximum retention capacity has been reached but also because the Hg species in gas phase leaving the sorbent bed is Hg^0 and not Hg^{2+} . Figure 5 shows the mercury adsorption curves in the fly ash samples for the entire gas mixture ($10\%\text{O}_2+16\%\text{CO}_2+0.2\%\text{SO}_2+50\text{ppmHCl}+3\%\text{H}_2\text{O}+\text{N}_2$). The background line was only reached by the raw fly ashes, but when the samples were analyzed after the retention experiments at different times all of them were found to be saturated. Thus, the shapes of the curves reveal that Hg oxidation has taken place in the enriched carbon fractions and that, at least, a part of the Hg^{2+} has not been retained. It can also be seen from Figure 5 that the behaviour of the two enriched carbon fractions is different: The oxidation is greater in the fly ash with a high unburned carbon content and Hg retention capacity (CTL-EC) (Table 1). To explain this different behavior it is necessary to distinguish between the Hg oxidation resulting from reactions with the gases present in the atmosphere (homogeneous oxidation) and the oxidation caused by the fly ashes enriched in carbon (heterogeneous oxidation).

3.2.1. Homogeneous oxidation

As already mentioned homogeneous oxidation was tested in the lab-scale experimental device (Figure 1) by replacing the fly ash sorbent bed with an empty reactor and using an Ontario Hydro impinger train device instead of a VM 3000 analyzer. Figure 6 shows the results for Hg^0 and Hg^{2+} in each one of the gas compositions studied. The results indicate that

no significant homogeneous oxidation reactions occur in the single gases under the experimental conditions of this study. However in the gas mixtures in which O₂ + SO₂ is present approximately 20% of oxidation was observed. From this, it can be inferred that SO₂ mixed with oxygen is the main factor responsible for the homogeneous oxidation of Hg. Although reactions (1) and (2) between Hg and these gases are theoretically possible, reaction (2) does not take place because solid HgSO₄ was not identified. The only gas species that might be present is HgO which would form through the reaction (1).

When H₂O(g) or H₂O(g) + HCl(g) were present in an atmosphere of O₂ + CO₂ + SO₂ the Hg oxidation percentages were found to be similar (Figure 6). Because the formation of HgSO₄ (reactions 2 and 4) can be discarded, in the absence of HCl, Hg oxidation would result from the formation of HgO(g) according to reaction (1) and/or through reaction (3). In the case of the atmosphere containing HCl, oxidation may also result from the formation of HgCl₂(g). Since HCl is more reactive, it is more likely that HgCl₂ to be the species formed through reactions (5-8)



3.2.2. Heterogeneous oxidation

Heterogeneous oxidation was evaluated in a series of tests in the lab-scale experimental device using sorbent beds of enriched carbon fly ash fractions (CTL-EC and CTE-EC). Figures 7-8 show the percentages of Hg²⁺ and Hg⁰ detected in the gas leaving the reactor, and the percentage of Hg that is retained in the ash which is referred to as particulate mercury (Hg^P). The atmospheres employed for CTL-EC were N₂, O₂, HCl, O₂+CO₂+SO₂,

$O_2+CO_2+SO_2+H_2O$ and $O_2+CO_2+SO_2+H_2O+HCl$ (Figure 7). In the case of CTE-EC only the atmospheres of principal interest (O_2 , $O_2+CO_2+SO_2+H_2O$ and $O_2+CO_2+SO_2+H_2O+HCl$) were evaluated (Figure 8).

