Differential Partitioning and Speciation of Hg in Wet FGD

Facilities of two Spanish PCC Power Plants

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Abstract

This paper evaluates the speciation and partitioning of mercury in two Spanish pulverized coal combustion power plants (PP1 and PP2), equipped with wet limestone-based flue gas desulphurization facilities (FGD) operating with forced oxidation and recirculation of FGD water streams. These plants are fed with coal (PP1) and coal/pet-coke blends (PP2) with different mercury contents. The behaviour, partitioning and speciation of Hg were found to be similar during the combustion processes but different in the FGD systems of the two power plants. A high proportion (86-88%) of Hg escaped the electrostatic precipitator in gaseous form, Hg^{2+} being the predominant mercury species (68-86%) to enter the FGD. At this point, a relatively high total Hg retention (72 and 65%) was achieved in the PP1 and PP2 (2007) FGD facilities respectively. However, during the second sampling campaign for PP2 (2008), the mercury removal achieved by the FGD was much lower (26%). Lab-scale tests point to liquid/gas ratio as the main parameter affecting oxidised mercury capture in the scrubber. The partitioning of the gaseous mercury reaching the FGD system in the wastes and by-products differed. In the low mercury input power plant (PP1) most of the mercury (67%) was associated with the FGD gypsum. Moreover in PP2 a significant proportion of the gaseous mercury reaching the FGD system remained in the aqueous phase (45%) in the 2007 sampling campaign while most of it escaped in 2008 (74%). This may be attributed to the scrubber operating conditions and the different composition and chemistry of the scrubber solution probably due to the use of an additive.

Keywords: Mercury partitioning, speciation, wet FGD

1. Introduction

Mercury is an element of special environmental concern because of its toxicity, persistence and bioaccumulation in the environment (US EPA, 2011). Today about 66% of total worldwide mercury emissions come from coal-fired power plants and future predictions point to an increase in this contribution due to the important role of coal combustion in electricity generation in developing countries (Pacyna et al., 2010). The major pathways for mercury release from coal combustion are via air and wastes. Unlike most other heavy metals, the majority of the mercury in the exhaust gas from combustion remains in gas phase (Meij, 1991; Clarke and Sloss., 1992; Sloss, 1995; Miller et al., 2002; Park et al., 2008). During combustion, most of the Hg bound in the coal is released as gaseous elemental mercury. Subsequent cooling of the combustion gas and interactions between the gaseous Hg^0 and other combustion products convert Hg^0 to gaseous oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg_p) (Sloss, 1995; Park et al., 2008;). The extent of this transformation depends on the characteristics of the coal and combustion conditions (Park et al. 2008). Particle-bound mercury can be retained in particle control devices such as electrostatic precipitators (ESPs). However, gaseous elemental and oxidized mercury are emitted to the environment in different proportions.

The 1990 Clean Air Act Amendments listed mercury compounds as hazardous air pollutants and required the Environmental Protection Agency (EPA) to establish technology-based standards for certain sources that emit these air toxics. In line with this requirement, EPA is developing air toxics emissions standards for power plants and intends to propose air toxics standards for coal- and oil-fired electric generating units by March 10, 2011 and finalize a rule by November 16, 2011 (US EPA, 2011). In Europe, the European Commission launched the EU Mercury strategy in 2005 (EC, 2005). In this document coal burning is identified as one of the largest sources of mercury release.

Coal burning in plants above 50 MWth is covered by the Integrated Pollution Prevention and Control and 2001/80/EC Directives.

