Mercury capture by a structured Au/C regenerable sorbent under oxycoal combustion representative and real conditions

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ABSTRACT

The environmental implications of mercury do not correspond only to the emissions to the atmosphere; the quality of the captured CO₂ to be transported and sequestered has been subject of research, concerning trace quantities of heavy metals participating in mineralization and precipitation reactions in sequestration conditions. For oxycoal combustion, mercury is not an environmental issue alone but also an operational issue, particularly about where mercury could accumulate within the CO₂ processing unit. Therefore, Hg removal is necessary to prevent its attack on the aluminium heat exchangers. In this work, a regenerable sorbent based on carbon supported Au nanoparticles (0.1% wt) has been used for Hg capture under oxycoal combustion atmosphere. The influence of the presence of O₂, NO, SO₂ and HCl in a gas containing Hg and CO₂ on the sorbent as well as on the Hg oxidation (Au can act as an oxidation catalyst) has been evaluated under a simulated flue gas. The presence of either NO or HCl in the simulated flue gas led to mercury oxidation, with oxidized mercury not evolving in the gas, indicating that it is retained on the sorbent; the oxidized mercury is well stabilized on Au surfaces of the sorbent and favours the Hg-Au amalgam formation. This sorbent has been also evaluated in 3 kWth oxycoal bubbling fluidized bed combustor. A lignite with high sulphur content was burned in presence of limestone. Despite high SO₂ concentration that reached the Au/C sorbent, high capture efficiency was achieved and breakthrough occurred after 3.5 h and 10% breakthrough is not reached during the experiments. Bearing in mind that regeneration time can be adjusted near 1 h, two swing sorbent beds could be used to control mercury emissions under oxycoal combustion conditions.

Keywords: mercury retention; regenerable sorbent; oxycoal combustion

1. INTRODUCTION

The fate of mercury during coal combustion has been deeply studied and it has been reported that it depends on combustion system, coal type, and existing APCD (Air Pollution Control Devices) configuration, which affect the form and speciation of mercury that is emitted to the atmosphere and the difficulty in controlling the emission of mercury to the atmosphere [1].

Hg speciation changes from pure Hg^0 vapour at the furnace exit to different mixtures of Hg^0 , Hg^{2+} , and Hg_p (particle-bound mercury) as the flue gas moves through the APCDs depending on the levels of Cl and unburned carbon [2]. If the power plant is provided with particulate matter control and desulphurization systems, Hg^0 should be the main form that could be released to the atmosphere [2].

The environmental implications of mercury do not correspond only to the emissions to the atmosphere; the quality of the captured CO_2 to be transported and sequestered has been subject of research, concerning trace quantities of heavy metals participating in mineralization and precipitation reactions in sequestration conditions [3]. In addition, for oxycoal combustion mercury is not only an environmental issue but also an operational issue, particularly about where mercury could accumulate within the CO_2 processing unit and attack the aluminium heat exchangers [4, 5].

Up to now, there is not an accepted value of mercury emissions that could be tolerated in the CO_2 processing unit; however, the standard of $0.01 \mu\text{g}/\text{m}^3$ set by the natural gas industry is one of the considered values, despite the differences among both type of industries: in natural gas processing, a failure of aluminium based equipment could cause an explosion due to the release of combustible natural gas but the release of CO_2 rich flue gas would not cause this fatal consequence [4].

Because the concentration of mercury is higher under oxyfuel combustion due to the recycling of the flue gases, this could be moderated for oxidized mercury, which could condense on the fly ash. In addition, it has been reported that the relationship between $\text{Hg}^0/\text{Hg}^{2+}$ in pulverized coal boilers shifts from 75/25 in air combustion to 70/30 in oxycombustion [6]; this fact would lead to an enhancement of oxidized mercury retention in WFGD (Wet Flue Gas Desulphurisation) systems. However, such low mercury limits, $0.01 \mu\text{g}/\text{m}^3$, would not be accomplished by mercury capture in APCDs. The Activated Carbon Injection (ACI) is the only specific control measure for mercury at commercial level for conventional pulverized coal boilers, but a large amount of residue is generated and the marketability of fly ash is lost [7]. In addition, it is not clear if ACI technology could achieve those low mercury emission levels.

Oxy-fuel demonstration projects have proposed different solutions to clean mercury prior to CO_2 liquefaction, usually combined with the removal of N- and S- compounds. The sour compression technology implies dissolving mercury in the nitric acid formed as condensate and hence is directly linked to the capture of NO_x and SO_x [8]. On the other hand, the inclusion of an activated carbon bed before or in the compression system was one of the first methods used: Schwarze Pumpe pilot plant worked with an adsorbing tower of S-doped activated carbon positioned before the CO_2 processing unit; but there is a risk of a thermal explosion within the bed at high pressure.

Alternative methods in the natural gas process plant could be used in the CO_2 compression process to remove mercury [9] such as silver-promoted molecular sieve adsorbents. In this context, regenerable sorbents based on supported noble metal nanoparticles can be a waste-free process because the regenerability of the sorbent (with only recovered mercury for commercial recycling or disposal) accomplishing high mercury removal capacity [10, 11].

