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SPECIATION, BEHAVIOUR, AND FATE OF MERCURY UNDER OXY-FUEL COMBUSTION CONDITIONS

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ABSTRACT

The work presented here reports the first study in which the speciation, behaviour and fate of mercury (Hg) have been evaluated under oxy-fuel combustion at the largest oxy-Pulverized Coal Combustion (oxy-PCC) demonstration plant to date during routine operating conditions and partial exhaust flue gas re-circulation to the boiler. The effect of the CO$_2$-rich flue gas re-circulation on Hg has also been evaluated. Results reveal that oxy-PCC operational conditions play a significant role on Hg partitioning and fate because of the continuous CO$_2$-rich flue gas re-circulations to the boiler. Mercury escapes from the cyclone in a gaseous form as Hg$^{2+}$ (68%) and it is the prevalent in the CO$_2$-rich exhausts flue gas (99%) with lower proportions of Hg$^{0}$ (1.3%). The overall retention rate for gaseous Hg are around 12%; Hg$^{0}$ is more prone to be retained (95%) while Hg$^{2+}$ shows a negative efficiency capture for the whole installation. The negative Hg$^{2+}$ capture efficiencies are due to the continuous CO$_2$-rich exhaust flue gas recirculation to the boiler with enhanced Hg contents. Calculations revealed that 44 mg of Hg were re-circulated to the boiler as a result of 2183 re-circulations of CO$_2$-rich flue gas. Especial attention must be paid to the role of the CO$_2$-rich exhaust flue gas re-circulation to the boiler on the Hg enrichment in Fly Ashes (FAs).

Keywords: Mercury, oxy-PCC, CO$_2$-rich flue gas re-circulation, capture efficiencies, FAs
1. INTRODUCTION

Oxy-fuel combustion is one of the most promising technologies for the capture of carbon dioxide (CO₂) from power plants (Toftegaard et al., 2010) with an expected CO₂ reduction of 14-19% (equivalent to CO₂ savings up to 5000 Mtn/year by 2050, European Zero Emissions Platform, 2013). Oxy-fuel combustion is based on the combustion process in O₂ stream and, in most concepts, re-circulated flue gas to lower the flame temperature. Whilst H₂O is removed, a proportion of the gas stream highly enriched in CO₂ is recycled to the boiler to improve the heat transfer and the remaining CO₂ follows a compression process for its subsequent transport, and geological storage (Toftegaard et al., 2010). However, during oxy-fuel combustion, H₂O and CO₂, are also produced, as well as CO, SOₓ, and NOₓ, particulate matter (PM) and minor and trace levels of other gaseous pollutants such as HF, HCl, Hg, Br, As, Se, and B, etc (Toftegaard et al., 2010). While there have been relatively few studies on the effects of oxy-combustion on PM formation (Zhuang et al., 2011), studies on the speciation and fate of trace pollutants potentially released during oxy-fuel combustion are based on modelling and lab studies (Zheng et al, 2003; Zheng and Furimsky, 2003; Gharebaghi et al., 2011; Jiao et al., 2011; Contreras et al., 2013; Roy et al., 2013; Jano-Ito et al., 2014; Fernandez-Miranda et al., 2014a,b) or small oxy-pilot plants (Suriyawong et al, 2006; Font et al., 2012; Spörl et al., 2014).

Gharebaghi et al (2011) developed a homogeneous-heterogeneous kinetic model of the transformation of Hg in air-fired and oxy-fuel combustion and found a higher amount of particulate mercury in the case of oxy-fuel combustion. Contreras et al (2013) and Roy et al (2013) used thermodynamic equilibrium calculations to study the speciation behaviour of Hg in air-fired and oxy-fuel systems. The former reported an increase of total Hg vaporisation during oxy-firing in comparison to air-combustion, whereas the latter authors found that elemental Hg (Hg⁰) was predicted as the main form of Hg. More recent work (Fernandez-Miranda et al., 2014) focused on the effect of the gases present in a typical oxy-coal combustion atmosphere on Hg speciation found that the minor constituents SO₂, NOₓ, and HCl significantly modify the percentages of Hg²⁺ in the gas, NOₓ being the main species involved in oxidation of Hg. However, neither these studies have reproduced full-industrial operating conditions, nor have ascertained the CO₂-rich re-circulated flue gas stream effect on Hg and other trace elements.
Concentrations of SO$_X$, HCl, HF, and specially Hg in the CO$_2$-rich re-circulated flue gas stream are expected to be around 3-4 times higher than that under conventional air-firing conditions due to the lack of dilution of the flue gas by airborne nitrogen in oxy-fuel operation (Wall et al., 2009; Scheffknecht et al., 2011; Stanger and Wall, 2011). High Hg concentrations in an oxy-fuel process may have potential implications on corrosion of Aluminium (Al)-alloys (Bessone, 2006), which could particularly be problematic in the CO$_2$-processing unit of an oxy-fuel combustion power plant (Santos, 2011) where Al-alloys are applied e.g. for heat exchangers (Bessone, 2006). Therefore, a study based on the potential effect of re-circulation of a CO$_2$-rich flue gas stream with high Hg impurities is of paramount importance as it may cause problems in the boiler components and oxy-fuel combustion process (Scheffknecht et al., 2011).

