**Influence of a CO₂-enriched flue gas on mercury capture
by activated carbons**

M.A. Lopez-Anton*, M. Rumayor, M. Díaz-Somoano, M.R. Martínez-Tarazona

Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe, 26, 33011, Oviedo, Spain

*Corresponding author:

Phone: +34 985 119090

Fax: +34 985 297662

Email: marian@incar.csic.es

Abstract

The main environmental problem caused by the production of energy from coal combustion is the emission of CO₂. One emerging technology designed for CO₂ capture is oxy-combustion. Among other issues to be solved in oxy-combustion power plants is the presence of mercury as this may damage the CO₂ compression unit. Hence the study of the behavior of mercury in oxy-combustion is of great interest both from an environmental and a technological point of view. The present study performed at laboratory scale evaluates the retention of mercury in a CO₂-enriched flue gas using the same activated carbon before and after it has been impregnated with sulphur and proposes a mechanism to explain the interactions between mercury and activated carbons. The results show that carbonyl and quinone groups are responsible for mercury oxidation and retention in the carbons. Although the contact time between mercury and the activated carbon surface limits the amount of mercury that can be captured, high retention capacities can be achieved in an oxy-combustion atmosphere. The presence of water, in high concentrations in oxy-combustion, may compete for the same active sites (carbonyl groups) as mercury, thereby inhibiting mercury adsorption on the surface of the activated carbons. Moreover, the presence of sulphur in the impregnated material, which is the key to mercury capture in other atmospheres, does not modify mercury capture in oxy-combustion.

Keywords: mercury retention; activated carbons; oxy-combustion

1. Introduction

It is well known that CO₂ is the main greenhouse gas emitted through human activities. In 2012, 6.5 million metric tons of CO₂ were emitted to the air [1] even considering that 2012 was a relatively good year in which emissions increased by only 1.1%, less than half of the average annual increase of 2.9% over the last decade [2]. The main anthropogenic source of CO₂ emissions is the combustion of fossil fuels, mostly coal. Between 2009 and 2010, CO₂ emissions from the combustion of coal increased by 4.9% due mainly to the growing energy demand of developing countries such as China and India [3]. The use of more efficient plants and end-use technologies as well as the increased use of renewables and carbon capture and storage (CCS) technologies could help to reduce CO₂ emissions from coal.

Oxy-combustion is a candidate technology for CCS. The basic concept behind oxy-combustion is the replacement of combustion in air by combustion in a mixture of oxygen and recycled flue gas and/or water for temperature control. The remaining flue gas is rich in carbon dioxide and water vapor, and is easily separated, producing a stream of CO₂ ready for utilization or sequestration. However, oxy-combustion still presents many challenges that need to be analyzed and investigated before its commercial application, such as capital cost, energy consumption, operational challenges of supplying O₂ to the combustion system, air infiltration that dilutes the flue gas with N₂, etc. [4]

A significant part of the risk associated with oxy-combustion comes from the trace species present in the stream of CO₂. These traces make it necessary to apply gas-cleaning protocols in oxy-combustion in order to remove emissions and corrosion problems. This is the case of mercury species which can form an amalgam with aluminium resulting in the corrosion of the heat exchanger elements in the CO₂

processing units of oxy-combustion plants [5,6]. Mercury is also an element of environmental concern. Coal-burning power plants are the largest human-caused source of mercury emissions to the air since they are responsible for emitting approximately 475 tonnes of mercury per year [7]. Furthermore, once in the environment mercury can be transported over long distances through the atmosphere. Not surprisingly the environmental problems of mercury have led to the implementation of stringent regulations by different countries [8-11].

Until now the principal process studied and employed to reduce mercury emissions in power plants has been the use of solid sorbents, mainly activated carbons. Numerous studies have been carried out at laboratory and industrial scale in the search for economically feasible activated carbons able to retain mercury efficiently [12-14]. Activated carbons from different raw materials have been used to capture reactive mercury species [15-17], but to retain elemental mercury (Hg^0) chemical impregnated sorbents are generally necessary [18-21]. The efficiency of these activated carbons depends on characteristics such as particle size, surface area, porosity, etc., but it is also conditioned by the conditions in which the process of coal combustion is carried out, such as gas composition, temperature, etc. that may modify not only mercury speciation in the gas stream but also the functional groups present on the activated carbon surface. Several studies have shown the important influence that the gas composition has on the behavior of activated carbons for mercury capture [19,20,22]. O_2 improves mercury retention [20,23] whereas reactive gases such as SO_x and NO_x may modify the surface of the carbons and favor or inhibit mercury adsorption [24-27]. Other gases such as H_2O may also play an important role in the mechanism of Hg adsorption on the surface of the activated carbon [20,28-30], and it has also been suggested that CO_2 might compete with Hg for the same adsorption sites [22]. In general, the study of the mechanism of