In this work, a regenerable sorbent based on gold nanoparticles supported on a structured carbon has been evaluated under oxy-coal combustion conditions. The novelty of this work is the assessment of the influence of NO, SO₂, HCl and water vapour, separately, under CO₂ rich atmospheres, on the characteristics of the sorbent and on the mercury capture performance, from a fundamental study by in situ XPS experiments to a more realistic study simulating different oxycombustion atmospheres as a preliminary step before extending the research to real flue gas conditions in a 3 KWth combustor.

2. EXPERIMENTAL

2.1. Sorbent preparation and characterization.

A cordierite honeycomb structure (from Corning Inc.) was impregnated with a phenolic resin (Novolak type delivered by Ilarduya, from Hüttenes Albertus group), thermally cured at 150 °C for 1h and subsequently carbonized at 700 °C for 1h.

The method for gold deposition onto the carbon support involved the direct reduction of gold salt (HAuCl₄•3H₂O) by the carbon surface without the addition of reducing or protective chemicals, by immersion of the support on a highly diluted gold salt solution. After gold deposition, the sorbent were subjected to Reducing Thermal Treatment (RTT) at 300 °C for 1 h under a flow of N₂ containing 4% H₂. More details of the preparation procedure are given in [12].

The bulk gold content of the sorbent was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Gold nanoparticle size distribution and average particle size were determined by analyzing several images obtained by Scanning Electron Microscopy with Field Emission (FE-SEM), according the procedure given elsewhere [13]. X-ray diffraction (XRD) was used to obtain information regarding the crystalline structure of the gold. The influence of the presence of different gases, NO, SO₂, HCl, on the sorbent, in

the presence and absence of mercury, was studied by X-ray Photoelectronic Spectroscopy (XPS).

2.2. Mercury capture

2.2.1. Experimental facility for mercury capture tests under simulated oxy-coal combustion atmosphere.

A bench-scale plant was specifically designed and built to test the performance of the sorbent for mercury capture. The experimental installation is described elsewhere [12]. A battery of flow meters was used to control the composition and flow-rate of the simulated flue gas. A certified Dynacal Hg^0 permeation device with an accuracy of ± 0.01 °C was used to generate a constant feed of Hg^0 . The resulting gas mixture was sent to the quartz reactor tube, with an internal diameter of 16 mm, where the sorbent was fitted between two ceramic pieces. A furnace surrounding the reactor was used to control the temperature. An on-line elemental cold vapour atomic absorption spectroscopy mercury analyzer (CVAAS, VM3000, from Mercury Instruments) continuously monitored Hg^0 evolution downstream the sorbent. The reactor was provided with a bypass which allows measuring the Hg concentration before starting and after finishing the experiment. At the end of the line, a battery of impingers was placed to capture the oxidized mercury following a modified Ontario Hydro Method (OHM) [14]. The fittings and tubings, where mercury was present, were made of Teflon to prevent possible mercury attack on the steel.

Hg breakthrough curves were obtained at a ratio of W_{Au}/Q of 1.6×10^{-5} g h l⁻¹, where W_{Au} was the weight of Au on the sorbent and Q was the total gas flow. Space velocity was calculated considering volume of the block sorbent monolith, and it was 42850 h⁻¹ in all the cases. Tests were performed at 50 °C and at Hg inlet concentration of 100 µg/m³ under CO₂ atmosphere, in presence of O₂, NO, SO₂, HCl and water vapour. Table 1 reports the

experimental test performed. Study of mercury capture under SO₂ containing atmosphere (no other component) was carried out elsewhere [12].

Some experiments were performed two or three times under the same operation conditions in order to test reproducibility. The total amount of Hg⁰ retained was calculated by integration of the breakthrough curve.

Regeneration of exhausted sorbents was carried out at 250°C during 1 h. After this period of time, the sorbent was cooled down to the desired temperature to be used in a new mercury capture test.

Exhausted samples of sorbent were analyzed by an Automatized Mercury Analyzer LECO AMA254 gold amalgam atomic absorption spectrometer to determine the mercury captured on them. The total amount of sample used for the mercury capture experiment was crushed and aliquots were analyzed in the AMA254 device. These results were compared with those obtained from the mercury breakthrough curves. Aliquots from the impinger solutions were also analyzed with the AMA254 device.

Table 1. Experimental tests performed under simulated oxycoal combustion conditions.

Test number	Hg μg/m ³	O ₂ %	SO ₂ ppm	NO ppm	HCl ppm	H ₂ O %	CO ₂ %
1	100	0	0	0	0	0	Balance
2	100	3	0	0	0	0	Balance
3	100	3	0	0	0	10	Balance
4	100	0	0	200	0	0	Balance
5	100	0	0	1000	0	0	Balance
6	100	3	0	200	0	0	Balance
7	100	0	0	200	0	10	Balance
8	100	3	0	200	0	10	Balance
9	100	0	0	0	200	0	Balance
10	100	3	0	0	200	0	Balance
11	100	0	0	0	200	10	Balance
12	100	3	0	0	200	10	Balance
13	100	3	0	200	200	0	Balance
14	100	3	2500	200	0	0	Balance
15	100	3	2500	0	200	0	Balance

2.2.2. Bubbling FB combustor of 3 kWth working under oxy-coal combustion conditions.

The experimental installation consists of a fluidized bed reactor, different auxiliary systems for gas supply (O_2 , CO_2 , H_2O , NO and SO_2), solid feeding (coal, limestone and sand as inert solid) and gas analysis. The BFB combustor and the experimental method are described elsewhere [15, 16].

