

## **FATE OF TRACE POLLUTANTS IN PCC-FGD POWER PLANTS**

**Oriol Font<sup>1</sup>, Maria Izquierdo<sup>1</sup>, Raquel Ochoa-Gonzalez<sup>2</sup>, Carlos Leiva<sup>3</sup>,  
Maria Antonia López-Antón<sup>2</sup>, Xavier Querol<sup>1</sup>, Mercedes Díaz-  
Somoano<sup>2</sup>, M. Rosa Martinez-Tarazona<sup>2</sup>, Constantino Fernandez<sup>3</sup>,  
Silvia Rico<sup>1</sup>, Alfredo Tomás<sup>4</sup>, Pedro Gómez<sup>4</sup>, Antonio Giménez<sup>4</sup>,  
Esther Alvarez<sup>5</sup>**

<sup>1</sup>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

<sup>2</sup>Instituto Nacional del Carbón (INCAR-CSIC), Francisco Pintado Fe, 26 - 33011 - Oviedo - Spain

<sup>3</sup>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

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

<sup>5</sup> Instituto de Recursos Naturales y Agrobiología de Salamanca (IRNASA-CSIC). Sede: C/Cordel de Merinas, 40-52. Salamanca. E-37008 (España)

**KEYWORDS:** partitioning, FGD, trace pollutants

### **ABSTRACT**

The partitioning and abatement capacity of trace pollutants in wet limestone-based flue gas desulphurization (FGD) facilities were investigated in two Spanish pulverized coal (co) combustion (PCC) power plants. The results were obtained from simultaneous sampling of solid, liquid and gaseous streams during two days in the power plants. High abatement of most pollutants (>90% as fly ash and slag) is allowed by the electrostatic precipitators (ESP) but Hg, Cl and F (78-98 %) and As, Se and B (0.01-7 %) still displaying a highly and displayed a volatile behavior. The different ESP temperature between power plants mainly account for an unlike volatile/particulate matter (PM) ratio for Se, As and Hg. Together with a high S capture (80-95 %), both FGD facilities showed high retention efficiencies (in gypsum and effluent) for gaseous Cl, F, and B (>95 %), As (78-90 %), Se (84-94 %) and relatively high for Hg (64-74 %) and PM (55-74 %). The high retention allowed reducing their volatile fractions down to 0.01-20 %, upon trace pollutant. The FGD gypsum also retains high fractions (76 -100 %) of Ca, Nd, Ti, Ce, La, Y, Nb, Fe, Pb, Sr, Rb, Ba, V, Cr, Cu, K and U. The PM emitted included the usual fly ash components while Mg, Na, Mn, Co, Sc, Cd, Zn, and Mo are water soluble being retained in the effluent (re-circulated to the scrubber). Major differences were produced in the partitioning of F, Hg, As, Ni, Li, Mo, Sn, Zr, Ga and Al, depending on operational conditions of the power plants (co-combustion of coal/pet-coke, purity of limestone and use of additives (Al) in the scrubber.

## INTRODUCTION

The incoming power generation scenario in the European Union (EU), with a new free electrical market and new environmental regulations promoted the implementation of co-combustion techniques and Flue Gas Desulphurization facilities (FGD). The high abatement of  $\text{SO}_x$  emissions by FGD facilities promoted the use of inexpensive but S-rich co-matters, such as pet-coke. The co-combustion of coal and pet-coke or other inexpensive fuels (sewage sludge or biomass) has environmental and economical benefits and allowed PCC-FGD plants to be competitive. The organic affinity of trace pollutants and potential high Cl contents of these fuels may account for increasing volatility of a number of trace pollutants (B, Se, F, Sn, Zn, among others) in co-combustion [1]. Furthermore the organic affinity and high contents of V, Ni and Mo in pet-coke produced a high volatilization-condensation of these metals with the subsequent occurrence of fine and soluble V, Ni and Mo species in fly ash [1-2]. The FGD facilities trap  $\text{SO}_x$  using alkaline sorbents, by wet or dry processes. The wet limestone-based process is the most widely used due to the high desulphurization abatement. The limestone/lime process, originated in 1909 in the U.S. by methods for purifying burner gases using milk of lime, is based in the reaction of the  $\text{SO}_2$ -rich flue gas flow with aqueous slurry of limestone or lime, to form  $\text{CaSO}_4$  (and Ca-sulfite). The FGD systems of PCC plants may capture significant proportions of other trace pollutants (such as F, As, B, Cl, Se or Hg) incoming the scrubber as fine particulate matter or in the gas phase [3-5]. The retention capacity is influenced by the mode of occurrence of the pollutant, but also on the characteristics of the retention facility (pH, free Ca content and temperature, additives, among others). The partitioning of these trace pollutants among gaseous, liquid and solid streams may influence the potential industrial uses and environmental features of the FGD by-products [6]. The capture of trace pollutants in FGD facilities may reduce the environmental impact of atmospheric emissions but may also cause an increase in the bulk content of trace pollutants in the final FGD gypsum end-product.