In N_2 and O_2 , no oxidised Hg was detected in gas phase with CTL-EC, which means that, if Hg oxidation occurs, all the Hg^{2+} was retained in the sample (Figure 7). In the HCl atmosphere, where there was no homogeneous oxidation (Figure 6) most of the Hg was retained in the fly ash (Hg^p), the remaining Hg leaving as Hg^{2+} . Therefore, CTL-EC must have been involved in the oxidation of Hg in the HCl atmosphere. In the atmosphere containing $O_2+CO_2+SO_2$ the amount of Hg^{2+} collected at the exit of the reactor was similar (~20%) to that estimated in the case of homogeneous oxidation (Figures 6-7). This shows either that heterogeneous oxidation did not occur in this atmosphere or that all of the Hg^{2+} produced in heterogeneous oxidation was retained in CTL-EC. In the mixture of gases where HCl was absent, approximately 30% of the Hg in gas phase was in oxidised form (Figure 7), demonstrating that heterogeneous oxidation had occurred. Finally in the atmosphere containing all of the gases evaluated, the Hg^0 in gas phase constitutes 2% of the total amount (Figure 7), confirming that CTL-EC promotes Hg oxidation in the presence of HCl. This behavior can be attributed to one of several different mechanisms:

a) One mechanism is based on the assumption that the carbon particles catalyze the reaction between Hg and HCl following the reactions (9-11) [24]. According to this mechanism chlorine binds itself to the surface of the carbon particles and reacts with Hg^0 to form $HgCl$ which is later released as $HgCl_2$ after reaction with $HCl(g)$. The $HgCl_2$ thus formed may be released in gas phase when it reaches saturation or it may be displaced by other gaseous species present in the atmosphere.





b) Another possible mechanism of reaction between Hg and HCl in the presence of carbon particles is the oxidation of Hg^0 by the ion carbenium formed by the addition of a proton to a carbene [30-31].

The results obtained (section 3.1.2.) by treating the fly ash samples with HCl before the Hg retention experiments confirm that HCl binds itself to the surface of carbon particles prior to Hg is bonded (Figure 4). Moreover, as we saw, the Hg retention was lower in the mixture with HCl than in the same atmosphere without HCl (Table 1) as a consequence of a competition of the gases for the bond sites which displaces the Hg retained, giving rise to the high amount of Hg^{2+} in gas phase found in the atmosphere $\text{O}_2+\text{CO}_2+\text{SO}_2+\text{H}_2\text{O}+\text{HCl}$ (Figure 7).

In the case of the mixture of gases without HCl ($\text{O}_2+\text{CO}_2+\text{SO}_2+\text{H}_2\text{O}$), the amount of $\text{Hg}^{2+}(\text{g})$ leaving the reactor increases in the presence of carbon concentrates compared to that emitted in absence of fly ash (Figures 6-7). In addition to reactions (1) and (3) which explain the homogenous oxidation, when fly ash is present it may act as support for the formation of HgSO_4 . As already was mentioned, HgSO_4 should be in the form of a solid condensed on the fly ash, which would explain the larger amount of Hg retained by the fly ashes in this atmosphere than in other atmospheres such as O_2 or N_2 (Table 1). Although the most thermodynamically likely reaction in the $\text{O}_2+\text{CO}_2+\text{SO}_2+\text{H}_2\text{O}$ atmosphere is the formation of HgSO_4 , Hg could also be partially released as $\text{HgO}(\text{g})$. In the presence of HgSO_4 , $\text{HgO}(\text{g})$ may remain in gas phase, because the HgSO_4 may prevent it from binding itself to the fly ash. This would explain the increase in the amount of Hg^{2+} emitted (30%) in $\text{O}_2+\text{CO}_2+\text{SO}_2+\text{H}_2\text{O}$ gas mixture, in the presence of CTL-EC (Figure 7).

The CTE-EC carbon concentrate fraction showed a lower Hg retention capacity than CTL-EC (Table 1), and it might therefore be expected to have a lower capacity for

influencing the oxidation of Hg. In fact, when oxidation was evaluated in oxygen and in the gaseous mixtures both with and without HCl, a smaller percentage of Hg^{2+} was observed to leave the sorbent bed (Figure 8). The amount of Hg^{2+} emitted in the $\text{O}_2+\text{CO}_2+\text{SO}_2+\text{H}_2\text{O}$ and $\text{O}_2+\text{CO}_2+\text{SO}_2+\text{H}_2\text{O}+\text{HCl}$ atmospheres, was around 10 and 15%, respectively. These values are lower than those recorded for CTL-EC (Figure 7) which not only displayed twice as much Hg retention capacity as CTE-EC but also twice the unburned carbon content. This would also explain the different mercury adsorption curves obtained for CTL-EC and CTE-EC in the atmosphere containing all the gases (Figure 5). The oxidation values for CTE-EC were lower than those obtained during homogeneous oxidation (Figure 6) indicating that the Hg^{2+} species were retained in the carbon concentrates. Consequently, heterogeneous oxidation followed by retention cannot be ruled out, since the retention of Hg in the fly ash (Hg^{P}) would result from both homogeneous and heterogeneous oxidation.