Elemental mercury (Hg^0) was monitored on-line by the VM3000 analyzer. Since SO_2 is a spectral interferant, CVAAS signal was previously tested at different SO_2 concentrations in order to subtract its contribution to real Hg^0 measurement [12, 17]. Oxidized mercury (Hg^{2+}) was recovered in impingers with KCl dissolution 1 M according to Ontario Hydro Method (OHM) [14]. In some experiments the complete train of impingers according to OHM was used in order to confirm the continuous Hg^0 measurement. Mercury contents in solids (Hg_p) elutriated from the combustor (recovered in a cyclone) as well as in the bed (recovered in a drainage deposit) were determined for each operating condition in order to follow mercury speciation before a mercury capture experiment. Mercury contents were directly analyzed on solids and impingers solutions using the AMA254 spectrometer.

A lignite from Teruel basin, Spain, with a particle size of 0.2–1.2 mm was burned in this facility. The Ca-based sorbent used for SO_2 in-situ capture was a Spanish limestone, Granicarb, with a particle size ranging from 0.3 to 0.5 mm. Table 2 shows the composition and main properties of the materials used.

Table 2. Characteristics of the coal and the Ca-based sorbent.

Composition, wt%	Lignite	Composition, wt%	Limestone
Moisture	12.6	$CaCO_3$	97.1
Ash	25.2	$MgCO_3$	0.2
Volatiles	28.7	Na_2O	1.1
Fixed C	33.5	SiO_2	<0.1
C	45.4	Al_2O_3	<0.1
H	2.5	Fe_2O_3	<0.1
N	0.6		
S	5.2		
Cl (mg/kg)	189	Cl (mg/kg)	1,116
Hg (mg/kg)	0.11	Hg (mg/kg)	0.0002
LHV (kJ/kg)	16,252		

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Au/C sorbent.

The bulk gold content of the sorbent determined by ICP-OES was 0.1 wt%; previous studies showed that gold was mainly decorating the surface of the support [18]. The analysis image of micrographs obtained by FE-SEM according to procedure described in [18] gave an average particle size of 61 nm. Moreover, the images showed that gold nanoparticles decorated homogeneously the support. Whole XRD pattern decomposition was performed using the LeBail method to obtain an average gold crystallite size of 24 nm, lower than that of gold nanoparticle size, indicating that particles are composed by various crystals. In addition, XRD study showed that the only gold phase present was Au^0 . However, a more detailed study of the chemical state of gold was carried out by XPS, indicating that near 90% of the deposited gold is its elemental state. This is an important fact, because mercury can only amalgamate with Au^0 , so most of the deposited gold is available for mercury capture. The thermal stability of the sorbent under simulated long-term adsorption-desorption cycles at high temperature, being equivalent to 60 days of operation, can be found in [12].

3.2. Hg capture under simulated oxy-coal combustion atmosphere.

One of the main components of flue gas during oxy-coal combustion is CO_2 , which makes the difference from conventional air coal combustion where N_2 is one of the main components.

Hence, Hg breakthrough curves depicted in Figure 1 were obtained at 50 °C and at Hg inlet concentration of $100 \mu\text{g}/\text{m}^3$, under either CO_2 or N_2 atmospheres, at the same experimental conditions: space velocity and W_{Au}/Q , set in the experimental section.

Figure 1. Hg breakthrough curves for sorbent tested under CO₂ or N₂ atmosphere.

As can be seen in Figure 1, breakthrough time was lower for the experiment under CO₂ atmosphere. It has been described that the carrier gas influences the kinetics of amalgam process [19]. It has been established that common carrier gases do not adsorb on annealed gold surface; thus, the studied carrier gases in present work are expected to have no influence on the reaction of amalgam formation, but they influence solely Hg diffusion in the gas phase. At the very low Hg partial pressure used, 2.2×10^{-5} , it has been stated that the number of Hg atoms collision with the Au surface and consequently the rate of adsorption will be determined by the flux of mercury [19]. The gas phase composition has influence on the kinetics of the amalgamation process, i.e. different rate of Hg atoms' diffusion from the mercury source through the gas phase to the Au nanoparticles. In addition, it was also observed differences of electrical resistance of the alloy Hg-Au formed under some atmospheres [19]. Accordingly, it is supposed that the kinetics of the amalgamation is less favoured under CO₂ atmosphere, as can be seen in Figure 1.

Figure 2 depicts the Hg breakthrough curve under different atmospheres with the initial concentration of $100 \mu\text{g}/\text{m}^3$, according to the labelling shown in Table 1.

Figure 2. Hg breakthrough curves for sorbent tested under different atmospheres (test number in Table 1).

