

DIFFERENTIAL PARTITIONING AND SPECIATION OF Hg IN WET FGD FACILITIES OF PCC POWER PLANTS

Raquel Ochoa², Mercedes Díaz-Somoano², Oriol Font¹, Carlos Leiva³, Maria A. López-Antón², Maria Izquierdo¹, Xavier Querol¹, M. Rosa Martínez-Tarazona², Constantino Fernández³, Alfredo Tomás⁴, Pedro Gómez⁴, Antonio Giménez⁴, Silvia Rico¹, Esther Álvarez⁵

¹ Institute of Environmental Assessment and Water Research ((IDÆA-CSIC), and Institute of Earth Sciences "Jaume Almera", (ICTJA-CSIC), Jordi Girona 18-26, E-08034, Barcelona, Spain and Lluís Solé Sabarís, s/n, 08028 Barcelona, Spain

² Instituto Nacional del Carbón (INCAR-CSIC), Francisco Pintado Fé, 26, 33011, Oviedo, Spain

³ Escuela Superior de Ingenieros de Sevilla, Departamento de Ingeniería Química y Ambiental, Camino de los Descubrimientos, s/n. Isla de la Cartuja, 41092 Sevilla, Spain

⁴ ENDESA GENERACIÓN, S.A. Ribera del Loira, 60, planta 2, sector E, 28042, Madrid, Spain

⁵ *Department of Environmental Geochemistry, IRNASA, CSIC, Apto. 257, 37071 Salamanca, Spain*

Keywords: mercury, FGD, partitioning

Abstract

The speciation and partitioning of mercury from two Spanish pulverized coal (co) combustion (PCC) power plants equipped with wet limestone-based flue gas desulphurization facilities (FGD) have been evaluated in this work. The results were obtained by simultaneously sampling the solid, liquid and gaseous streams in the power plants and by determining the mercury content in the representative samples in two laboratories. The behavior, partitioning and speciation of Hg were found to be similar during the combustion processes but different in the FGD system of the power plants. A high proportion (86-88 %) of Hg escapes the ESP in gaseous form, Hg²⁺ being the predominant mercury species (75-86 %) entering the FGD. A similar and relatively high potential for total Hg retention (64-74 %) was achieved in both FGD facilities, Hg²⁺ being the prevalent Hg species retained by the desulphurization process (72-90 %). A low abatement capacity was observed for Hg⁰ (close to 25 %). The prevalent Hg species after FGD, depends on the input of mercury, 71 % Hg⁰ at low mercury inputs and 66 % Hg²⁺ at high mercury inputs. Furthermore, the partitioning of mercury is different in each FGD system. In the low mercury input power plant, 38% of the total Hg input escaped in gas phase. In the FGD byproducts, more than half of the mercury (52 %) was retained by the gypsum whereas only low amount (9 %) was captured in the aqueous fraction of the slurry. Conversely, a very high fraction (80 %) of the incoming mercury was found to be water soluble while only 6 % was captured by gypsum in the power plant with a high mercury input. In this plant only 14 % of the mercury was emitted into the atmosphere. Most probably this is not only because the different input and/or mode of occurrence of Hg but also because the different operational conditions, which modifies the partitioning of this pollutant in wet FGD systems.

Introduction

The coal combustion process has been identified as the largest anthropogenic source of mercury emissions to the atmosphere.¹⁻² During combustion, most of the Hg bound in the coal is released as gaseous elemental mercury (Hg^0). 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). Particle-bound mercury is mainly retained in the particle control devices. However, gaseous elemental and oxidized mercury may be emitted to the environment in different proportions depending on the amount that is captured in the gas cleaning systems installed in the Pulverized Coal Combustion (PCC) power plants. Unlike elemental mercury which is not water-soluble oxidized mercury compounds such as HgCl_2 dissolve in water.

Mercury is a global issue and needs to be considered at this level. However, until now there have been no specific limits for mercury emissions from coal combustion. Current EU regulations that affect large power plants, such as ETS, IPPC, LCPD and NECD will inevitably reduce the amount of coal burned in power production and, as a result, reduce the amount of mercury emitted from power plants. Periodic reviews of the impact that these directives are having on mercury emissions will probably lead to additional measures on mercury emission control.