3.3. Hg desorption

To evaluate the stability and to identify the Hg species retained in the carbon concentrates a series of desorption tests were carried out after Hg retention in different atmospheres by the Ontario-Hydro method. In this way it was possible to identify the Hg species that had been desorbed. N_2 was used as the carrier gas. The temperature selected for the experiments was 180 °C, higher than that of the retention experiments (120°C) and low enough to minimize the thermal reduction of the desorbed Hg. The desorption test was carried out using the carbon particle concentrate that had shown the highest capacity of Hg retention (CTL-EC) (Table 1) to minimize the risk of error arising from the use of the Ontario-Hydro method. Figure 9 shows the results as percentages of the Hg^0 and Hg^{2+} desorbed and the Hg remaining in the CTL-EC (Hg^{P}). As can be seen, Hg^{2+} was emitted from all the samples post-retention in all the atmospheres tested, including N_2 , confirming that this fly ash had retained oxidised mercury. The amount of $\text{Hg}^0+\text{Hg}^{2+}$ desorbed at 180°C ranged between 50 and 80 %

(Figure 9), whereas when the same sample was heated up to 240°C, approximately 65% of Hg remaining in the sample was desorbed as Hg⁰. Therefore, some of the Hg retained by the fly ash can be considered to be stable. The possibility of a thermal reduction of Hg²⁺ to Hg⁰ at 180°C was evaluated in a new run of retention and desorption experiments employing a permeation tube of HgCl₂ instead of Hg⁰ in the N₂ atmosphere. Hence any Hg retained and then desorbed would have to be HgCl₂. The results of desorption at 180°C showed that 69% of Hg was desorbed as Hg²⁺ (12%) and Hg⁰ (57%). Therefore, Hg²⁺ can be reduced to Hg⁰ during the retention-desorption experiments. Although the results of the desorption study demonstrate that heterogeneous oxidation did take place in this fly ash, the results are qualitative rather than quantitative.

4. Conclusions

The findings of this study indicate that the retention of Hg by the fly ashes occurs mainly as a result of a reaction between the Hg, the components of the ashes and the gases. In other words, it is essentially a chemical adsorption process that may be accompanied by the condensation of oxidized mercury in gas phase when homogeneous oxidation occurs. This would explain why it is the ashes with the highest Hg retention capacity that produce the highest Hg oxidation.

The species present in the gas are able to bind themselves to the surface of the fly ashes and alter their Hg retention capacity. Sometimes the retention capacity increased as in the case of the binding of chlorine whereas at other times it decreases as the case of SO₂ or H₂O(g).

Of all the gaseous species tested, HCl and SO₂ (the latter only in the presence of O₂) exerted most influence on Hg retention and oxidation. The homogeneous oxidation of Hg⁰ at 120°C occurred in a gaseous atmosphere containing O₂ + SO₂. In addition to SO₂ and O₂, if

the atmosphere also contained CO₂ and H₂O the proportion of Hg²⁺ emitted increased significantly in the presence of fly ash. The atmosphere containing only HCl increased Hg retention considerably and promoted Hg oxidation in the presence of fly ash. However, in the absence of ash there was not apparent reaction to Hg in the conditions studied in this work.

Carbonaceous matter was involved in most of the interactions between Hg and fly ash. This organic matter not only played an important role in Hg retention. It was also the principal medium via which the oxidation of Hg⁰ occurred.

Acknowledgments

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Table 1. Mercury retention by the fly ashes CTL-O, CTL-EC, CTE-O and CTE-EC in different atmospheres.