The aforementioned changes in volatility and mode of occurrence of trace pollutants by co-combustion pet-coke and other fuels may produce changes in the gas composition incoming the scrubber and consequently in the abatement and emissions of trace pollutants as well as in the composition of the FGD gypsum end-product.

The main objectives of this study are to determine the partitioning of trace pollutants in the PCC-ESP and FGD systems and in the whole installation of PCC plants, to evaluate of the abatement capacity for trace pollutant emissions of wet FGD facilities and establish the potential influence of the co-combustion of pet-coke and use of additives in the above features. To complete the objectives simultaneous sampling of solid, liquid and gaseous streams (including the particulate matter (PM) entrained by the gas were carried out in two 1200 MW Spanish power plants (PP1 and PP2), fed with coal and coal/pet-coke blends, respectively.

## EXPERIMENTAL

A simultaneous sampling of solid, liquid and gaseous streams (including PM) were carried out in two 1200 MW Spanish PCC power plants (PP1 and PP2) equipped with a wet limestone-based with forced oxidation FGD facility. The PP1 is 100 % fed with coal (60:40 mixture of imported bituminous and local coal). The PP2 is fed with an 80:20 coal/pet-coke blend. The feed coal is a blend of Spanish anthracitic coals and a blend of imported South African bituminous coal. The feed pet-coke is a blend of Spanish and imported pet-coke. An Al additive is used in the scrubber of PP2 to improve the SO<sub>x</sub> sorption. The PP2 is also equipped with a gas gas heater (GGH).

The samplings were carried out at 100% MCR (maximum capacity) and 100 % desulphurization in a 337 MW units of the plants, during two consecutive days on September and November 2007, respectively. The sampling of solid streams included coal, pet-coke, feed fuel blend, slag, pulverised fly ash (PFA), fly ash from ESP1, limestone and FGD gypsum. The sampling of liquid streams and slurries included the water from slag drainage, the process water (arising from a lake), the recovered water from gypsum slurry filtration and limestone and gypsum slurries (solid and liquid fractions). In both power plants the recovered water from slurry filtration is re-circulated to the scrubber and mixed with the limestone slurry. The limestone slurry is made with the process water in the proportions required to supply the proportion of water lost as moisture of the gas leaving FGD (OUT-FGD) and of the FGD-gypsum. The samples of coal and pet-coke were collected in the feeders while for feed fuel blend an automatic sampler were used. This apparatus allowed take sample in periods of 6 minutes. PFA was collected in the discharge vessel several times per hour if available (only when trucks transporting the fly ash to the cement industry were in operation). Regarding fly ash from ESP, only fly ash retained in the ESP1 was possible to collect. This fly ash was sampled using an automatic sampler which collect continuously the fly ash produced. Slag was collected once per day when discharged from the vessel. The limestone and gypsum were collected in the limestone feeder and after filtering in the conveyors, respectively. The limestone and gypsum slurries, slag, process and recovered water were sampled in the respective tanks. Different sub-samplings of each stream were performed along each sampling day to obtain representative samples burned and produced during the sampling period. For solid streams a total of 54 samples (raw coals, feed fuel prior sampling, coal, pet-coke, feed fuel blend, slag, pulverised fly ash (PFA), limestone and FGD gypsum) were collected, obtaining a global sample for each stream and sampling day for subsequent mass balance determination. A total of 74 liquid samples were collected for subsequent analysis, corresponding to 5 liquid streams (slag, process and output water and limestone and gypsum slurry). For the slag, process and output waters 3 sub-samplings per day were carried out and 5 sub-samplings per day were performed for limestone and gypsum slurries.