Wet FGD technologies designed for the removal of SO_2 can also result in the co-removal of highly-soluble oxidized mercury,³⁻⁶ a portion of which may be retained in the FGD slurry and its solid by-products including synthetic gypsum. As a consequence, FGD facilities can be regarded as potential systems for mercury reduction emissions, i.e. for the co-capture of sulphur and mercury species in flue gases. However, it should also be pointed out that the amount of mercury retained in FGD products could be increased if these units are optimized for co-capture. Other issues that need to be considered include the possibility of atmospheric and groundwater release of mercury species during subsequent manufacturing processes, or from the manufactured products themselves or from wallboards and similar products post disposal. For these reasons, it is important to have a clear understanding of the speciation and partitioning of mercury in wet FGD facilities.

The main aim of this work was to evaluate the speciation and partitioning of mercury species from two Spanish PCC power plants equipped with wet limestone-based FGD facilities. These plants are fed with coal and coal/pet-coke blends with different mercury contents. The results were obtained from the simultaneous sampling of solid, liquid and gaseous streams and their subsequent analysis in two different laboratories for purposes of comparison

Experimental

Power stations and sampling procedures

Two 1200 MW Spanish Pulverised Coal (co) Combustion (PCC) power stations (labelled PP1 and PP2) equipped with wet-limestone based FGD facilities and fed with different fuel and mercury inputs (15 g/h and 30 g/h respectively) were selected for this study. The sampling was carried out at 337 MW units from the mentioned power stations. The PP1 power plant was fed with 100 % of coal (60:40 local sub-

bituminous coal and a bituminous coal blend with a relatively low mercury input (15 g/h per unit). The PP2 co-combustion power plant was fed with a coal and coke blend (80:20). The feed coal was a blend of anthracitic coal and imported South African bituminous coal. In this PP2 plant, Aluminum additive was used in the scrubber to improve SO_x removal efficiency.

The sampling campaigns at PP1 and PP2 were carried out at 100% maximum capacity and 100% desulphurisation during 2 consecutive days in September and November 2007 respectively. Solid, liquid and gaseous streams were collected simultaneously from each power plant in order to calculate the mass balance of trace pollutants. 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. K₂Cr₂O₇ was employed to stabilize the mercury in these solutions. All the samples were divided for analysis in two laboratories.

The gas measurements were carried out for two different sampling points, upstream, (IN)-FGD, and downstream, (OUT)-FGD, the FGD unit. The gas trapping system was devised for mercury speciation (Hg⁰ and Hg²⁺) using the Ontario Hydro method (ASTM D6784-02).⁷ A sample of 1 m³ (or higher) was withdrawn from the flue gas stream through a filter system, maintained at the right temperature, followed by a series of impingers and placed in an ice bath. Particle-bound mercury was collected at the front half of the sampling train using quartz micro filters. Due to the high solubility of Hg²⁺ in water, this species was collected by impingers containing a chilled aqueous potassium chloride solution. Hg⁰ was collected in the subsequent bottles, one of which contained a chilled aqueous acidic solution of hydrogen peroxide (5% HNO₃ in 10% H₂O₂) and the three other bottles chilled aqueous acidic solutions of potassium permanganate (4% KMnO₄ in 10% H₂SO₄).

Analysis

The mercury content in the solid, liquid, gaseous and particulate matter samples was measured by means of an Automatic Mercury Analyser (AMA-254) in two different laboratories for comparison following the ASTM Standard D 6722-01 method. The solid samples and filters of particulate matter were previously acid digested following the method prompted by Querol (1995).⁹ Due to the high correlation between the results obtained in both laboratories only the mean values are reported in this study.

Results and discussion

The results of the analysis of mercury obtained from laboratories (a) and (b) showed a high agreement. A representative sample of the results is presented in Table 1. This table shows the Hg content of a number of solid and liquid streams collected from the PP1 power plant during sampling day 1. The differences (d) between the mercury concentrations of the two laboratories are indicated, as well as the reproducibility value (R) estimated in accordance with the ASTM, D-6722-01 standard method.⁸ The R value is considered as an indication of the deviations between the results from two laboratories. According to ASTM rules, the mercury content range needs to be between 0.017 and 0.586 µg g⁻¹.

Table 1. Reproducibility of the results obtained in the two laboratories. Samples from the first day of sampling in PP1