Atmosphere	Hg retention ($\mu\text{g g}^{-1}$)			
	CTL-O	CTL-EC	CTE-O	CTE-EC
N ₂	1.7	20	1.0	9.0
12.6% O ₂	1.8	20	1.1	8.5
20% O ₂	1.9	20	1.2	9.2
16% CO ₂	2.2	22	1.0	8.7
0.2% SO ₂	1.7	19	1.0	5.7
50 ppm HCl	21	250*	9.9	200*
3% H ₂ O	1.7	20	0.9	5.6
10%O ₂ + 16%CO ₂ + 0.2%SO ₂	2.1	29	1.1	8.9
10%O ₂ + 16%CO ₂ + 0.2%SO ₂ + 3% H ₂ O	1.7	310*	0.9	160*
10%O ₂ + 16%CO ₂ + 0.2%SO ₂ + 3% H ₂ O + 50 ppm HCl	8.5	35	4.4	17

* retention at 67 hours, no saturation.

Table 2. Elemental composition of the inorganic components of the fly ashes.

	CTL-O	CTL-EC	CTE-O	CTE-EC
SiO₂ (%)	55.8	36.1	58.5	41.0
Al₂O₃ (%)	27.6	23.8	23.7	25.7
Fe₂O₃ (%)	7.78	0.85	10.5	8.38
MgO (%)	0.89	0.43	1.03	0.67
Na₂O (%)	0.36	0.35	0.88	0.41
K₂O (%)	0.62	0.61	1.54	1.05
CaO (%)	0.38	1.55	0.32	3.53
TiO₂ (%)	0.55	0.30	0.66	0.33
SO₃ (%)	0.21	0.27	0.83	0.62

Figure captions

Figure 1. Schematic diagram of the experimental device used for mercury retention and oxidation at laboratory scale

Figure 2. Mercury retention by CTL-EC and CTE-EC in a N₂ and a SO₂ atmosphere and in N₂ after treatment of the fly ashes with SO₂.

Figure 3. Water vapor isotherms at 298K corresponding to CTL-EC and CTE-EC

Figure 4. Mercury retention by CTE-O and CTL-EC in a N₂ and a HCl atmosphere and in N₂ after treatment of the fly ashes with HCl.

Figure 5. Mercury adsorption curves in raw (O) fly ashes and enriched unburned carbon (EC) fly ash fractions in a coal combustion atmosphere (10%O₂+16%CO₂+0.2%SO₂+50ppmHCl+3%H₂O+N₂)

Figure 6. Percentages of Hg⁰ and Hg²⁺ in the different atmospheres studied.

Figure 7. Mercury speciation in different gas compositions in the presence of fly ash CTL-EC.

Figure 8. Mercury speciation in different gas compositions in the presence of fly ash CTE-EC.

Figure 9. Mercury speciation after the desorption tests carried out on mercury retained in fly ash CTL-EC in different gaseous atmospheres.