mercury capture on activated carbon is based not only on the interactions between mercury and carbon but also on the competitive reactions of these gases with the solid. Special attention has been paid to the role of SO_x and the formation of sulfuric acid (H₂SO₄) [22,24-27] which may condensate on the carbon surface in different amounts preventing the adsorption of Hg⁰ or favouring the reaction with mercury to form Hg₂SO₄ [20]. Most of the knowledge acquired until now on Hg-activated carbon interactions has been obtained from studies carried out in atmospheres typical of coal combustion in air but there is a lack of similar knowledge on the interactions of Hg-activated carbons in oxy-combustion atmospheres. In these atmospheres, CO₂ is the main component but there is also a high amount of H₂O vapor (up 30%) [31] and SO₂ and SO₃ are present in different proportions [32-33].

As previously pointed out, oxy-combustion plants still need to address several problems, one of which is the potential change in the behaviour of Hg with respect to combustion in air. This issue needs to be addressed not only for environmental but also for technological reasons. In this work, a laboratory scale study was carried out to evaluate the capacity of an activated carbon to capture elemental mercury in oxy-combustion conditions before and after being impregnated with sulfur. The main goal is to understand the mechanism of interaction between mercury and activated carbon in these conditions.

2. Experimental part

Two previously characterized [21,34] commercial activated carbons were used as mercury sorbents: Norit RB3 and Norit RBHG3. The peculiarity of these carbons is that Norit RBHG3 was prepared by impregnating Norit RB3 (a peat-based, steam-activated

carbon) with sulphur compounds to be used for mercury retention. These activated carbons were employed in a particle size of 0.2-0.5 mm.

The laboratory device used for mercury experiments is shown in Figure 1. The experimental device consists of: i) a system to generate a stable concentration of Hg^0 in gas phase, ii) a gas blending station where the gas composition is prepared, iii) a glass reactor heated by a furnace and fitted with a thermocouple and iv) a system for analyzing the mercury species. Bronkhorst mass flow controllers were used to control the gas flow into the system. The transfer lines for the mercury are made of PTFE (polytetrafluoroethylene) and, for the rest of the gases, of 316 stainless steel tubes with a diameter of $\frac{1}{4}$ in.

The following experimental conditions were applied: i) a Hg^0 concentration of $100 \mu\text{g}\cdot\text{m}^{-3}$ obtained by means of a VICI Metronic calibrated permeation tube, ii) a synthetic gas mixture consisting of one of the compounds O_2 , SO_2 , NO , NO_2 , HCl , H_2O , CO_2 and N_2 , or any combination of them in identical proportions, iii) a sorbent bed prepared with 1000 mg of activated carbon and maintained at 150°C , and iv) a continuous Hg gas analyzer (VM 3000) used to monitor the Hg^0 . The Hg^{2+} was determined by capturing it in an ion exchanger resin (Dowex® 1x8), suitable for the selective extraction of Hg^{2+} species [35]. The resin was conditioned with a solution of $\text{HCl}:\text{H}_2\text{O}$ (1:1) at 90°C for 30 minutes and then filtered and dried. The resin was placed prior to the Hg^0 continuous analyzer (Figure 1) in such a way as to ensure that the mercury balance was closed. The Hg^{2+} in the resin at the end of the experiments was determined by means of an automatic mercury analyzer (AMA 254). The total mercury content of the sorbent after the retention experiments was determined by AMA.

The following gas compositions were used to carry out the mercury retention experiments: i) 100% N_2 , as the inert atmosphere, ii) 4% O_2 , 1000ppm SO_2 , 1000ppm

NO, 100 ppm NO₂, 25 ppm HCl, 12% H₂O, 64% CO₂ and 20% N₂, as the simulated oxy-combustion atmosphere, iii) 100% N₂, after the samples had been subjected to an oxy-combustion atmosphere as the N₂(treat.oxycomb) atmosphere iv) 4% O₂, 1000ppm SO₂, 1000ppm NO, 100 ppm NO₂, 25 ppm HCl, 6% H₂O, 16% CO₂ and 74% N₂, as simulated coal combustion in air and v) 4% O₂, 1000ppm SO₂, 1000ppm NO, 100 ppm NO₂, 25 ppm HCl, 64% CO₂ and 32% N₂, as the dry oxy-combustion atmosphere.