Owing to the environmental relevance of this element, the Hg emissions from oxy-fuel combustion are also an important issue to deal with in view of the forthcoming implementation of this technology at an industrial scale. In Europe the emissions of Hg from power plants have not been regulated for many years. The Pollutant Release and Transfer Register (PRTR) of Industrial Emissions into air, water, and land (EC Regulation Nº166/2006) established threshold limit values for the atmospheric emissions of 86 pollutants only for information purposes without a legally binding. However, in an attempt to reduce air pollution, the European Union (EU) is updating air pollution standards for industrial installations, including for coal power plants. In April 2015, the European Integrated Pollution Prevention and Control (IPPC) Bureau published its proposed definitions of best available techniques (BAT), and a set of proposed Hg standards that will be examined by an EU working group later this year, before formal adoption in early 2016. The draft EU standard for Hg emissions based on lignite burning is set at 10 μg/Nm$^3$ for existing plants and 4 μg/Nm$^3$ for new plants (annual average), whereas those for hard coal are set at 4 μg/Nm$^3$ for existing plants and 2 μg/Nm$^3$ for new plants (annual average).

The potential environmental and operational impacts of Hg, particularly its ability to form an amalgam with Al, make its measurement, speciation and ultimate fate of Hg a high priority for oxy-fuel combustion. Accordingly, the aims of this work are to: 1) determine the speciation and fate of Hg during routine operating conditions and partial CO$_2$-rich exhaust flue gas re-circulation in a 20MWth
ox-Pulverised Coal Combustion (ox-PCC) demonstration plant; 2) establish the mass balance and the partitioning of Hg for the whole installation (combustion unit and depuration train); 3) determine the effect of the CO₂-rich flue gas re-circulated to the boiler on Hg; and to 4) evaluate the abatement capacity of the ox-PCC whole installation for Hg.

2. MATERIALS AND METHODS

2.1 The ox-PCC facility

This research was conducted in the largest ox-PCC (20MWth) demonstration plant to date owned by Fundación Ciudad de la Energía (CIUDEN). This 20MWth ox-PCC operates under partial CO₂-rich exhaust flue gas re-circulation to the boiler and it is fed with bituminous coal. The capture process incorporates (Figure 1): Pulverised Coal (PC) boiler, 20 MWth operating from air to full ox-model, which also includes a fuel preparation unit where coals are ground, milled and dried; flue gas depuration train consisting of a cyclone followed by a Boiler Feed Water heater (BFW-heater) and a Bag Filter (BF); recirculation of flue gases (FRGs); and CO₂ capture: processing and purification train (oxy-mode)/absorption unit (air-mode).

At this ox-PCC, pulverised coal is introduced into the boiler through burners by a primary oxidiser that supplies part of the oxidant stream required for the ox-PCC. The ox-PCC oxidant stream is obtained from mixing O₂ with a proportion of CO₂-rich re-circulated flue gas and it is introduced mainly in the boiler by a secondary oxidiser. During ox-PCC, which occurs at 1000°C, the coarse fraction of ashes (boiler slags) are removed from the bottom of the ox-PCC boiler. The flue gas, which ranges from 350°C to 425°C, passes through a cyclone in order to remove the finest fraction of ashes, Fly Ashes (FAs). The outgoing cyclone (OUT-cyclone) flue gas is lead through the BFW heater; where it is cooled down to enter in the BF at a temperature of 200°C (Figure 1) where most of the FAs are removed. A proportion of the outgoing BF (OUT-BF) CO₂-rich exhaust flue gas is re-circulated to the boiler to maintain the temperature and improve the heat transfer whilst the remaining CO₂-rich exhaust flue gas proportion pass through the Capture and Purification Unit (CPU).

2.2 Sampling campaign
The sampling campaign at the 20MWth oxy-PCC was performed on 1st - 3rd July 2014 at 100% MCR (maximum capacity) during routine operating conditions in terms of boiler operation and performance, load, flame temperature, etc, and under partial CO₂-rich exhaust flue gas re-circulation to the boiler.

Isokinetic samplings of flue gas streams were performed before and after each PM and gas control device (Figure 1). At each sampling point, two different trains of sampling systems were assembled in parallel for simultaneous sampling with specific trapping solutions, one for the measurement of levels and speciation of Hg, and another one for the measurements of anions and cations. The measurements of levels and speciation of gaseous Hg was devised according to UNE-EN 13211 and Meij and Winkel (2006). This standard system is based on the determination of Hg⁰, oxidised Hg²⁺, particle-bound (Hgp) and total Hg in flue gas generated from coal-fired stationary sources. In such a system, a sample is withdrawn from the flue gas stream isokinetically through probe/filter system, maintained at the flue gas temperature, followed by a series of impingers in an ice bath. The filter within a heated filter chamber collects Hgp associated with the gas phase while the impingers solutions allow the transfer of Hg gaseous species from the gas to aqueous phase in an ice bath, which promotes the condensation of volatile species. Hence, at each sampling point, the Hg sampling system assembled a train of sampling system consisted in quartz-fibre filter within a heated filter chamber followed by a train of dark glass impingers in an ice bath. A first impinge was filled with 100 mL of HCl to capture Hg²⁺ (Meij and Winkel, 2006), the second impinge containing 3 w% H₂O₂ for SO₂ removal (Meij and Winkel, 2006), and the two last impingers containing 4 w% K₂Cr₂O₇ with 20 w% of HNO₃ for Hg⁰ trapping.