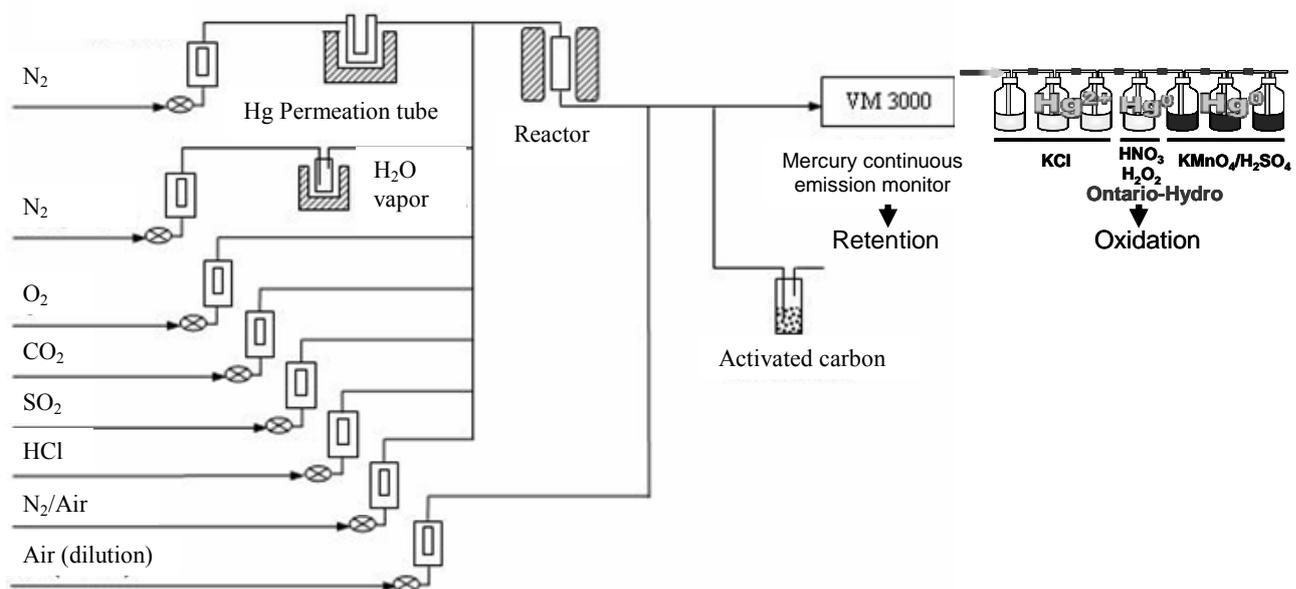


Figure 1.

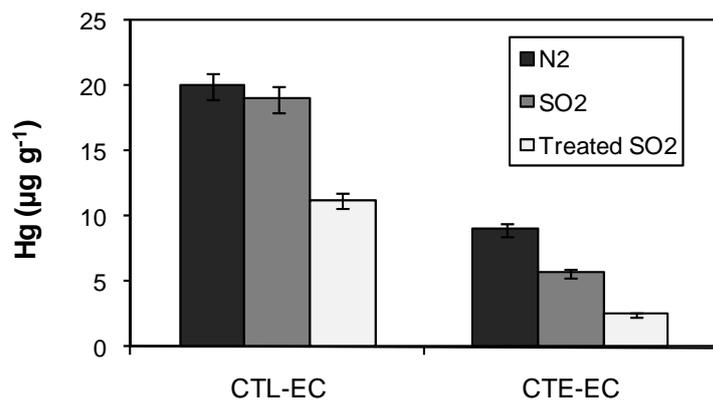


Figure 2.

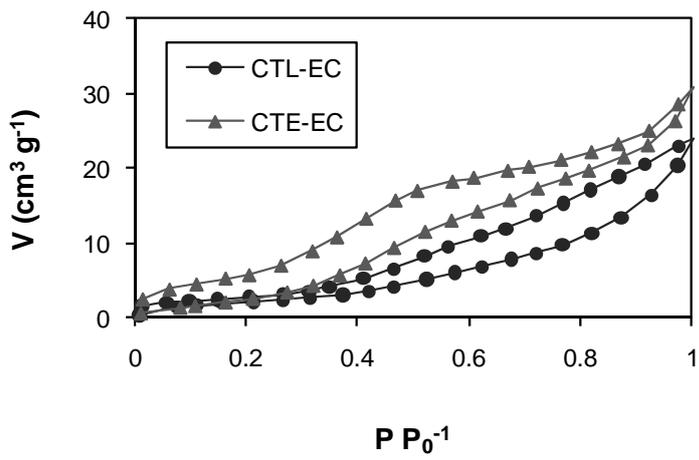
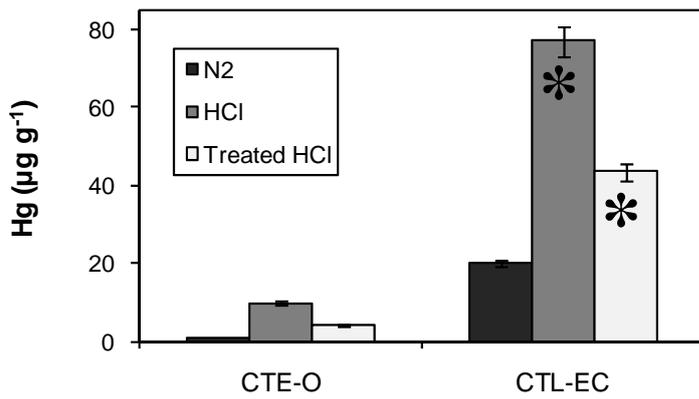


Figure 3.