In the presence of NO, mercury breakthrough is reached after more than 24 h and saturation is not reached after 96 h. This fact could be explained in terms of mercury oxidation. The breakthrough curves were obtained with the VM3000 analyzer, which does not detect oxidized mercury. So, the integration of the curves could overestimate the calculated amount retained by the sorbent and, consequently, the reliable amount of mercury captured by the sorbent is that shown in Table 3, which was measured directly on the sorbent by AMA254 spectrometer, as well as the amount of oxidized mercury captured in the KCl impingers. It can be seen that only a little amount of the oxidized mercury formed is evolved with the gas stream and retained in the impingers. This fact means that oxidized mercury is retained by the sorbent.

Table 3. Amount of mercury captured by breakthrough curve integration (basis 70 h for NO, SO₂ or HCl containing atmospheres, basis 18 h for only O₂ and/or H₂O containing atmospheres) and amount of

mercury and oxidized mercury captured in the sorbent and trapped in the impinger solutions obtained by AMA254 spectrometer (per g of sorbent).

Test number	Gas composition (100 $\mu\text{g Hg/m}^3$, balance CO_2)	$\mu\text{g Hg/g}$ (integration)	$\mu\text{g Hg}^0/\text{g}$ (in exhausted sorbents)	$\mu\text{g Hg}^{2+}/\text{g}$ (from impinger*)	Total Hg ($\mu\text{g Hg/g}$)
1	Hg+CO ₂	34.7	33.0	0.0	33.0
2	Hg+O ₂ +CO ₂	33.5	32.2	0.0	32.2
3	Hg+O ₂ +H ₂ O+CO ₂	22.2	29.2	0.2	29.4
4	Hg+NO+CO ₂	263.9	234.9	8.0	242.9
5	Hg+NO+CO ₂	274.4	285.7	9.3	295.0
6	Hg+O ₂ +NO+CO ₂	338.7	283.3	13.4	296.7
7	Hg+H ₂ O+NO+CO ₂	252.8	261.2	2.3	263.5
8	Hg+O ₂ +H ₂ O+NO+CO ₂	247.9	218.6	0.9	219.5
9	Hg+HCl+CO ₂	327.8	360.5	1.0	361.5
10	Hg+O ₂ +HCl+CO ₂	290.6	276.6	3.3	279.9
11	Hg+H ₂ O+HCl+CO ₂	295.5	217.2	3.0	220.2
12	Hg+O ₂ +H ₂ O+HCl+CO ₂	226.9	177.3	2.2	179.5
13	Hg+O ₂ +NO+HCl+CO ₂	305.7	323.8	0.9	324.7
14	Hg+O ₂ +SO ₂ +NO+CO ₂	252.0	248.2	4.9	253.1
15	Hg+O ₂ +SO ₂ +HCl+CO ₂	305.0	298.7	1.5	300.2
Ref.[12]	Hg+3% O ₂ +2500 ppm SO ₂ +CO ₂	38.7	27.8	5.6	33.4

*referred to sorbent mass

Two different mechanisms could be involved in the mercury oxidation. The presence of NO in the simulated flue gas would lead to mercury oxidation that could be enhanced by a catalytic effect of Au [20, 21, 22]. In situ XPS experiments determined that the presence of gold favour the dissociative adsorption of NO at room temperature [23]. Once mercury is in the oxidized form it can be chemisorbed on the carbon support. What is more, carbon surface could oxidize adsorbed NO to NO₂ on oxygen surface groups [24, 25] creating new sites; carbon surface can reduce (NO)₂ dimers to N₂, oxidizing carbon surface again [26] and this oxidized surface can thus chemisorb not only Hg²⁺ but also Hg⁰. It has been previously reported that there is low affinity between non-treated activated carbons (without specific active sites) and elemental mercury [27, 28], but treated activated carbons have shown high mercury retention performance [29].

In order to test the influence of NO on the mercury oxidation, a new experiment was performed (Figure 3a). In the first step an stream containing 100 $\mu\text{g Hg/m}^3$, 3% O₂, 2500 ppm SO₂ and CO₂ as balance was introduced into the reactor. When the breakthrough was about

25%, NO was added to the gas to obtain a concentration of 200 ppm. The introduction of NO led to a decrease in Hg concentration, which increases again when NO is removed from the stream, indicating the mechanism of Hg oxidation and/or retention previously mentioned. During a Hg retention long term experiment in presence of SO₂ and NO (Figure 3b), only 10% of breakthrough is reached after 190 h.

Figure 3. a) Hg breakthrough curves for the sorbent tested changing the gas composition during the experiment; b) long-term experiment with sorbent under Hg+NO+SO₂+O₂+CO₂ atmospheres.

Because the amount of mercury retained by amalgamation on the gold nanoparticles and by chemisorption on the carbon support cannot be determined separately, some thermal desorption experiments with the exhausted sorbents (TPD-Hg) were conducted to follow the mercury evolution with the temperature. Figure 4 depicts mercury evolution during a TPD-Hg experiment on a previously used sorbent sample (corresponding to the mercury capture experiment under NO containing atmosphere). As can be seen, two peaks are obtained: first of them can be attributed to the evolution of mercury associated to gold nanoparticles and the second one can be attributed to chemisorbed mercury onto the carbon support. However, these results are surprising when comparing with baseline, i.e. only Hg and CO₂ are present in the gas stream. The amount of Hg captured by the sorbent through amalgamation mechanism seems to be enhanced by the presence of NO. It is important to emphasize that only elemental mercury can amalgamate with gold. This fact should mean that NO could favour the exposition of gold surface to new Hg atoms entering in the Au crystalline network.