The gas sampling system for measuring levels of anions and cations was devised according to UNE-EN 1911:1998 and UNE-EN 14385:2004. In such a system, two impingers 100mL of de-ionized H₂O (or MilliQ grade water) and two filled with 6 w% HNO₃ and 10 w% H₂O₂ were assembled to determine the concentrations of anions and cations, respectively, in an ice bath. Each sampling run lasted about 2.5 h.

The sampling of flue gases also included CO₂, CO, SO₂, and NOₓ by a mobile unit equipped with an automatic and continuous measurement system (HORIBA PG-250), which was simultaneously carried
out to the sampling of gaseous Hg and of cations and anions of interest. The measurement principles used by HORIBA PG-250 are Non-Dispersive Infra-Red (NDIR) for CO and SO$_2$; NDIR (pyro-sensor) for CO$_2$; chemiluminescence (cross flow modulation) for NOx; and galvanic cell for O$_2$ measurements. The flue gas measurement settings with PG-250 included ranges for NOx extending up to 2500 ppm, four ranges for SO extending up to 3000 ppm, five ranges for CO over the span of 0 to 5000 ppm and three ranges each for CO$_2$ and O$_2$. In each sampling point, the velocity (m/s), temperature (ºC), humidity (%v), and O$_2$ (%v dry basis) of the gaseous stream were also measured. The operational conditions over the sampling period are summarised in Table 1.

A total of 3 solid (feed coal blend, boiler slag, FAs) and 2 water (process water and boiler slag water) streams were collected, mixed, and homogenised. Three sample sets consisting of two samples for each material were collected during the 3 sampling days under the progressive increase of CO$_2$-rich flue gas re-circulations to the boiler. Inputs and outputs streams involved in the oxy-PCC process and sampling points are shown in Figure 1.

2.3 Chemical analysis

Mercury analyses were carried out directly on flue gas trapping solutions, solid and liquid streams samples using a LECO AMA 254 gold amalgam atomic absorption spectrometer (GA-AAS). The analyses and certified values of Hg (NBS 1633b (>0.01) and SARM 20) were also measured to determine the accuracy of the results.

Duplicate of the solid samples were acid-digested by using a two-step digestion method (Querol et al., 1993). The resulting solution was then analysed by Inductively-Coupled Plasma Atomic-Emission Spectrometry (ICP-AES) for Sulphur (S) determination using the Advantage Radial ER/S Iris device from Thermo Jarrell-Ash. A semi-quantitative analysis was performed to determine the range of element concentrations as well as the matrix and the possible spectral interferences. The calibration was performed by means of the international certified standard (1000 and 10.000 ppm). The fly ash and coal international reference material (NBS1633b and SARM19) were also digested to determine the accuracy of the analytical and digestion methods. Chlorine (Cl) contents in solid samples were determined by applying Eschka (Chakrabarti, 1978) method. The solutions were subsequently
analysed by sensitive Cl electrode. Eschka method and subsequent analysis by selective electrode of reference material Coal 1632c for Cl was also carried out. Cl concentrations in water streams and trapping solutions used for isokinetic flue gas measurements were directly determine by High Performance Liquid Chromatography (HPLC).

The mineralogy of coal samples was determined by X-ray powder diffraction (XRD). XRD patterns were collected using a Bruker D8 Advance diffractometer with monochromatic Cu Ka1, 2 radiation (k = 1,5405) operated at 40 kV and 40 mA. The primary parallel X-ray beam was generated by a Göbbel mirror and the scattered beam was analysed by a Sol-X detector with the following scanning parameters: from 4 at 60° of 2h, a step size of 0.05°, and time per step of 3 s.