Among the different systems proposed for the reduction of mercury emissions in power stations, multi-pollutant gas cleaning systems are considered a valuable option in terms of efficiency and low investment (Niksa and Fujiwara, 2005; Álvarez-Ayuso et al., 2006; Meij and Te Winkel, 2006; Díaz-Somoano et al., 2007; Meij and Te Winkel, 2007; Senior, 2007; Cao et al, 2008; Hutson et al., 2008; Stergarsek et al., 2008; Tao et al., 2009). In this approach, the wet flue gas desulfurization (wet FGD) units installed in power plants for SO₂ capture could be optimized for the co-capture of pollutants other than sulphur, including some mercury species. Unlike elemental mercury, which is not water-soluble, oxidized mercury compounds such as HgCl₂ dissolve in water. Therefore, wet FGD technologies could be used for the co-removal of highly-soluble oxidized mercury (8-72%) (Niksa and Fujiwara, 2005; Meij and Te Winkel, 2006; Díaz-Somoano et al., 2007; Senior, 2007; Hutson et al., 2008; Stergarsek et al., 2008; Tao et al., 2009), a portion of which could be retained in the FGD slurry and FGD gypsum end-product. Accordingly, FGD facilities should be regarded as potential systems for mercury reduction emissions. However, this fact makes that high amount of toxic species could be present in the produced gypsum. For these reasons, it is important to have a clear understanding of the speciation and partitioning of mercury in wet FGD facilities and to determine which parameters influence mercury behaviour in these facilities. It is known that the efficiency of FGD plants for mercury emission reductions may vary considerably even among similar units due to the wide range of operational parameters and to the different pollution control devices employed (ESP and De-NO_x).

The objective of this study was to evaluate the speciation and partitioning of mercury in two Spanish Pulverised Coal Combustion (PCC) power plants equipped with

wet limestone-based FGD facilities operating with forced oxidation and re-circulation of FGD water streams. These plants are fed with coal and coal/pet-coke blends that have different mercury contents. The results were obtained from the simultaneous sampling of solid, liquid and gaseous streams and their subsequent analysis in two separate laboratories to ensure the accuracy of the quantitative analysis. On the basis of the results mercury retention efficiency in wet FGD facilities operating with recirculation of FGD water streams was evaluated.

2. Materials and methods

2.1. Power stations and sampling procedures

Three sampling campaigns were undertaken in two large (1050 and 1200 MW) Spanish PCC power stations (labelled PP1 and PP2, respectively) equipped with wet limestone-based with forced oxidation FGD systems (Ochoa et al., 2009). The PP1 power plant was fed with a 100% coal blend (60:40 local sub-bituminous coal: bituminous coal), containing a relatively low mercury input (16 g h^{-1} per unit). The PP2 power plant was fed with 82:18 and 84:16 coal:petroleum coke blends for the 2007 and 2008 samplings respectively. These combustible blends provided a relatively high mercury input ($30\text{-}31 \text{ g h}^{-1}$).

Both FGD systems use limestone as reagent and operate in forced oxidation mode in order to ensure the conversion of the captured SO_2 to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The gypsum slurry was discharged over filters, previous separation of the liquid fraction by hydro-cyclones which was re-used in the scrubber. In PP1 the limestone slurry was prepared by mixing the pulverised limestone with the process water (taken from a nearby reservoir and subsequently treated to reduce the content of salts) and a fraction of the re-circulated water in the reagent tank. The remaining filtered water (45%) was

sent directly to the spray nozzles of the scrubber. In PP2 the filtered water was sent directly to the spray-nozzles and was not used in the preparation of the limestone slurry. In this plant the limestone slurry is prepared with process water also arising from a nearby reservoir. Furthermore, an aluminium additive was injected into the scrubber of PP2 plant in order to improve the sorption of SO_x by Ca and to favour the reaction of F with the Al preventing the presence of F in the gypsum (Álvarez-Ayuso et al., 2008; Font et al., 2008). It should be pointed out that the amount of additive dosed to the scrubber was in 2007 twice the amount added in 2008.

The sampling campaigns were carried out at 100% maximum capacity and 100% desulphurisation over two consecutive days. Solid, liquid and gaseous streams were collected simultaneously from each power plant in order to calculate the mass balance of mercury. The solid samples were mixed, crushed, milled and rafted and representative samples of each sampling day were analysed. The water streams and gas trapping solution samples were filtered in situ. $\text{K}_2\text{Cr}_2\text{O}_7$ was employed to stabilize the mercury in the solutions. All the samples were divided into two groups for analysis in two separate laboratories [a] and [b].