The water vapour at the outlet of the reactor was condensed and collected in two flasks prior to the VM analyzer. The content of mercury condensate in this water was determined by AMA. The sulphate retained in the condensate was determined by ionic chromatography.

The activated carbons were characterized before and after the mercury experiments. The surface oxygen groups were analyzed by temperature-programmed desorption (TPD) using an Autochem II analyzer coupled to an OmnistarTM mass detector in an argon atmosphere.

3. Results and discussion

The main characteristics of the activated carbons have been evaluated in previous works [21,34]. They have an ash content close to 6% and the sulphur content in RB3 is 0.4% whereas it is 6% (wt) in the carbon impregnated RBHG3. RB3 was impregnated by making the surface of the activated carbon a reactive medium for elements capable of reacting with sulphur [21]. The textural parameters indicate that the activated carbons are microporous materials. The adsorption isotherms of nitrogen belonged to type I of the BDDT classification (typical of microporous solids), with only minor participation of type IV. The nitrogen adsorption isotherms yielded BET surface area values of 1183 m²g⁻¹ (RB3) and 868 m²g⁻¹ (RBHG3). Fitting the Dubinin-Radushkevich (DR) equation

to the CO₂ adsorption isotherms at 273 K yielded micropore volumes of 0.37 cm³g⁻¹ (RB3) and 0.30 cm³g⁻¹ (RBHG3), and equivalent micropore surface areas of 1009 m²g⁻¹ (RB3) and 830 m²g⁻¹ (RBHG3) [21,34].

Information about the functional groups that decompose below 1200°C was obtained by means of TPD analysis. Carboxylic acids and lactone groups evolve CO₂ upon heating, while carboxylic anhydride produces both CO and CO₂. CO is derived from phenols, ethers and carbonyl/quinone groups [36,37]. Previous studies have suggested that oxygen functional groups, such as, lactone and carbonyl, may be active sites that favour mercury adsorption whereas phenol groups inhibit mercury adsorption [15,28,38,39]. To identify the functional groups on the carbon surface and to clarify the modifications that occur during the process due to interaction with the components of the oxy-combustion atmosphere, the TPD profiles of i) the raw materials (RB3 and RBHG3), ii) RB3 and RBHG3 after being subjected to an atmosphere free of mercury (RB3/RBHG3 treat.oxycomb), iii) the carbons subjected to the same atmosphere containing Hg (RB3/RBHG3 oxycomb_Hg), and iv) the solids obtained after being subjected to an oxy-combustion atmosphere but now in an inert atmosphere containing mercury (RB3/RBHG3 treat.oxycomb_Hg), were evaluated and compared (Figures 2,4,5).

Figure 2 shows the TPD profiles for the raw activated carbons (RB3, RBHG3) and the activated carbons treated for 24 h in the oxy-combustion atmosphere free of mercury (RB3/RBHG3 treat.oxycomb). The TPD plots for RB3 and RBHG3 are similar. In fact RBHG3 is the same carbon as RB3 except that it is impregnated with sulphur. CO is more abundant than CO₂, and an appreciable peak corresponding to the evolution of CO can be observed at 700-1000°C. The surface chemical structures that correspond to these peaks are likely to be quinines and carbonyl groups (black line). The peak

evolution of RB3 and RBHG3 treated in the oxy-combustion atmosphere (grey line) indicates an increase in oxygenated groups. A peak centred at 250°C due to the release of CO₂ can be attributed to the decomposition of carboxylic acid. However, this sharp peak could also correspond to the decomposition of acidic groups formed as a result of the acid atmosphere to which activated carbons were subjected. From the release of CO, carbonyls and quinones (peaks centered at 850°C) can be identified and the peak centred at low temperatures up to approximately 800°C, probably corresponds to the decomposition of phenols and ethers.

The percentage of mercury retained in the carbon and the percentages of the total oxidized mercury (Hg²⁺) in the gas stream resulting from homogeneous (gas-gas interaction) and heterogeneous (gas-solid interaction) oxidation are presented in Table 1. The rest of the mercury remains as elemental mercury (Hg⁰(g) out). The mercury adsorption curves in the N₂ and oxy-combustion atmospheres are shown in Figure 3. RBHG3 retains Hg⁰ with an almost 100% efficiency in the N₂ atmosphere (Figure 3b), as might be expected of an activated carbon impregnated with sulphur in which chemisorption and/or reaction between the sulphur compounds and mercury occur mainly via the formation of HgS. Mercury oxidation does not occur in the inert atmosphere. However, when the activated carbons are tested in the oxy-combustion atmosphere they show a different behaviour that may be described as follows: i) the mercury retention obtained with RBHG3 is lower than that obtained in the N₂ atmosphere and ii) a high oxidation (75-80%) is produced in both activated carbons. As already mentioned Hg²⁺ is a result of homogeneous and heterogeneous oxidation. In a previous study carried out by the authors [40] in which homogeneous mercury oxidation in the same oxy-combustion atmosphere was evaluated, 30±10% Hg²⁺ was formed. Therefore both activated carbons (with and without sulphur), oxidize mercury in similar