2.4 Mass balances

Mass balances (MB) were calculated by normalising the concentration of Hg in a given stream with the corresponding stream flow for the oxy-PCC (boiler + cyclone), BFW heater, and BF, independently, and for the whole installation. MB calculations were devised according to standard MB principles considered for air-combustion processes (ABETRAP, 2006) but in accordance with oxy-fuel operational conditions. The flows considered for MB calculations are detailed as follow:

\[
\text{oxy-PCC MB} = \frac{[(\text{Flow FA } \times \text{ C}_{\text{Hg FA}}) + (\text{Flow BSW } \times \text{ C}_{\text{Hg BSW}}) + (\text{Flow BS } \times \text{ C}_{\text{Hg BS}}) + (\text{Flow PM OUT-cyclone } \times \text{ C}_{\text{Hg PM OUT-cyclone}}) + (\text{Flow OUT-cyclone gas } \times \text{ C}_{\text{Hg OUT-cyclone gas}})]}{[(\text{Flow Feed fuel } \times \text{ C}_{\text{Hg FF}}) + (\text{Flow PW } \times \text{ C}_{\text{Hg PW}})]} \tag{1}
\]

\[
\text{BFW MB} = \frac{[(\text{Flow FA } \times \text{ C}_{\text{Hg FA}}) + (\text{Flow PM OUT-BFW } \times \text{ C}_{\text{Hg PM OUT-BFW})} + (\text{Flow OUT-BFW gas } \times \text{ C}_{\text{Hg OUT-BFW gas}})]}{[(\text{Flow OUT-cyclone PM } \times \text{ C}_{\text{Hg OUT-cyclone PM})} + (\text{Flow OUT-cyclone gas } \times \text{ C}_{\text{Hg OUT-cyclone gas}})]} \tag{2}
\]

\[
\text{BF MB} = \frac{[(\text{Flow FA } \times \text{ C}_{\text{Hg FA}}) + (\text{Flow PM OUT-BF } \times \text{ C}_{\text{Hg PM OUT-BF})} + (\text{Flow OUT-BF gas } \times \text{ C}_{\text{Hg OUT-BF gas}})]}{[(\text{Flow OUT-cyclone PM } \times \text{ C}_{\text{Hg OUT-cyclone PM})} + (\text{Flow Gas OUT-cyclone } \times \text{ C}_{\text{Hg Gas OUT-cyclone})}]} \tag{3}
\]

\[
\text{TOTAL MB} = \frac{[(\text{Flow FA } \times \text{ C}_{\text{Hg FA}}) + (\text{Flow BSW } \times \text{ C}_{\text{Hg BSW}}) + (\text{Flow BS } \times \text{ C}_{\text{Hg BS}}) + (\text{Flow OUT-BF PM } \times \text{ C}_{\text{Hg OUT-BF PM})} + (\text{Flow OUT-BF gas } \times \text{ C}_{\text{Hg OUT-BF gas}})]}{[(\text{Flow Feed fuel } \times \text{ C}_{\text{Hg FF}}) + (\text{Flow PW } \times \text{ C}_{\text{Hg PW}})]} \tag{4}
\]
Where the output and input flows (Flowx) are the flows for a given stream IN and OUT of the oxy-PCC, depuration train (BFW heater + BF) and for the whole installation and for mass balance calculations; and $C_{\text{Hg}}$ is the mean concentration of Hg in the inputs and outputs streams (feed fuel, oxy-FAs, boiler slag, etc).

Because the continuous CO$_2$-rich flue gas re-circulation to the boiler could lead to an increase of Hg input gas in the depuration train, net MBs were performed by excluding the total proportion of Hg re-circulated with the CO$_2$-rich flue gas from the gas output stream considered for MB calculations. The total proportion of Hg re-circulated with the CO$_2$-rich flue gas was calculated by considering the: 1) concentration of Hg in the CO$_2$-rich exhaust flue gas re-circulated to the boiler; 2) % CO$_2$-rich exhaust flue gas re-circulated to the boiler; and the 3) oxy-PCC operational conditions during the sampling campaign (gas velocity; flow gas; gas sampled volume; oxy-PCC dimensions).

Because CIUDEN’s CO$_2$ operates at a demonstration phase, the effect of the CO$_2$-rich flue gas re-circulation on Hg was determined by estimating the number of CO$_2$-rich flue gas re-circulations to the boiler during the sampling campaign. Owing to the impossibility of determining the number of CO$_2$-rich flue gas re-circulations to the boiler during the sampling campaign in the first operating cycle of the CO$_2$-rich flue gas re-circulation, an estimation of this cycle was carried out. This estimation was performed by considering operating hours of work of the oxy-PCC from steady operational conditions (controlled together with the power plant staff), the average velocity (m/s) of the CO$_2$-rich flue gas along the depuration train during routine operating conditions, and the oxy-PCC dimensions.

3. RESULTS AND DISCUSSION

3.1 Feed fuel

The bituminous coals are characterised by middle ash content (12-14%) with relatively high-N (1.5%) and low-S (0.7 %). Quartz, kaolinite, and traces of calcite, albite, and dolomite are the main mineral phases. Gypsum which is of secondary origin from the weathering of sulphide minerals is also detected in samples of these coals.
The bituminous feed coals show major enrichment in Cl and Hg compared to the Yudovich and Ketris (2006) and Swaine’s (1990) worldwide values (Table 2). Chlorine reached concentrations (768-1495 mg/kg) relatively close to the highest of Swaine’s (1990) worldwide values (50-2000 mg/kg), whereas Hg reached concentrations (0.1 mg/kg) in between the maximum and minimum of Swaine’s (1990), and the similar to those of Yudovich and Ketris (2006).