This enhancement effect would be superior to the adverse effect of the presence of SO_2 , studied previously [12].

Figure 4. Mercury evolution during TPD-Hg experiments on used samples of sorbents after Hg capture experiments: (1) under NO atmosphere; (2) baseline ($\text{Hg} + \text{CO}_2$).

In order to separate the catalytic effect of gold, a series of experiment were carried out on the support under the same experimental conditions than those used to test the sorbent. Figure 5 depicts breakthrough curves for support and sorbent. In absence of NO, the support cannot retain mercury but in presence of mercury the breakthrough occurred after 7 h. However, the breakthrough for the sorbent started after 50 h, indicating that other mechanism than that of mercury retention on the support because oxidation mechanisms is involved.

In order to gain insight of the retention mechanism, XPS spectra of $\text{Hg}4f$ region for sorbent and support after the experiments carried out in presence of NO were analysed (Figure 5b).

For support, $\text{Hg}4f_{7/2}$ peak is shifted at high binding energies (101.2 eV), indicating that mercury is present in oxidized form; for sorbent, $\text{Hg}4f_{7/2}$ peak is found at 99.8 eV, typical of elemental mercury but it is supposed the presence of some oxidized mercury according the peak shape. These results suggest that in presence of NO, the Au enhances its capacity of mercury adsorption. It has been reported that the establiity of adsorbed mercury on gold is increased if the former interacts to form HgX (i.e. $\text{X}=\text{O}$) in Au surfaces (111) with hollow type defects [30, 31]. In addition, in those studies it was described the need to form an

oxidized mercury monolayer on the gold surface to enhance the formation of Hg-Au amalgam. This would explain the lower sorbent performance when those oxidation mechanisms are not present.

Figure 5. a) Hg breakthrough curves of sorbent and support; b) XPS spectra of the Hg4f_{7/2} region for sorbent and support after experiment under NO containing atmosphere.

In presence of HCl containing atmospheres, the sorbent exhibited similar Hg breakthrough curves to that in presence of NO containing atmospheres. It has been described a mechanism of halides-carbon materials interaction creating points on the surface acting as Lewis acids [32] available for elemental mercury acting as Lewis base [33], enhancing mercury oxidation. In addition, the homogeneous oxidation mechanism Hg-HCl does not take place under 600 °C; however, it has been found that chlorine binds preferentially on steps, vacancies, and gold adatoms [34] and a high chlorine coverage on gold surface led to evolution of gold atoms from (111) planes to further binding to the surface as Cl-Au [35]; at low chlorine coverage on gold surface the binding Cl-Au occur without previous Au atoms evolution from (111) planes [36]. This mechanism could favor the formation of a oxidized mercury layer on the Au surface to enhance the formation of Hg-Au amalgam, as in the case of NO containing atmospheres, according to the mechanism previously described [30, 31].

In order to study the influence of the presence of HCl on the support when mercury is not present, fresh support was subjected to an in situ treatment in the XPS equipment with 3% O₂, 200 ppm HCl and CO₂ as balance. In addition, Hg breakthrough curve for the support in presence of HCl was obtained (Figure 6b) in the experimental installation. Figure 6a depicts region O1s for fresh and treated sorbent indicating the formation of carboxyl-type groups, which are available for mercury retention; quantification gave an increase of oxygen content, from 2.3 at% for fresh support to 8.5 at% for treated support, and after treatment the presence of chlorine can be quantified as 1 at%, in agreement with the mechanism proposed previously [33].

Figure 6. a) XPS spectra of the O1s region for fresh support and after in situ treatment under HCl containing atmosphere; b) Hg breakthrough curves of support under an atmosphere containing 3%O₂, 200 ppm HCl and CO₂ as balance.

3.3. Sorbent regeneration.

In previous work [10] it was found that temperature for maximum Hg evolution was around 220 °C for amalgamated mercury. The temperature needed to completely remove mercury from the sorbent, around 450 °C, is too high and could cause gold nanoparticles sintering (thermal stability at 300 °C of the particles over 30 days was established previously in [12]). So, the mercury retained in the support is not removed during the regeneration of the sorbent along cycles of Hg capture/regeneration. This fact would lead to a decrease in Hg capture

capacity in the second cycle, because sites for chemisorption are occupied. But after this second cycle, the Hg capture capacity would be maintained. Figure 7 shows the cycles of Hg capture-regeneration at the following conditions: capture was carried out under Hg-200 ppm NO-3% O₂-CO₂ atmosphere and regeneration was carried out at 250 °C under inert atmosphere.

Figure 7. Mercury capture-regeneration cycles.

As can be seen, after the first Hg capture experiment with the fresh sample of sorbent, the breakthrough time decreases, being similar for the following Hg capture cycles. The Hg breakthrough curve for fresh sample corresponds to the Hg capture by amalgamation on the gold nanoparticles as well as chemisorption on the carbon support. After this, during regeneration at 250 °C only amalgamated mercury is evolved from the sorbent, remaining the sites for mercury chemisorption occupied, as it was shown in Figure 4. So, in the following Hg capture experiment, mercury is retained by amalgamation and chemisorption in the remaining chemisorption sites on the support: breakthrough time and, consequently, Hg capture capacity decreases. On the other hand, the amount of oxidized mercury evolved after the first cycle increases as can be seen in Table 4; the sites for chemisorption are already occupied, oxidized mercury cannot be fixed and is evolved and retained in the impingers.