proportions (~45-50%) but retain very little of it. This can be appreciated from Figure 3. The concentration of Hg^0 arriving at the VM analyser is $25 \pm 3 \mu\text{g m}^{-3}$ (the baseline) (dotted line). When the sorbent reaches its maximum retention capacity and/or no oxidation is produced the signal should have reached this baseline. Therefore, in the case of RB3 in the oxy-combustion atmosphere and RBHG3 in both the N_2 and oxy-combustion atmospheres, the mercury may have been retained or oxidized. From the results obtained with the resin suitable for the selective extraction of Hg^{2+} (Table 1), in the case of RB3 and RBHG3 in oxy-combustion it appears to be mainly due to mercury oxidation (75-80%).

The ability of the carbon surfaces to catalyse mercury oxidation has been explained by equilibrium considerations on the carbon surface [41-42]. Hg^0 can be converted to Hg^{2+} losing its two 6s electrons of the electronic configuration. Therefore, the mechanism of oxidation is favoured by reactions of type I (quinonoid complexes) which can accept mercury electrons.

The oxygenated surface groups, such as lactones and carbonyls or quinones, will then act as electron acceptors facilitating the electron transfer process (mercury oxidation) on the activated carbon surface which acts as an electrode [15,28].

Figure 4 shows the TPD plots for the activated carbons after being used as mercury sorbents in the oxy-combustion atmosphere (RB3/RBHG3 oxycomb_Hg). It can be seen that the number of oxygenated groups has increased notably and that CO decomposition is now centred at 700°C (phenols and ethers) instead of at 850°C (carbonyls and quinones) as in the case of the RB3/RBHG3 treat-oxycomb samples (Figure 2). This fact corroborates the reaction: quinines + $2\text{H}^+ + 2\text{e}^- \rightarrow$ phenols (I) which will facilitate the electron transfer process, i.e. mercury oxidation [15,28,38,39]. To explain the

decrease in mercury retention in activated carbons in the oxy-combustion atmosphere different competitive reactions need to be taken into consideration: i) the high proportion of CO₂ present in the gas composition might be occupying a part of activated carbon microporous structure competing for the same adsorption sites as mercury [22], ii) the H₂O molecules in the flue gas (in oxy-combustion they may be present in concentrations of up to 30%) might be adsorbed into the micropore structure of the activated carbon reducing the number of active sites for mercury adsorption [12,24,43-45], (iii) a higher proportion of oxidation of SO₂ to SO₃ that could occur during oxy-combustion [33,46] will inhibit mercury adsorption because SO₃ will be competing with mercury for the same binding sites [19,25,30,47]. The role of SO₃ is not clear. In some research works it has been found that SO₃ in flue gases can originate H₂SO₄ on the surface of the activated carbon, which will enhance Hg⁰ adsorption. The discrepancies found in the literature in relation with this phenomenon have been ascribed to kinetic limitations in the reaction between Hg and H₂SO₄ or to pore blockage of the binding sites for mercury adsorption caused by the H₂SO₄ present on the surface [20].

To clarify these matters a series of experiments was carried out. The first involved a test in which the mercury retention capacity of activated carbons was evaluated in an atmosphere with small concentrations of CO₂ and H₂O (1000 ppm SO₂, 1000 ppm NO, 100 ppm NO₂, 25 ppm HCl, 4%O₂, 16%CO₂, 6%H₂O and N₂). This can be considered an atmosphere similar to one of coal combustion in air. The results obtained were similar to those of oxy-combustion and the same oxygen functional groups were identified by TPD. Therefore, it can be concluded that the high concentration of CO₂ present in oxy-combustion does not inhibit the adsorption of mercury on the activated carbons studied.

The second set of mercury retention experiments was carried out in a dry oxy-combustion atmosphere to evaluate the effect of water. With the absence of water in the flue gas, a higher mercury retention ($15\pm 5\%$) was achieved. Therefore, it can be concluded that the presence of water vapour in the flue gas, even in relatively low percentages of around of 6%, reduces the number of active sites on the activated carbons available for mercury removal.