3.2 Solid by-products

Oxy-FAs consist of an alumina-silicate glassy matrix with minor amounts of mullite, maghemite, hematite, and traces of anhydrite, calcite, and lime. Similarly, slag is characterised by the predominance of an alumina-silicate glass matrix, with lower contents of quartz, albite, hematite, mullite, and traces of anorthite.

There are significant differences in the chemical composition of oxy-PCC FAs. Thus, higher concentration of Hg (Hg concentration 3rd FA/ Hg concentration 1st and 2nd FA) by a factor of 8.0 and 4.0 were determined in 3rd FA set with respect to 1st and 2nd FAs, respectively (Table 2). The progressive increase of Hg concentration in oxy-FAs can be ascribed to the CO₂-rich exhaust flue gas continuously re-circulated to the boiler with relatively high impurities of Hg leading to an increase of Hg input along the depuration train. This together with the decrease of the flue gas temperature through the BFW heater in order to enter in the BF at a temperature of 200ºC, results in a high condensation of Hg on FA surfaces (Table 2). Multi-year studies (Ghorishi and Gullett, 1998; Butz et al., 2000a; 2000b; Gibb et al., 2000; Hower et al., 2005; 2006; 2010) have demonstrated the relationship between decreasing flue gas temperature and Hg capture. The capture of Hg on FAs is progressively increased as the flue gas temperature is reduced below 400ºC and is increased by extending the effective contact time between flue gas and FA. A similar concentration pattern in oxy-FAs is shown by Cl, showing a factor of 7.1 in the 3rd FAs sample set with respect to 1st FAs (Table 2). This is also indicative of the formation of gaseous Cl- species of Hg, primarily HgCl₂, in the CO₂-rich flue gas stream and progressive concentration increase in FAs. Such effects were mainly observed by Qiu et al (2007) and Ueno et al (2008) in lab scale studies. The former reported that elevated CO₂ concentrations potentially enhance Hg retention on FAs, whereas the latter indicated an additional Hg oxidation under oxy-fuel combustion conditions as a result of Hg chlorination.
Because few studies on the speciation and fate of Hg during oxy-fuel combustion at demonstration phase have been carried out and existing test facilities and experimental approaches are considerably different, the comparability of values generated under oxy-fuel conditions is limited. However, it is should be mentioned that a research performed by Liu and Okazaki (2003), Kull et al (2008) and others on the composition of the FA, indicated S enrichment of particles with factor 1.5-3 in comparison with the conventional air case. In this regard, compared to FAs under air-firing conditions, FAs from oxy-PCC show a high concentration in Hg and Cl. The lowest concentration of Hg and Cl in these FAs (1st sample set) is higher by a factor of 2 and 12, respectively, than those from an air co-firing power plant (Córdoba et al., 2012a) and by a factor of 5 and 76, respectively, compared to those from an air-firing power plant (Córdoba et al., 2012b). The highest concentration of Hg and Cl in these FAs (3rd sample set) is higher by a factor of 18 and 62, respectively, than those from the air-firing co-combustion power plant, and by a factor of 40 and 546, respectively, than those from the air-firing power plant. The high Hg concentration in the oxy-PCC FAs subjected to the CO₂-rich flue gas continuously re-circulated to the boiler with relatively high levels of Hg and Cl indicates that the change in the flue gas composition and temperature between oxy-PCC (1000°C) and air PCC (1300-1700°C) has a significant effect on the FAs composition and quality.

Boiler slags show no significant differences in their Hg concentration. However, compared to boiler slags under air-firing conditions (Córdoba et al., 2012a; 2012b), these also show a high concentration in Hg and Cl, which could be due in addition to the CO₂-rich flue gas recirculation, to the flame temperature under oxy-PCC (1000°C). Combustion under oxy-fuel takes place under a lower adiabatic flame temperature compared to that of PCC and hence a reduction of the coal burning rate compared to combustion in air, which decreases vaporization of both volatile and moderately volatile elements as well as particle formation rates (Suriyawong et al., 2006). Compared to the oxy-PCC boiler slag composition, oxy-PCC FAs are highly enriched (FA/slag>2.8) in Hg and Cl (Table 2).

3.3 Composition of flue gas

SO₂ is the dominant acidic gaseous pollutant outgoing the cyclone (IN-BFW), reaching concentrations around 1931 mg/m³N (Table 3). Such high levels rise after BF (OUT-BF) to 2225 mg/m³N, which indicate that SO₂ emissions are not reduced. NOx species reach levels up to 603 mg/m³N in the OUT-
cyclone flue gas (IN-BFW), increasing to 640 mg/m$^3$N OUT-BF. Hydrochloric acid levels in the IN-BFW flue gas (OUT-BFW) exceeded 49 mg/m$^3$N and are slightly reduced to ~40 mg/m$^3$N OUT-BF (18% retention). The progressive increase of the SO$_2$ and NOx concentration of in the CO$_2$-rich flue gas along the depuration train, opposed to decrease concentration along the depuration train, was confirmed by the automatic and continuous measurement system carried out by PG-250 during the 3 consecutive sampling days. Hence, the progressive increase of the SO$_2$ and NOx concentration of in the CO$_2$-rich flue gas along the depuration train, and therefore, negative SO$_2$ and NOx capture efficiencies (Table 3) can be attributed to the continuous CO$_2$-rich flue gas re-circulation with significant quantities of SO$_2$, NOx, and HCl to the boiler after number of re-circulations.