The concentration of mercury in the gas was measured at two different sampling points, upstream, (IN)-FGD, and downstream, (OUT)-FGD, in the FGD unit. The speciation of mercury emissions were determined according Ontario-Hydro method (ASTM D6784-02, 2008). In such a method a sample of 1 m^3 (or higher) was withdrawn from the flue gas stream through a filter system. Due to the high solubility in water of oxidised mercury, it was trapped in bottles containing a chilled aqueous solution of KCl. Elemental Hg is collected in the subsequent bottles containing chilled solutions of 5% HNO_3 in 10% H_2O_2 and 4% KMnO_4 in 10% H_2SO_4 .

2.2. Mercury analysis

The mercury content of the solid, liquid, gaseous and particulate matter (PM) samples was measured by means of an Automatic Mercury Analyser (AMA-254) in two separate laboratories, [a] and [b], following the ASTM Standard D 6722-01 method (ASTM, 2006). The solid samples were previously acid digested following the method devised by Querol et al. (1995) whereas the particulate Hg contents were determined directly from the quartz filter samples.

2.3. Lab-scale tests

In order to investigate the different mercury behaviour observed during the two sampling campaigns carried out in PP2, a lab-scale device was built (Fig. 1). The apparatus consists of a closed glass vessel in a thermostat system to ensure a constant temperature. A calibration gas generator system (HOVACAL, IAS GmbH) coupled with an evaporator was used to generate oxidised mercury in gas phase.

Limestone slurry was prepared using sulphuric acid and the limestone collected during the sampling campaign in PP2. A simulated flue gas containing nitrogen, oxygen and a known amount of mercury was passed through the slurry solution. When sulfite ions were added to the reaction vessel flue gas only contained mercury and nitrogen in order to favour Hg^0 formation. A continuous mercury emission monitors (VM3000) was used to follow elemental mercury concentration in gas phase. The continuous mercury analyser was replaced by Ontario-Hydro sampling train when mercury speciation at the gas outlet was necessary.

3. Results and discussion

3.1. Mercury analysis

The results of the mercury analysis obtained by the two laboratories [a] and [b] were in good agreement. The differences between the mercury concentrations obtained

in the two laboratories are calculated, as well as the reproducibility value (R) both in accordance with the ASTM, D-6722-01 standard method (ASTM, 2006). The differences between results obtained for mercury concentrations in both laboratories were lower than 0.01 ppm except for gypsum samples in which the values ranged between 0.02 and 0.04 ppm. The R value provides an indication of the deviations between the results from the two laboratories but it is based only on the mercury content range between 0.017 and 0.586 $\mu\text{g g}^{-1}$ in accordance with ASTM rules. Due to the high correlation between the results obtained in both laboratories the results of all the mercury analyses are reported as mean values.

3.2. Mercury mass balances

In order to validate the design of the sampling campaign and to assure the reliability of the results, the following mass balance calculations were performed: i) through the entire installation (total) ii) around the Boiler + ESP and iii) around the FGD system. The different stream flows are based on information provided by the power plant.

Table 1 shows all the inputs and outputs considered for the mass balance calculations therefore the achieved mass balance closure. In general good mass balance closures were achieved, with Out/In ratios ranging from 0.8 to 1.0 (Table 1). Mercury flows of the different sampled streams are shown in Fig. 2. As expected, the feed fuel blend is the main source of mercury in the combustion process. In PP1 this input was 16 g h^{-1} of mercury and it was higher in PP2, close to 30 g h^{-1} (Table 1). An additional contribution to mercury input in PP2 came from the re-circulated water (45 to 50 g h^{-1}), but this was compensated for by the mercury output from the scrubber, the gypsum slurry (water + solid gypsum), 60 and 53 g h^{-1} in PP2 (2007) and PP2 (2008), respectively (Table 1). The high concentration of mercury in the water is a consequence

of its accumulation as it dissolves over consecutive cycles. If all the inputs are added up, the total mercury input to FGD amounted to 16 and almost 80 g h⁻¹ in the PP1 and PP2 plants respectively though it should be remembered that in PP2 a 45% of the water is returned to the plant.