Table 4. Amount of mercury captured by breakthrough curve integration and amount of mercury oxidized and trapped in the impinger solutions (per g of sorbent).

	$\mu\text{g Hg/g sorbent}$ (integration)	$\mu\text{g Hg}^{2+}/\text{g}$ (from impinger)*
Cycle 1	328.3	4.8
Cycle 2	287.4	8.3
Cycle 3	317.8	9.9
Cycle 4	311.8	7.9

*referred to sorbent mass

3.4. Hg capture in a 3 kWth bubbling FB combustor operating under oxycoal combustion conditions.

Before starting the experiment of mercury capture, steady conditions at the FB combustion facility had to be reached. To start-up, the bed was filled with silica sand and hot air was introduced (from a pre-heater) to heat the bed up to the ignition temperature of the lignite. The lignite was fed at a rate of 0.7 kg/h and the bed temperature increased rapidly due to the coal combustion. After the working temperature of 925 °C was reached, the preheating system was turned off and the air was replaced by a mixture of $\text{O}_2/\text{CO}_2=35/65$. The limestone introduced was equivalent to a molar ratio $\text{Ca/S}=3$. The control of the temperature was carried out by means of a heat exchanger inside the bed. More details of the experimental procedure are given elsewhere [16]. When steady state for SO_2 retention was achieved, sampling of gaseous mercury, Hg^0 and Hg^{2+} , in the gaseous outlet stream was carried out according to section 2.2.2.

Two Hg retention experiments were carried out in the 3 kWth BFB combustor operating under oxycoal combustion conditions. Experiment#1 was performed with Au/C fresh sorbent and experiment#2 was carried out with Au/C regenerated sorbent (after use in first experiment).

Before starting the first experiment, Hg emission (Figure 8a) was measured when steady state was reached. As can be seen, SO_2 interference in Hg signal measured in the VM3000 device was corrected point by point to obtain the real elemental mercury concentration, being the

average value $6.9 \mu\text{g Hg}^0/\text{m}^3$, as can be seen in Table 5. On the other hand, Hg^{2+} was directly determined from the impingers solution (in the AMA254 device) after 2 h of operation, before starting the Hg retention experiment#1 giving a value of $0.4 \mu\text{g Hg}^{2+}/\text{m}^3$.

In order to maintain the same value of W_{Au}/Q used for experiments carried out under simulated oxycombustion atmosphere, a total of 8 units of fresh sorbent were placed in series in the reactor placed before the VM3000 analyzer. Mercury breakthrough curve for experiment#1 is depicted in Figure 8c. It can be seen that breakthrough occurred after 3 h and 20% of breakthrough was not reached during the experiment. After the trend of breakthrough curve was clear, the experiment was stopped. The sorbent was submitted to regeneration at 250°C for 1 h. During this time, the operation conditions were changed and the recirculation of SO_2 was simulated in the oxycoal combustion facility, increasing its concentration as can be seen in Figure 8b and Table 5. This fact led to an increase in the concentration of Hg^0 , as can be seen in Figure 8b and Table 5, explained in terms of SO_2 inhibiting mercury oxidation from Hg^0 to Hg^{2+} in combustion flue gas because Cl-free radicals, main responsible for this oxidation mechanism, were scavenged [37]. Hg^0 concentration at steady state, before starting mercury capture experiment#2 with the regenerated sorbent, was $16.2 \mu\text{g Hg}^0/\text{m}^3$. As can be seen in Figure 8c and Table 5, the breakthrough time was lower than that in experiment#1 with fresh sorbent, and 10% of breakthrough is not reached during the experiment#2. This decrease of performance after 1st cycle was previously exhibited under simulated oxycombustion atmosphere. Accordingly, it is expected that this low breakthrough values are long-term maintained and, as it was shown under cycles of mercury retention under simulated oxycombustion atmosphere-regeneration, also maintained along further cycles. These results would make this Au/C based sorbent a worthwhile and promising basis for a free waste mercury retention process.

Table 5. Experimental conditions for mercury retention in the oxycoal combustion facility

	Experiment#1 (fresh sorbent)	Experiment#2 (regenerated sorbent)
Hg ⁰ initial concentration ($\mu\text{g}/\text{m}^3$)	6.9	16.2
Hg ²⁺ initial concentration ($\mu\text{g}/\text{m}^3$)	0.4	0.0002
SO ₂ concentration (ppm)	2792	3753
NO concentration (ppm)	344	316
Hg breakthrough (min)	180	165
Hg ²⁺ conc. during experiment (ppm)	0.0009	0.0003
Hg sorbent efficiency (%)	93.3	95.8

Figure 8. a) Hg⁰ concentration before experiment #1 (with fresh sorbent) in the oxycoal combustion facility; b) Hg⁰ concentration before experiment #2 (with regenerated sorbent) in the oxycoal combustion facility; c) Hg breakthrough curves for experiment #1 (with fresh sorbent) and experiment #2 (with regenerated sorbent) in the oxycoal combustion facility.