3.4 Concentration and speciation of gaseous Hg under oxy-PCC conditions

Different gaseous Hg patterns are observed along the depuration train (Table 4). The total concentration of Hg OUT-BFW heater is higher (by a factor of 1.7) than at OUT-cyclone but it decreases at the OUT-BF. These results can be interpreted as an increase of Hg input along the depuration train leading to higher Hg concentrations at the BFW heater outlet than at the inlet (OUT-cyclone) because of the continuous re-circulation of the CO$_2$-rich flue gas with relatively high concentrations of Hg to the boiler. The lower concentration of Hg in OUT-BF than at OUT-BFW heater can be attributed to a relatively high retention of Hg in the BF. The adsorption of Hg on FAs as a result of the decrease of the flue gas temperature through the BFW to reach the BF at a temperature of 200ºC can be considered the cause of the moderate retention (48%) of total Hg in the BF (Table 4).

Results evidence that Hg escapes from the cyclone in a gaseous form as Hg$^{2+}$ (68%) and it is the prevalent Hg species OUT-BWF (97%) as well as in the CO$_2$-rich exhausts flue gas (OUT-BF, 99%) with lower proportions of Hg$^0$ (1.3%). The speciation of Hg under oxy-fuel conditions at this oxy-PCC is the opposite than that reported for conventional air PCC plants after FGD (Córdoba et al., 2012a; 2012b; 2012c) and for oxy-fired laboratory and pilot scale studies (Suriyawong et al., 2006; Font et al., 2012) (with no CO$_2$-rich flue gas re-circulation) but in line with a previous pilot scale study under oxy-fuel conditions (Farzan et al., 2003; Gharebaghi et al., 2011). These results are also in line with thermodynamic equilibrium predictions on trace element speciation in oxy-fuel combustion (Jano-Ito et al., 2014), showing gaseous Hg$^{2+}$ as the predominant gaseous Hg species at equilibrium for
temperatures below 400°C. The very high Hg²⁺/Hg⁰ in the flue gas during oxy-PCC and the depuration train can be due to: 1) an increase of O₂(g) content during oxy-fuel combustion accounting for Hg; 2) a continuous interaction of Hg with enriched HCl leading to an increase of Hg oxidation as Hg chlorination, the reaction of Hg⁰(g) with HCl(g) or Cl₂(g) to form HgCl₂(g), is the main mechanism of Hg oxidation (Galbreath et al., 2000); 3) a change in the flue gas composition between oxy-PCC and air PCC as a higher oxidation of Hg in the presence of NO, CO₂ and O₂ via the formation of a high proportion of NO₂ which would react with Hg⁰ to form oxidised Hg species (Fernández-Miranda et al., 2014a); and 4) the lower flame temperature under oxy-PCC (1000°C) than conventional air PCC (1300-1700°C) leading to the occurrence of unburned coal particles, which also promote Hg oxidation (Meij and Te Winkel, 2006; Meij, 2008).

The overall retention rate for gaseous Hg when considering the whole installation (oxy-PCC+BF) reach 12% (Table 4), but this value is markedly dependant on Hg speciation. Elemental Hg is more prone to be retained (95%) while Hg²⁺ shows a negative efficiency capture for the whole installation because of the higher Hg²⁺ concentration at the BFW heater outlet than at the inlet (OUT-cyclone). The continuous CO₂-rich flue gas re-circulations to the boiler with high Hg impurities can be considered as the cause of the Hg²⁺ concentration increase along the depuration train as it is discussed in the next section, whereas the retention of Hg⁰ in FAs by oxidation on unburned coal particles in FAs could be considered as the Hg⁰ retention mechanism as a high occurrence of unburned carbon (12-20%) in these FAs has been found. Multi-year studies (Sakulpitakphon et al., 2000; Hower et al., 2005; Mardom and Hower, 2004; Hower et al., 1999; 2006; 2010) under air-combustion conditions have demonstrated relationships among amount FA carbon and Hg capture and FA carbon type and Hg capture.

The concentration of Hgp decreases in the CO₂-rich flue gas along the depuration train, which can be interpreted as a result of the progressive enrichment of Hg in FAs as the continuous CO₂-rich flue gas re-circulation progresses (Table 4).

3.5 Effect of CO₂-rich flue gas re-circulation on Hg
Mass balances were conducted for each sampling day and no significant differences were observed. The very high repeatability provided us with reliable raw data for the MB closure and an overall MB, which comprises the mean values of each day, is reported in this study.