Mercury behaviour during combustion was similar in the two power plants. A very low proportion of the incoming mercury was retained in the slag (< 0.1%), whereas in the pulverised fly ash only 10% was captured. Due to the high volatility of mercury, most of this element (86 at PP1 and 78-89% at PP2) escapes the ESP in gas phase. As a result 11 and 25-27 g h⁻¹ of mercury reached the FGD system in gas phase in PP1 and PP2, respectively (Table 2).

3.3. Mercury removal in FGD systems

Significant differences were observed for mercury behaviour in the FGD plants and as a consequence, after passing through the FGD system (OUT-FGD) different mercury concentrations were emitted in gas phase, 3.6, 9.3 and 21 g h⁻¹ in PP1, PP2-2007 and PP2-2008, respectively (Table 2). The concentrations of Hg in the gaseous streams IN and OUT-FGD in the three samplings are summarised in Table 2. As previously mentioned most of the mercury escapes the ESP in gas phase, 7.8 and approximately 20 µg m⁻³ of mercury input in the gas phase to the FGD system in PP1 and PP2, respectively (Table 2). These concentrations represent a flow of 11 and approximately 25-27 g h⁻¹ of gaseous mercury input to the FGD in PP1 and PP2, respectively. Most of this gaseous mercury was found to be in oxidised form. In PP1, 74% of the incoming mercury was Hg²⁺ whereas in PP2 it was 85 and 88% for each sampling campaign. These results agree with the generally held view that HgCl₂ can be expected to be the predominant species under the typical operating conditions of ESP prior to entry into the FGD plant (Meij and Te Winkel, 2006).

A relatively high total mercury removal was achieved in the scrubber of PP1 (72%) and PP2 (2007) (65%). However a lower total mercury abatement was attained during the second sampling campaign in PP2 (26%) (Table 3). As was expected, due to the different solubility of Hg species, elemental mercury passed through the FGD systems being emitted in gaseous form. The emission of elemental mercury represents 3-5% of the total mercury input. The fact that the quantity of elemental mercury at the FGD outlet and inlet was found to be similar implies that oxidised mercury reduction and re-emission as elemental mercury that take place in some FGD plants (Meij and Te Winkel, 2006; Díaz-Somoano et al., 2007; Senior, 2007; Hutson et al., 2008; Stergasek et al., 2008) did not occur in the plants evaluated in this study. The main mercury species retained in the FGD was oxidised mercury with retention efficiencies ranging from 67 to 62% in PP1 and PP2 (2007) respectively, although it was found to be notably lower (23%) in PP2 (2008). These different mercury abatements could be due to the different mercury concentrations in the scrubber. The highest oxidised mercury abatement occurred in PP1 where the mercury concentration input in gas phase was low. However, this variation in mercury concentration cannot explain the different mercury behaviour in the FGD plant in the two sampling campaigns of PP2. In order to explain this fact, a thorough investigation on mercury behaviour in FGD systems has been carried out using a lab-scale device (Fig. 1). As a first approach it was considered that in these Spanish power plants an important flow of water coming from the scrubber is re-circulated. As a consequence, a high concentration of mercury can be reached in the FGD water stream, representing a serious drawback because equilibrium between the aqueous and gas phases would lead to the formation of the gaseous form of mercury according to the Henry's Law. So a sequence of tests has been carried using different mercury concentration in the scrubber solution. The results (Fig. 3a) show that in the

experimental conditions an increase in mercury concentration in flue gas favours mercury reduction and re-emission. However no correlation with the amount of Hg^{2+} in gas phase was observed. Consequently the variation in mercury concentration cannot explain the different mercury behaviour in the FGD plant in the two sampling campaigns of PP2.