4. CONCLUSIONS

A regenerable sorbent based on carbon supported Au nanoparticles (0.1%wt) has been used for Hg capture under oxycoal combustion atmosphere. The influence of the presence of O₂,

NO, SO₂ and HCl in a gas containing Hg and CO₂ on the sorbent as well as on the Hg oxidation has been evaluated under a simulated flue gas. In addition, this sorbent has been also evaluated in a 3 kWth oxycoal bubbling fluidized bed combustor.

Under CO₂ major component atmospheres the Hg retention capacity was slightly lower than under N₂ major component atmospheres due to the different rate of Hg atoms' diffusion from the mercury source through the gas phase to the Au nanoparticles.

In presence of NO in the simulated flue gas less than 20% Hg breakthrough was maintained for, at least, 72 h. Three different mechanisms seem to be involved. On one hand, nitric oxide can oxidize the carbon support creating active sites for Hg chemisorption. On the other hand, mercury can be oxidized in presence of NO and the catalytic effect of Au; as oxidized mercury was evolved in low extent, it is supposed to be retained on the sorbent. Finally, an oxidized mercury monolayer on Au surface seems to be created, which enhances the formation of Hg-Au amalgam; this would explain the lower performance of the sorbent when the described oxidation mechanisms were not present.

In presence of HCl in the simulated flue gas the sorbent exhibited similar behaviour than that described in presence of NO; in this case, Cl can be found on the sorbent after use.

Long-term experiments in presence of NO y SO₂ in the simulated flue gas showed values of less than 10% Hg breakthrough after 180 h, which made this sorbent a candidate for pilot plant scale-up.

Mercury retention under flue gas atmosphere coming from the oxycombustion of a lignite in a BFB combustor maintained the trend observed under simulated flue gas, indicating the initial feasibility of this Hg retention waste free process based on the presented Au/C sorbent.

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6. REFERENCES

1. Senior C. Mercury Behavior in Coal Combustion Systems. In: E. J. Granite HWP, C. Senior, editor. Part III Mercury Chemistry in Coal Utilization Systems and Air Pollution Control Devices. Weinheim, Germany: Wiley-VCH Verlag GmbH; 2015. p. 109-132.
2. Sloss LL. Legislation, standards and methods for mercury emissions control. Report n° CCC/195. IEA Clean Coal Centre. London, UK, 2012.
3. Adams D. Flue gas treatment for CO₂ capture. Report n° CCC/169. IEA Clean Coal Center. London, UK, 2010.
4. Davidson RM, Santos SO. Oxyfuel combustion of pulverised coal. Report n° CCC/168. IEA Clean Coal Centre, London, UK, 2010.
5. Wall T, Stanger R, Liu Y. Gas cleaning challenges for coal-fired oxy-fuel technology with carbon capture and storage. *Fuel*. 2013;108:85-90.
6. Suriyawong A, Gamble M, Lee M, Axelbaum R, Biswas P. Submicrometer particle formation and mercury speciation under O₂-CO₂ coal combustion. *Energy & Fuels*. 2006;20:2357-63.
7. Sloss LL. Trace elements and fly ash utilisation. Report n° CCC/122. IEA Clean Coal Centre. London, UK, 2007.
8. Stanger R, Ting T, Spero C, Wall T. Oxyfuel derived CO₂ compression experiments with NO_x, SO_x, and mercury removal-Experiments involving compression of slip-streams from the Callide Oxyfuel Project (COP). *International Journal of Greenhouse Gas Control*. 2015;41:50-59.
9. Eckersley N. Advanced mercury removal technologies. *Hydrocarbon Processing*. 2010;89:29-35.
10. Ballester D, Gómez-Giménez C, García-Díez E, Juan R, Rubio B, Izquierdo MT. Influence of temperature and regeneration cycles on Hg capture and efficiency by structured Au/C regenerable sorbents. *Journal of Hazardous Materials*. 2013;260:247-254.
11. Rodriguez-Perez J, Antonia Lopez-Anton M, Diaz-Somoano M, Garcia R, Rosa Martinez-Tarazona M. Development of Gold Nanoparticle-Doped Activated Carbon Sorbent for Elemental Mercury. *Energy & Fuels*. 2011;25:2022-2027.
12. Gomez-Gimenez C, Ballester D, Juan R, Rubio B, Izquierdo MT. Mercury capture by a regenerable sorbent under oxycoal combustion conditions: Effect of SO₂ and O₂ on capture efficiency. *Chemical Engineering Science*. 2015;122:232-239.
13. Ballester D, Juan R, Gomez-Gimenez C, Garcia-Diez E, Ruiz C, Rubio B, Izquierdo MT. Novel methodology for gold nanoparticles deposition on carbon monolith supports. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*. 2014;441:91-100.
14. Curtis K, Eagleson K. Speciation of mercury emissions from Ontario hydro's coal-fired generating stations. Report No. A-F-95-22-Con. Ontario Hydro Technologies. Toronto, 1995.
15. de las Obras-Loscertales M, Izquierdo MT, Rufas A, de Diego LF, Garcia-Labiano F, Abad A, Gayan P, Adanez J. The fate of mercury in fluidized beds under oxy-fuel combustion conditions. *Fuel*. 2016;167:75-81.
16. de Diego LF, de las Obras-Loscertales M, Rufas A, Garcia-Labiano F, Gayan P, Abad A, Adanez J. Pollutant emissions in a bubbling fluidized bed combustor working in oxy-fuel operating conditions: Effect of flue gas recirculation. *Applied Energy*. 2013;102:860-867.