Comparison of the results between MBs and net MBs over oxy-PCC, BFW heater, BF, and the whole installation for Hg brings to light the significant role of the CO₂-rich flue gas re-circulation on Hg partitioning and fate (Table 5). MB for Hg over oxy-PCC closes with excellent OUT/IN ratios (1.3); however, those over BFW heater (1.5), whole installation (1.5), and especially over BF (2.0) close with relatively high OUT/IN ratios, which is due to an excess of Hg in the output streams. Calculations reveal that 44 mg of gaseous Hg (43.5 mg Hg²⁺/ 0.4 mg Hg⁰) were re-circulated to the boiler during the sampling campaign as a result of 2183 re-circulations of CO₂-rich flue gas. This explains the increase of gaseous Hg²⁺ concentration in the CO₂-rich flue gas and therefore the negative retention efficiencies of gaseous Hg²⁺ along the depuration train.

Net MBs for Hg close with much better OUT/IN ratios, especially over oxy-PCC (0.8) and whole installation (1.1), than those considering CO₂-rich flue gas re-circulation, which indicates that oxy-PCC affects the partitioning, behaviour and fate of Hg because of the re-circulation of CO₂-rich flue gas to the boiler with relatively high levels of Hg (Table 5). Despite excluding the re-circulated proportion of Hg with the CO₂-rich flue gas, the MB over BF (1.7) still close with relatively high OUT/IN ratios. This relatively high Hg OUT/IN ratio is due to the enrichment of Hg in the FAs leading to an excess of Hg output even excluding the Hg re-circulated with the CO₂-rich flue gas. FAs constitute 77% of the Hg output in the BF. The excess of Hg output because of its enrichment in FAs cannot be discarded for MB calculations over BF.

The overall retention rate calculated by excluding the gaseous Hg²⁺ proportion re-circulated to the boiler reveal that Hg²⁺ concentrations at the OUT-BF (2.2 µg/Nm³) would be lower than at the OUT-cyclone (2.6 µg/Nm³) leading to 16% of gaseous Hg²⁺ retention efficiency.

These results bring to light that CO₂-rich flue gas re-circulation plays a significant role in the partitioning and fate of Hg. The continuous CO₂-rich re-circulations to the boiler increase Hg input in
the depuration train leading to negative retention efficiencies for gaseous Hg$^{2+}$ and Hg enrichment in FAs.

3.6 Partitioning and fate of Hg

In accordance with the volatile behaviour of Hg at the oxy-PCC (boiler + cyclone), Hg can be classified as highly volatile (75%) with a significant proportion in the FAs (21%) (Figure 2). In the BFW heater, the OUT-BFW gas (65%) is still the whole output of Hg followed by FAs (34%). However, Hg behaviour and partitioning are significantly modified by the operational conditions from the BFW heater to the BF. In the BF, FAs (77%) are the whole output for Hg, followed by the OUT-BF CO$_2$-rich flue gas re-circulated (15%) to the boiler and the OUT-BF gas (8.3%). Calculations based on experimental data demonstrate that the continuous CO$_2$-rich flue gas re-circulation increases the input of gaseous Hg in the depuration train. This together with the decrease of the CO$_2$-rich flue gas temperature from the BFW to the BF leads to the progressive Hg enrichment in FAs.

Mercury speciation in PCC under air-combustion conditions has been reported by Meij (1997; 1999), Gulli et al (1999), Galbreath and Zygarlicke (1999), Hower et al. (1999), Senior et al (2000), Gibb et al (2000), Meij and te Winkel (2006), and Park et al (2008), Córdoba et al (2012c), among others. All these studies concluded that, regardless of the manner in which Hg is present in coal, Hg$^0$ (g) is released during combustion. During post-combustion, and with decreasing temperature, Hg$^0$ (g) may remain as a monatomic species or may oxidise to Hg$^{2+}$ and Hg$^{2+}$ compounds, whereas under oxy-fuel combustion conditions, results reported here that Hg escapes from the cyclone in a gaseous form as Hg$^{2+}$ (68%) and it is the prevalent in the CO$_2$-rich exhausts flue gas (OUT-BF, 99%) with lower proportions of Hg$^0$ (1.3%).

Regarding Hg partitioning and fate, Hg leaves the power plants under air-combustion conditions mainly in the FA and flue gases; only a minor part is present in the FGD-gypsum, sludge of the waste water treatment plant, and effluent (Meijj, 1994). However, according to other works such as those presented by Álvarez-Ayuso et al (2006) and Cheng et al (2009), the partitioning of Hg OUT-FGD can vary greatly. These authors reported that 60 and 70% of Hg removed by the FGD was found in the FGD-gypsum, respectively, and about 35% and 4%, respectively, was emitted into the atmosphere.
This suggests that the partitioning of Hg OUT-FGD could depend on e.g. specific operational conditions of power plants. According to Meij (1991) the temperature of the ESP and the Cl content of the fuel appear to have a profound effect on the speciation of Hg, which in turn greatly affects the emissions. Gullit et al (1999) reported that calcium compounds can promote the adsorption of Hg$_2$Cl$_2$ on FA particles, thus increasing the removal in the ESP, and decreasing the incoming proportion of Hg to FGD system. Regarding the emission abatement capacity for Hg, measurements in US showed that the combination of SCR, ESP, and wet FGD gave rise to Hg removals of 84-89% (Withum et al., 2005).