In addition to mercury content, variations in the concentration of other components in the gas and aqueous phases may play an important role. The content of halogen in both the gases and water is also known to modify mercury behaviour and mercury oxidation (Senior, 2007). Although the proportion of mercury species and chloro input in the FGD were similar in the 2 samplings at PP2, the fluorine content differed (Table 2). In PP2 2008 sampling the amount of gaseous fluorine that reached the scrubber was 28.6 mg m^{-3} , while in PP2 2007 it amounted to 14.4 mg m^{-3} , as a consequence of the different F contents in the fuel blend (378 and 182 ppm, respectively). However, lab-tests show that no effect on oxidised mercury removal should be expected due to fluorine concentration in the scrubbing liquor. Experiments with fluorine concentrations of 0-4000 ppm have been carried out. However, no differences between oxidised mercury in the gas coming from the scrubber were detected.

Finally the influence of the liquid/gas ratio (L/G) has been tested. For the lab-scale tests the amount of liquid remained constant while the amount of gas passing through the system was increased. This parameter is directly related to residence time of the gases in the scrubber. Results show that oxidised mercury capture decreases when gas flow through the FGD increases (Fig. 3b). Most of the oxidised mercury is captured in the scrubber until a gas flow value in which the oxidised mercury capture decreased notably, probably due to the low residence time of the gas in the scrubber. This fact

reveals that the low oxidised mercury removal in PP2 (2008) is probably due to L/G ratio. Although the flow of the limestone slurry was quite similar in both sampling campaigns in PP2, the gas flow through the scrubber was a 16% higher in 2008 than in 2007 producing a decrease in the residence time of the gases in the scrubber and a lower oxidised mercury removal. The oxidised mercury that is not dissolve in the aqueous phase goes out to the FGD.

3.4. Mercury partitioning in the FGD by-products

Mercury partitioning in the FGD by-products was also observed to differ during the three sampling campaigns (Fig. 4). In PP1 most of the outgoing mercury was associated with the FGD gypsum (67%) while a low proportion was trapped by the gypsum slurry water (5%). The rest of the gaseous mercury input remained in gas phase (28%). The high retention of Hg in the gypsum by wet FGD plant in PP1 suggests that an insoluble Hg species, such as Hg-sulphate (Cao et al., 2008), may have been present in the scrubber. In the wet FGD plant of PP2 the partitioning was different from that of PP1 as most of the mercury was retained in the FGD water streams. In 2007 sampling 45% of the gaseous mercury that reached the FGD system was collected with the gypsum slurry water, while 20% was associated with the gypsum. A relatively high proportion of mercury remained in gas phase (35%). In the PP2 2008 sampling campaign, the mercury in the aqueous solution amounted to 16% against 10% for gypsum.

The difference observed between PP1 and PP2 is probably related with the use of Al-sulphate in PP2. This compound could favour the formation of soluble mercury species (HgO) instead of HgSO₄ which is commonly associated with calcium sulphate particles. Although more research is necessary, the different partitioning of mercury in PP1 and PP2 is probably related to the use of Al-sulphate.

4. Conclusions

The amount of mercury removed in a FGD unit is highly influenced by the mercury concentration entering the scrubber. This parameter is clearly related to the amount of mercury fed to the boiler and to the efficiency of the particle control device. However, it should be remarked that a high amount of mercury and other species such as halogens, are being introduced to the scrubber due to the recirculation of the water. Moreover, the results discussed in this work underline the importance of carrying out a thorough control of the working conditions in the scrubber, being the L/G ratio an important parameter related to the oxidised mercury removal due to mass transfer and the gas residence time in the scrubber.

The use of an additive in PP2 favours the presence of mercury in the aqueous phase avoiding its association with the resulting gypsum. However some precaution should be taken because this water can be partially re-circulated to the scrubber.