Hg $\mu\text{g g}^{-1}$		R	d	Hg $\mu\text{g g}^{-1}$		R	d
lab (a) IDAEA	lab (b) INCAR	ASTM D-6722	(a)-(b)	lab (a) IDAEA	lab (b) INCAR	ASTM D-6722	(a)-(b)
Solutions from the Ontario Hydro method				Water strams			
0.038	0.028	0.011	0.010	<0.001	<0.001		
<0.001	0.002		0.001	<0.001	0.002		
0.014	0.013		0.001	<0.001	0.002		
0.011	0.010		0.001	<0.001	<0.001		
<0.001	<0.003		0.002	0.038	0.043	0.012	0.005
<0.001	<0.003		0.002	<0.001	<0.001		
0.016	0.016		0.000	<0.000	<0.001		
0.010	0.010		0.000	Limestone samples			
<0.001	<0.001		0.000	<0.001	0.002		
0.013	0.012		0.001	0.002	0.003		0.001
0.015	0.015		0.000	0.002	0.003		0.001
<0.001	<0.001		0.001	0.002	0.008		0.006
<0.001	0.004		0.003	FGD-Gypsum samples			
<0.001	0.003		0.002	0.162	0.124	0.026	0.038
				0.167	0.144	0.027	0.022
				0.178	0.165	0.029	0.012
				0.190	0.165	0.030	0.025

R; reproducibility limit according to ASTM, D-6414 ($0.007 + 0.13\bar{x}$) for a concentration range 0.017-0.586 $\mu\text{g g}^{-1}$

d: differences between the results from the two laboratories

The mass balance of the mercury in both FGD facilities was calculated on the basis of the mercury content in the limestone and gypsum slurries (solid + liquid), and gas and solid particles at the FGD inlet and outlets (Table 2). Similar closures between 83 and 100% were obtained for the two plants. The total mercury inputs to FGD were 11 and 76 g/h in the PP1 and PP2 plants respectively. In PP1, due to the highly volatile behaviour of mercury during combustion (86 %), the gas leaving the ESP supplies the main input of mercury to the FGD system (11 g/h). In PP2, mercury is also evaporated in a similar proportion (88%), the mercury input in the gas being 25 g/h. However in PP2 the main source of mercury to the FGD system (51 g/h) was the filtered water that was re-circulated to the scrubber. The main output streams were the FGD gypsum (7.4 g/h) in PP1 and the filtered water (51 g/h) in PP2.

The proportions of Hg^0 and Hg^{2+} found in the gas at the inlet of FGD in both power stations were similar. In PP1 80% of the incoming mercury was Hg^{2+} and in PP2 85%. These results indicate that HgCl_2 can be expected to be the predominant species under typical operating conditions of electrostatic precipitators (ESP) (between 180 and 150 °C in the power stations studied), prior to entry into the FGD plant.

A relatively high retention potential for total Hg (67-72 %) was achieved in both FGD facilities (Table 3), Hg^{2+} being the prevalent species retained (i.e. 73 to 86 % of the Hg^{2+} entering the system). In contrast a low abatement capacity was obtained for

Hg⁰, this being 26 and 14 % in PP1 and PP2, respectively. The prevalent mercury species in the gas phase leaving the FGD depended on the input of mercury species, which was 68 % for Hg⁰ in PP1 and 67 % for Hg²⁺ in PP2. Furthermore, the partitioning of Hg differs in each FGD system. In PP1, the highest retention of Hg (67 %) was achieved by the FGD gypsum, whereas only 33 % was emitted as gaseous Hg. Conversely in the PP2 power plant, the highest proportion (83 %) of incoming Hg was retained in the effluent (filtered water, re-circulated to the scrubber), while only 7 % was captured by FGD-gypsum. Only 10% of the Hg was emitted into the atmosphere

Table 2. Mass balances in the FGD systems of the PP1 and PP2 power stations.

		PP1		PP2	
		g h ⁻¹	SD	g h ⁻¹	SD
Hg in FGD	Limestone	N.D.	-	N.D.	
	Effluent	N.D.	-	N.D.	
	Filtered water	N.D.	-	51	6
	Particles prior to FGD	0.002	0.001	0.009	^a
	Gas at the inlet of FGD	11	0.6	25	6
	Total	11		76	
Hg out FGD	Gypsum	7.4	0.8	4.2	0,1
	Filtered water	0	-	52	6
	Particles out FGD	0.015	0.005	0.01	^a
	Gas at the outlet of FGD	3.7	0.5	7	2
	Total	11		63	
Out/in balance (%)		100		83	
SD		6		2	

a: not available N.D: not detected, SD; standard deviation

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

		Hg ²⁺ (µg/m ³)	Hg ⁰ (µg/m ³)	Total Hg (µg/m ³)
PP1	In FGD	5.7	2.0	7.8
	Out FGD	0.7	1.5	2.2
	Retention (%)	88	25	72
PP2	In FGD	18	3.0	21
	Out FGD	5.0	2.5	7.5
	Retention (%)	72	17	64

The FGD facilities of the PP1 and PP2 plants removed 88 and 72% of the total mercury at the inlet. The distribution of the total mercury in the outlet products is represented in Figure 1. The mercury content in the flue gas at the outlets of FGD is equivalent to 11% and 34% of the total mercury at the outlet in PP2 and PP1 power plants respectively, whereas the rest of the mercury is distributed among the products in different proportions. In the PP2 power station a high proportion of

mercury is dissolved in the filtered water, whereas in PP1 a significant fraction is retained in the FGD gypsum.