17. Baldwin DP, Bajic SJ, Eckels DE, Zamzow DS, Miller GP, Tao S, Waggoner CA. Testing of continuous sampling air-ICP and mercury systems as Continuous Emission Monitors at the diagnostic instrumentation and analysis laboratory. Report n° IS-5144. US-DOE, Ames, 2001.
18. Ballesterio D, Juan R, Ibarra A, Gomez-Gimenez C, Ruiz C, Rubio B, Izquierdo MT. Effect of thermal treatments on the morphology, chemical state and lattice structure of gold nanoparticles deposited onto carbon structured monoliths. *Colloids and Surfaces a-Physicochemical and Engineering Aspects*. 2015;468:140-150.
19. Kobiela T, Nowakowski B, Dus R. The influence of gas phase composition on the process of Au-Hg amalgam formation. *Applied Surface Science*. 2003;206:78-89.
20. Hrdlicka JA, Seames WS, Mann MD, Muggli DS, Horabik CA. Mercury oxidation in flue gas using gold and palladium catalysts on fabric filters. *Environmental Science & Technology*. 2008;42:6677-6682.
21. Wu Z, Xu L, Zhang W, Ma Y, Yuan Q, Jin Y, Yang J, Huang W. Structure sensitivity of low-temperature NO decomposition on Au surfaces. *Journal of Catalysis*. 2013;304:112-122.
22. Presto AA, Granite EJ. Noble Metal Catalysts for Mercury Oxidation in Utility Flue Gas: gold, palladium and platinum formulations. *Platinum Metals Review*. 2008;52:144-154.
23. Bukhtiyarov AV, Kvon RI, Nartova AV, Prosvirin IP, Bukhtiyarov VI. In-situ XPS investigation of nitric oxide adsorption on (111), (310), and (533) gold single crystal faces. *Surface Science*. 2012;606:559-563.
24. Fierro V, Izquierdo MT, Schuurman Y, Rubio B, Mirodatos C. A novel approach for characterising carbon catalysts by TAP experiments. *Characterization of Porous Solids VI*. 2002;144:255-260.
25. Sousa JPS, Pereira MFR, Figueiredo JL. Modified activated carbon as catalyst for NO oxidation. *Fuel Processing Technology*. 2013;106:727-733.
26. Shen Y, Ge X, Chen M. Catalytic oxidation of nitric oxide (NO) with carbonaceous materials. *RSC Advances*. 2016;6:8469-8482.
27. Huggins FE, Yap N, Huffman GP, Senior CL. XAFS characterization of mercury captured from combustion gases on sorbents at low temperatures. *Fuel Processing Technology*. 2003;82:167-196.
28. Padak B, Wilcox J. Understanding mercury binding on activated carbon. *Carbon*. 2009;47:2855-2864.
29. Nabais JV, Carrott PJM, Carrott MMLR, Belchior M, Boavida D, Dially T, Gulyurtlu I. Mercury removal from aqueous solution and flue gas by adsorption on activated carbon fibres. *Applied Surface Science*. 2006;252:6046-6052.
30. Lim D-H, Aboud S, Wilcox J. Investigation of Adsorption Behavior of Mercury on Au(111) from First Principles. *Environmental Science & Technology*. 2012;46:7260-7266.
31. Lim D-H, Wilcox J. Heterogeneous Mercury Oxidation on Au(111) from First Principles. *Environmental Science & Technology*. 2013;47:8515-8522.
32. Qu Z, Chang J, Hsiung T-L, Yan N, Wang HP, Dod R, Chang S-G, Miller C. Halides on Carbonaceous Materials for Enhanced Capture of Hg⁰: Mechanistic Study. *Energy & fuels*. 2010;24:3534-3539.
33. Olson ES, Azenkeng A, Laumb JD, Jensen RR, Benson SA, Hoffmann MR. New developments in the theory and modeling of mercury oxidation and binding on activated carbons in flue gas. *Fuel Processing Technology*. 2009;90:1360-1363.
34. Baker TA, Friend CM, Kaxiras E. Chlorine interaction with defects on the Au(111) surface: A first-principles theoretical investigation. *Journal of Chemical Physics*. 2008;129: 104702-104705.
35. Baker T, Friend C, Kaxiras E. Effects of chlorine and oxygen coverage on the structure of the Au(111) surface. *The Journal of chemical physics*. 2009;130:84701-84708.
36. Gao W, Baker T, Zhou L, Pinnaduwa D, Kaxiras E, Friend C. Chlorine Adsorption on Au(111): Chlorine Overlayer or Surface Chloride? *Journal of the American Chemical Society*. 2008;130:3560-3565.

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37. Carey TR, Hargrove CW, Richardson CF, Chang R. Factors affecting mercury control in utility flue gas using activated carbon. Journal of the Air & Waste Management Association. 1998;48:1166-1174.