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389 **Table 1.** Mass balances around the boiler and ESP (PCC system); FGD (FGD) and the
390 whole installation (Total); Hg (g h⁻¹).

Stream		PP1	PP2 (2007)	PP2 (2008)
TOTAL				
Fuel Blend	IN	15.5	30.0	30.8
Limestone		0.09	0.00	0.02
Process Water		0.17	0.00	0.00
Recirculated water		0.14	49.3	44.8
Fly ash	OUT	1.58	3.11	3.07
Slag		0.02	0.04	0.01
Slag Water		0.00	0.05	0.05
Gypsum		6.90	3.95	3.62
Gypsum slurry Water		0.60	56.0	49.3
PM-OUT		0.01	0.01	0.00
Gas-OUT		3.57	9.31	21.1
ΣOUT/ΣIN		0.8	0.9	1.0
PCC				
Fuel Blend	IN	15.5	30.0	30.8
Fly ash	OUT	1.58	3.11	3.07
Slag		0.02	0.04	0.01
Slag Water		0.00	0.05	0.05
PM-IN		0.00	0.00	0.01
Gas-IN		10.9	24.9	26.6
ΣOUT/ΣIN		0.8	1.0	1.0
FGD				
Limestone	IN	0.09	0.00	0.02
Process Water		0.17	0.00	0.00
Recirculated water		0.14	49.3	44.8
PM-IN		0.00	0.00	0.01
Gas-IN		10.9	24.9	26.6
Gypsum	OUT	6.90	3.95	3.62
Gypsum slurry Water		0.60	56.0	49.3
PM-OUT		0.01	0.01	0.00
Gas-OUT		3.57	9.31	21.1
ΣOUT/ΣIN		1.0	0.9	1.0

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Table 2. Concentrations of main gaseous pollutants and mercury in the gas stream flowing IN and OUT of the FGD.

$\mu\text{g m}^{-3}$	IN-FGD			OUT-FGD		
(g h^{-1})	PP1	PP2 2007	PP2 2008	PP1	PP2 2007	PP2 2008
Hg_{total}	7.8 (11)	20.5 (25)	19.0 (27)	2.2 (3.6)	7.1 (9.3)	14.0 (21)
Hg^{2+}	5.8 (8.1)	17.5 (21)	16.8 (24)	0.6 (1.0)	4.7 (6.2)	12.3 (18)
Hg^0	2.0 (2.8)	3.0 (3.6)	2.2 (3.1)	1.6 (2.6)	2.4 (3.1)	1.7 (2.6)
$\text{Hg}_{\text{PM}}^{(1)}$	1.3	7.3	0.7	8.8	9.4	1.8
F^-	23.0 ⁽²⁾	14.4 ⁽²⁾	28.6 ⁽²⁾	370	78	147
Cl^-	6188	7191	6148	233	51	93
$\text{SO}_2^{(2)}$	14.6 ⁽²⁾	4319	4746	988	779	555
⁽¹⁾ ng m^{-3} ; ⁽²⁾ mg m^{-3}						

396 **Table 3.** Mercury retention in the FGD systems of the PP1 and PP2 power stations.

Hg removal (%)	Total Hg (%)	Hg²⁺ (%)	Hg⁰ (%)
PP1	72	67	5
PP2 (2007)	65	62	3
PP2 (2008)	26	23	3

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Figure captions

Figure 1. Schematic diagram of lab-scale scrubber used for the experimental tests.

Figure 2. Schematic diagrams of the mercury flows in the sampled power plants in (a) PP1; (b) PP2 (2007) and (c) PP2 (2008) sampling campaigns.

Figure 3. Lab-scale test results. (a) Influence of mercury concentration in elemental mercury emission and (b) influence of gas flow through the scrubber solution on oxidised mercury emission.

Figure 4. Mercury distribution in the FGD by-products.

Fig. 1

413

414 Fig. 2

Fig. 3

Fig. 4