* = retention at 15 hours, no saturation.

Figure 4.

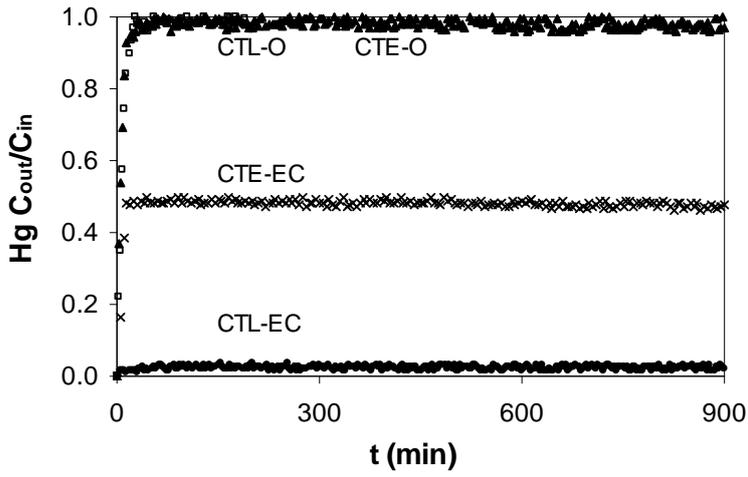


Figure 5.

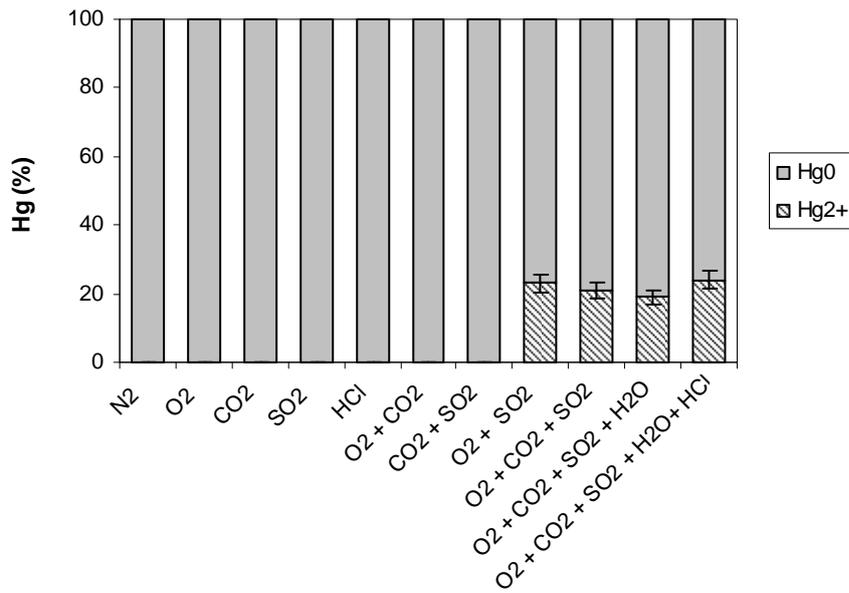


Figure 6.