After comparing our results with the above Hg patterns, it can be concluded that oxy-PCC operational conditions also modifies the behaviour and fate of Hg compared to that under air-firing conditions mainly due to the CO$_2$-rich flue gas re-circulation to the boiler. The partitioning for the whole installation (Figure 3) indicates that the whole output (as mean in %) of Hg is mainly in the FA (64%) followed by the CO$_2$-rich exhaust flue gas re-circulated (23%), CO$_2$-rich exhaust flue gas (13%), and boiler slag (0.3%). The gaseous emission of Hg (36%) is produced in a significant amount but it is still retained by the whole system with relatively high proportions (64%).

4. CONCLUSIONS

Based on these results, it can be concluded that oxy-PCC operational conditions modifies the speciation, behaviour and fate of Hg compared to that under air-firing conditions mainly due to the CO$_2$-rich flue gas re-circulation to the boiler. Calculations revealed that 44 mg of Hg were re-circulated to the boiler during the sampling campaign as a result of 2183 re-circulations of CO$_2$-rich flue gas leading to negative gas retention efficiencies of Hg for the whole installation and its enrichment in FAs.

Mercury escapes from the cyclone in a gaseous form as Hg$^{2+}$ (68%) and it is the prevalent in the CO$_2$-rich exhausts flue gas (OUT-BF, 99%) with lower proportions of Hg$^0$ (1.3%). The occurrence of Hg$^{2+}$ in the flue gas during oxy-PCC and the depuration train, opposite to that under air-conditions, are ascribed to: 1) increase of O$_2$ (g) content during oxy-fuel combustion accounting for Hg oxidation; 2) continuous interaction of Hg with enriched HCl leading to an increase of Hg oxidation as Hg.
chlorination is the main mechanism of Hg oxidation; 3) a change in the flue gas composition and
temperature between oxy-PCC and air PCC as a higher oxidation of Hg in the presence of NO, CO\textsubscript{2}
and O\textsubscript{2} via the formation of a high proportion of NO\textsubscript{2} which would react with Hg\textsuperscript{0} to form oxidised Hg
species; and 4) the lower flame temperature under oxy-PCC than conventional air PCC leading to the
occurrence of unburned coal particles, which promote Hg oxidation.

The overall retention rate for gaseous Hg when considering the whole installation are around 12%.
Elemental Hg is more prone to be retained (95%) while Hg\textsuperscript{2+} shows a negative efficiency capture for
the whole installation. The negative Hg\textsuperscript{2+} capture efficiencies are due to the increase of Hg input along
the depuration train as a consequence of the continuous CO\textsubscript{2}-rich exhaust flue gas recirculation to the
boiler with high impurities of Hg.

The partitioning for the whole oxy-PCC plant indicates that the gaseous emission of Hg (36%) is
produced in a significant amount but it is still retained by the whole oxy-PCC plant with relatively high
proportions (64%). Especial attention must be paid to the role of the CO\textsubscript{2}-rich exhaust flue gas re-
circulation to the boiler on the Hg enrichment in FAs. The enrichment of Hg in FAs because of re-
circulating CO\textsubscript{2}-rich stream with significant quantities of Hg is highly significant as it may reduce the
valorisation possibilities of this solid residue and/or lead to environmental leaching problems if FAs
are disposed in landfills.

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Institute of Environmental Assessment and Water Research, Spanish National Research Council
(ID\textdegreeEA-CSIC).

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FIGURES

FIGURE 1. 20MWth oxy-PCC demonstration plant for capture of CO₂

FIGURE 2. Partitioning of Hg over oxy-PCC, BFW, and BF

FIGURE 3. Partitioning of Hg for the whole oxy-PCC installation
FIGURE 1

- 20 MWth PC BOILER
- Coal
- Boiler slag
- CO₂-rich flue gas recirculation
- Cyclone
- BFW heater
- Bag Filter
- Fly Ash
- Fly Ash sampling point
- Sampling points
OXY-PCC: oxy-Pulverised Coal Combustion unit (boiler + cyclone)
BFW: Bag Filter water pre-heater
BF: Bag Filter
FIGURE 3

Total partitioning of Hg

- Fly Ash
- Boiler slag
- OUT-BF PM
- OUT-BF gas
- OUT-BF re-circulated gas
- Boiler slag water

Logarithmic scale (log scale)
TABLES

TABLE 1. Operational conditions during the sampling campaign
TABLE 2. Concentration of S, Cl, and Hg in solid streams
TABLE 3. Flue gas composition
TABLE 4. Concentration and speciation of Hg in the flue gas
TABLE 5. Mercury mass balances around oxy-PCC, BFW, BF and whole installation
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FC: Feed coal; FA: Fly ash; BS: Boiler slag
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