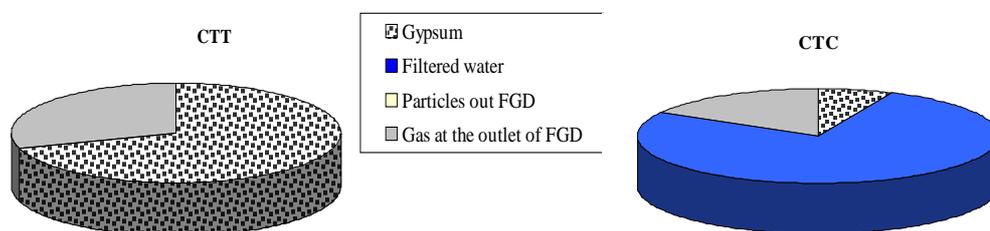


Figure 1. Mercury distribution in the FGD by-products.

The unexpected high proportion of Hg in the water stream entering the FGD system in the PP2 plant was a consequence of the dissolution of high proportions of mercury in the OUT-FGD effluent, and the recirculation of some of this water back into the system. As already mentioned, mercury entering the FGD plants occurs in high proportions in the form of water soluble Hg species, most probably HgCl_2 . Indeed, the main output of Hg from FGD is the effluent (78-81 %), with relatively high fractions of Hg (14 and 15 %) leaving the scrubber as volatile species and only 6-7 % being retained in gypsum.

The reasons for the different partitioning and speciation of Hg in the two power plants are currently being investigated. The higher Hg input from coal and the addition of Al-sulfate to the scrubber in PP2, may modify the interaction between the mercury and the solid fraction of the scrubber solution. The presence of other species such as sulfate and halide ions may also influence the mechanisms and kinetics of mercury re-emission, in some cases preventing the reduction of oxidized mercury to elemental mercury

Summarizing: A mercury measurement campaign was conducted at two coal-fired utilities equipped with limestone FGD scrubbers. The Hg mass balance closures were between 83 % and 100% for both plants. The mass balance data conform to the data quality objectives. Most of the mercury reaching the FGD system is present as oxidised species which is removed in the scrubber solution in different proportions. The removal of mercury in the FGD averaged 72 % for PP1 and 64 % for PP2. The outlet speciation data showed a very low proportion of oxidized Hg but significant levels of elemental Hg. Differences in the fate of the captured mercury were also observed. In PP1 the mercury was retained in the gypsum while in PP2 the mercury was captured in the aqueous solution, where it can be reduced and then re-emitted to the atmosphere. The higher mercury input and the addition of Al-sulphate though the interaction with other species achieving the scrubber solution i.e. halides may also have an effect.

References

1. www.epa.gov/mercury
2. Communication from the Commission to the Council and the European Parliament, 28th January 2005 – Community Strategy Concerning Mercury-COM (2005) 20.
3. Ruud Meij, Henk te Winkel, The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations, *Atmospheric Environment*, 41 (2007) 9262-9272.
4. E. Álvarez-Ayuso, X. Querol, A. Tomás. Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products, *Chemosphere*, 65 (2006) 2009-2017.
5. Liang Zhang, Yuqun Zhuo, Lei Chen, Xuchang Xu, Changhe Chen, Mercury emissions from six coal-fired power plants in China, *Fuel Processing Technology*, 89, (2008), 1033-1040.
6. Mercedes Díaz-Somoano, Sven Unterberger, K.R.G. Hein, Mercury emission control in coal-fired plants: the role of wet scrubbers, fuel processing technology, 88, (2007) 259-263.
7. ASTM D6784 - 02(2008) "Standard test method for elemental, oxidized, particle-bound and total mercury in flue gas generated from coal-fired stationary sources (Ontario Hydro Method)"
8. ASTM D6722 - 01(2006) "Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis".
9. X. Querol, J.L. Fernández-Turiel, A. López-Soler, Trace elements in coal and their behaviour during combustion in a large power station, *Fuel* 74 (1995) 331-343

Acknowledgements

This work was carried out with a grant from the research fund for coal and steel (RFCR-CT-2006-00006). We would like to thank to the staff from the power plants for their support, help and kind assistance before, during and after the sampling campaign.