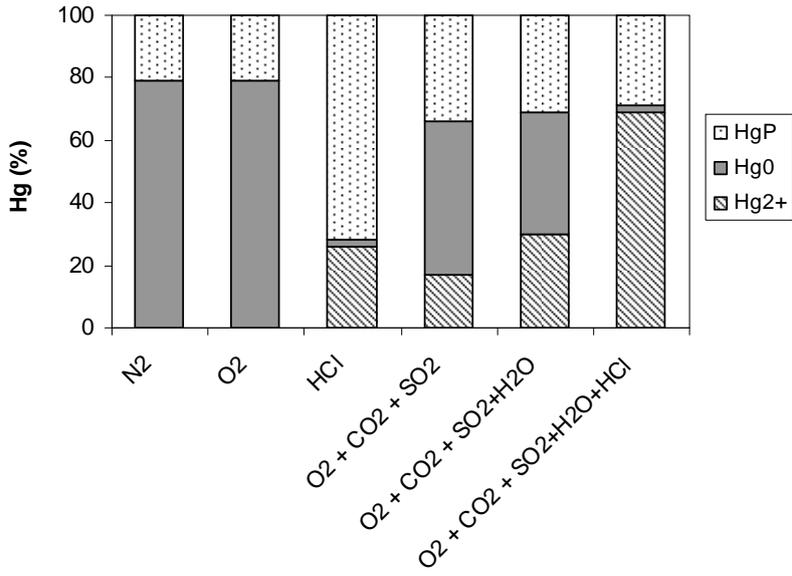


Figure 7

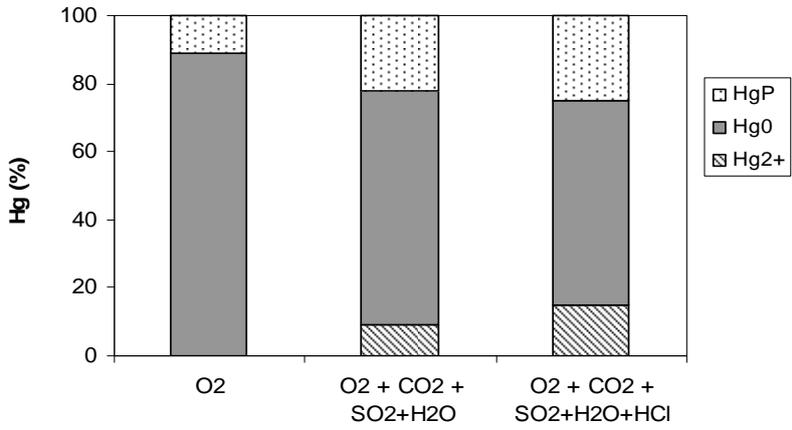


Figure 8

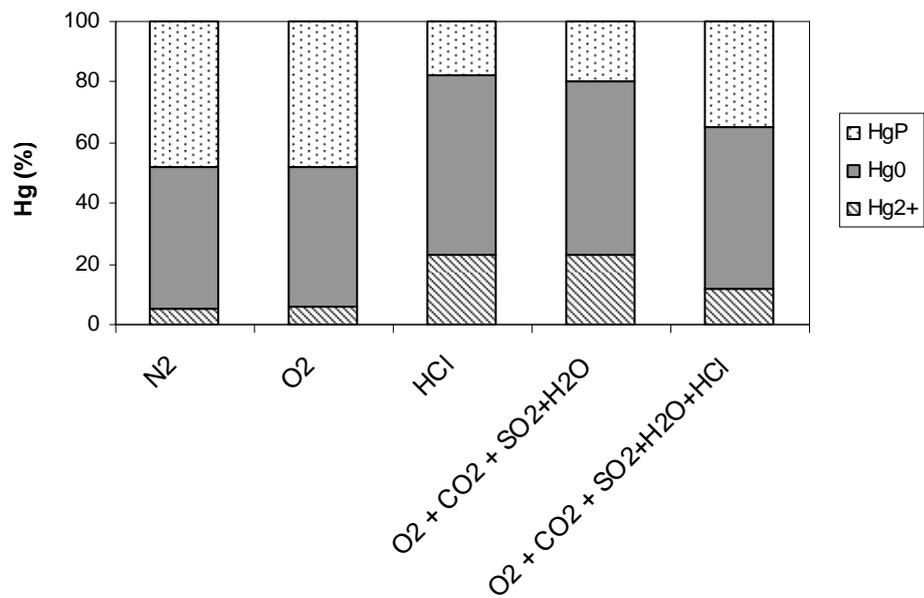


Figure 9