The gas measurements were performed simultaneously with the sampling of solid and liquid streams, at two different sampling points, upstream (IN)-FGD (P1) and downstream (OUT)-FGD unit (P2). Two samplings per day were performed, corresponding to the sampling points P1 (IN-FGD) and P2 (OUT-FGD), respectively. In

each set of sampling and sampling point, the levels of NO, NO<sub>2</sub>, O<sub>2</sub>, CO (major gaseous components) and the gas temperature were measured. Simultaneously with sampling three different gas washing bottle systems were assembled with specific trapping solutions for the capture of different gaseous pollutants (Hg, Cl, F, B, Se and metals). Furthermore, the gas trapping system was devised for the subsequent determination of the speciation of Hg (Hg<sup>0</sup> and Hg<sup>2+</sup>) using the Ontario Hydro method (ASTM D6784-02). In such a method a sample of 1m<sup>3</sup> (or higher) was withdrawn from the flue gas stream through a filter system, maintained at the right temperature, followed by a train of dark glass bottles in an ice bath. Due to the high solubility in water of Hg<sup>2+</sup>, it was trapped in bottles containing a refrigerated aqueous solution. Elemental Hg (Hg<sup>0</sup>) is collected in the subsequent bottles, containing a refrigerated solution of 5% HNO<sub>3</sub> in 10% H<sub>2</sub>O<sub>2</sub> and 4% KMnO<sub>4</sub> in 10% H<sub>2</sub>SO<sub>4</sub>.

The major, minor and trace element concentrations were determined in the collected solid streams. The samples were acid-digested in duplicate by using a special two-step digestion method devised by Querol et al [7] to retain volatile elements in coal and fly ash. The resulting solution was then analyzed by ICP-AES and ICP-MS for major and trace. The coal SARM19 and fly ash international reference material NBS1633b were also digested to check the accuracy of the analytical and digestion methods. The Cl contents were determined by following the ASTM D4208 method for coal samples, using a calorimetric bomb to obtain the chlorine in solution, which is measured by using an ion selective electrode. The determination of F was performed according to the pyrohydrolytic extraction method described in the ISO 11724 standard method and the subsequent analysis of fluorine in solution by using i) an ion selective electrode for high content samples or ii) IC for the low content samples. The concentrations of As and Se were also measured after a HNO<sub>3</sub> extract and further analysis by means of HG-AAS. A very good agreement was obtained with those arising from the acid digestion and subsequent ICP-AES and ICP-MS analysis. The Hg analyses were carried out directly on solid samples using a LECO AMA 254 gold amalgam atomic absorption spectrometer.

The liquid samples, including liquid streams and trapping solutions from flue gas sampling were directly analyzed by ICP-AES and ICP-MS for major and trace elements. Chloride contents were measured by means of high performance ion chromatography (HPLC), whereas fluorides were determined by ion selective electrode. Hg analyses were carried out directly on liquid samples using a LECO AMA 254 gold amalgam atomic absorption spectrometer.

The analysis of the PM was performed by the following procedures:

- The levels of PM IN and OUT-FGD were obtained by standard gravimetric methods.
- The levels of particulate Hg were determined by GA-AAS directly on filter samples.
- The contents of major and trace elements in the filters were determined by ICP-AES and ICP-MS. A prior filter digestion using HF:HNO<sub>3</sub>:HClO<sub>4</sub> was carried out to obtain the bulk dissolution of the samples for the analysis.

## RESULTS AND DISCUSSION

### Mass balance

The results on partitioning and mass balance of trace pollutants in the PP1 and PP2 power plants were performed by combining information on the analytical data obtained from the solid, liquid and gaseous streams and the operational parameters of the power plants during the sampling period. This analytical data were measured in duplicate at two labs. The mass balance was calculated for the 2 sampling days. Due to the very low variations on the concentrations of elements in each stream, no significant differences among the mass balances were observed and it was also calculated using the mean of the two sampling days.

The mass balance for the mean values in the PCC (boiler + ESP), FGD and in the whole installation was carried out for all the analyzed elements except for Cd, Tl, Bi and some REE's (Eu, Tb, Ho, Tm and Lu) not detected in the feed blend, coal and pet-coke. The input and output streams used for mass balance calculations are summarized in Table 1.

The mass balance for PP1 and PP2 power plants (Table 2) was closed with excellent well out/in ratios for the PCC system (0.93 and 1.00 for PP1 and PP2, respectively) and for the whole installation (1.03 and 0.99). The mass balance closure was relatively poor for the FGD (0.73 and 0.66). Generally a good mass balance was obtained for most of elements in the PCC system for both power plants, with the exception of Na and Sc in the PP1 and Se and Ta in PP1 and PP2. The out/in ratio for Se was 0.5-0.6 in both power plants. The mass balance in the FGD for most of elements is generally much poorer than obtained for PCC system, due to the very low concentrations of pollutants in the FGD streams.