Finally RB3 and RBHG3, previously treated in the oxy-combustion atmosphere, were tested for mercury retention in an inert atmosphere (N_2). Mercury retention capacities of the order of 80-85% were achieved with both carbons (Table 1). These results reveal that the formation of H_2SO_4 on the surface of the activated carbon does not lead to blockage of the pores but improves Hg^0 adsorption via oxidation on the carbon surface. This mechanism has been previously proposed [20]. The analysis of the condensates obtained by cooling the gases (Figure 1) corroborates the presence of sulphates in the water.

Kinetic limitations in the reaction between Hg and H_2SO_4 are the cause of the low mercury retention capacity obtained in the oxy-combustion atmosphere. The sorbent-gas contact time in this study is lower than 1 second, similar to the contact time when activated carbon is injected into a coal-fired power plant. This is not enough time for the reaction to take place. However, when the activated carbons were treated in the oxy-combustion atmosphere (RB3/RBHG3_{treat.oxy-comb}) previous to the Hg^0 retention test, adsorption was occurred. Moreover, the TPD plots obtained with these samples (RB3/RBHG3_{treat.oxycomb_Hg}) (Figure 5) show that mercury bonding on the carbon surface is probably associated with carbonyl/quinone groups. The signal corresponding to CO decomposition for RB3/RBHG3_{treat.oxycomb_Hg} sharply decreased (Figure 5) in contrast with the signal obtained for the RB3/RBHG3_{oxycomb_Hg} (Figure 4). The

fall of the signal might be due to mercury adsorption giving rise to new C-O groups (Figure 6) most of which would not decompose at 400-1000°C in the CO profile.

4. Conclusions

From the interaction between activated carbons and Hg^0 in a CO_2 -enriched flue gas typical of oxy-combustion, the predominantly formed species is Hg^{2+} . This is a consequence not only of homogeneous mercury oxidation by the gases present in oxy-combustion but also of the oxidation of Hg^0 on the activated carbons. The carbonyl and quinone groups are responsible for mercury oxidation and retention in the activated carbons with and without sulphur. Although the kinetic limitations of Hg and H_2SO_4 must be taken into consideration, high mercury retention capacities can be achieved in an oxy-combustion atmosphere. The presence of water in the flue gases is a limitation for mercury capture because the water may compete for the same active sites (carbonyl groups) as mercury, thereby inhibiting its adsorption.

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Table 1. Percentages of mercury retention and homogeneous and heterogeneous mercury oxidation corresponding to the activated carbons in different atmospheres.

Sample	N ₂			Oxycomb.			N ₂ (treat.oxycomb)		
	Hg ret. (%)	Hg ²⁺ (g) _{out} (%)	Hg ⁰ (g) _{out} (%)	Hg ret. (%)	Hg ²⁺ (g) _{out} (%)	Hg ⁰ (g) _{out} (%)	Hg ret. (%)	Hg ²⁺ (g) _{out} (%)	Hg ⁰ (g) _{out} (%)
RB3	<1	n.d	99±1	6±1	80±5	14±7	80±8	5±2	15±6
RBHG3	90±10	n.d	10±5	4±1	75±5	21±2	85±7	4±3	11±5

Oxycomb.: simulated flue gas of oxy-combustion; Hg ret.: mercury retention capacity; Hg²⁺(g)_{out}: mercury oxidized by homogeneous and heterogeneous oxidation; n.d.: not detected

Figure captions

Figure 1. Schematic diagram of the experimental device used for mercury retention

Figure 2. TDP profiles of (a) CO evolution and (b) CO₂ evolution in the raw activated carbons (RB3 and RBHG3) and activated carbons treated over 24 h in an oxy-combustion atmosphere (RB3/RBHG3 treat.oxycomb)

Figure 3. Mercury adsorption curves obtained for (a) RB3 and (b) RBHG3 activated carbons in N₂ and oxy-combustion atmospheres

Figure 4. TDP profiles of (a) CO evolution and (b) CO₂ evolution in the activated carbons employed as mercury sorbents in an oxy-combustion atmosphere (RB3/RBHG3 oxycomb_Hg)

Figure 5. TDP profiles of (a) CO evolution and (b) CO₂ evolution in the activated carbons treated in oxy-combustion after being used as mercury sorbents in a N₂ atmosphere (RB3/RBHG3 treat.oxycomb_Hg)

Figure 6. Mechanism of mercury adsorption on activated carbon

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6