### Partitioning in the PCC system (boiler+ESP)

The results allowed to classify the elements according to their volatile behaviour as follows: a) High volatile elements (S, Cl, Hg and F), b) Moderately volatile elements with high condensation potential in PFA (Se and As) and c) Low volatile elements (>80 % in fly ash): Zn, Hf, Pb, U, Zr, Th, Rb, Cs, Mo, Li, Ba, Sn, Mn, Ga, Al, Cr, Sr, Y, Ca, Ti, P, Ge, Be, Mg, Co, Fe, K, Sb, W, Na, Nb, and REEs.

The comparison of the partitioning in the PCC system between the PP1 and PP2 power plants (Table 3) revealed that the volatile proportion of S, Cl, F and Se are higher in the PP1 power station than in the PP2 plant, whereas that of Hg is slightly higher in PP2 than in PP1. Conversely in the PP2 the PM fractions escaping ESP are higher for all the elements than that obtained at the PP1. As a result, the whole fraction of Hg, B, Se and As escaping the ESP is higher in PP2 than in PP1. Bearing in mind that the ash content (29 and 28 % ash for PP1 and PP2, respectively), and the feed fuel input (202 and 142 tn/h) as well as the ESP efficiency (99.6 %), of both power plants are very similar, the differences on the PM fractions of the aforementioned pollutants have to be attributed to the lower ESP temperature of the PP2 (149 °C) than that of PP1 power plant (170-180 °C).

Table 1. Input and output streams used for mass balance calculations in the sampled Spanish power plants.

	<b>PCC</b>	<b>FGD</b>	<b>Whole installation</b>
	Coal-pet-coke blend	Limestone	feed blend
inputs	Process water	0.47/0.53 mixture of limestone slurry water and recovered water	Limestone
		fly ash (PM in FGD), Gas (IN-FGD)	mixture of limestone slurry water and recovered water
outputs	slag PFA, slag water, Fly ash (PM in FGD) gas (IN-FGD)	Gypsum recovered water (effluent) Gas OUT-FGD fly dust (PM OUT-FGD)	Slag PFA slag water, recovered water gas (OUT-FGD) fly dust (PM OUT-FGD)

Table 2. Mean and standard deviation (std) of the Out/In ratio from the mass balance closure for 56 elements in the sampling campaign in the two Spanish power plants.

Out/In	PCC (boiler+ESP)		FGD		Whole installation	
	mean	std	mean	std	mean	Std
PP1	0.93	0.15	0.73	0.54	1.03	0.90
PP2	1.00	0.14	0.66	0.23	0.99	0.13

Table 3. Volatile and PM fractions of S, Cl, Hg, F, B, se and As in the pp1 and PP2 power plants.

		% gas		% PM		gas +PM	
		PP1	PP2	PP1	PP2	PP1	PP2
Highly Volatile	S	98.8	96.9	0.01	0.2	98.9	97.2
	Cl	91.9	88.1	-	-	91.9	88.1
	Hg	86.3	87.6	0.01	0.03	86.3	87.6
	F	86.7	78.6	-	-	86.7	78.6
Moderately Volatile	B	5.7	7.4	0.03	0.1	5.8	7.5
	Se	7.3	3.9	1.02	10.9	8.4	14.8
	As	0.03	0.01	0.24	0.8	0.3	0.8

#### Partitioning of the FGD system

The input and output streams used for the partitioning in the FGD facilities of the PP1 and PP2 power plants are summarized in Table 1. It has to be noted that in PP2, Al is used as an additive being an important source of this metal.

According to their partitioning on IN and OUT-FGD streams and their behavior during desulfurization the elements in the FGD facilities may be classified as follows: a) Partially volatile elements, b) Elements reaching and leaving (emitted) the FGD as PM c) Elements retained in FGD gypsum and d) Water soluble elements (in the FGD water

streams). The proportions and partitioning of elements in the FGD facilities of both power plants are summarized and compared in Table 4.

Table 4. Partitioning of trace pollutants in the FGD system of the PP1 and PP2 power plants. In bold the elements with a different classification.

<b>PP1</b>	
Partially volatile (0.3-39 % volatile OUT-FGD %)	S, Cl, F, Hg, B, As and Se
Retained in FGD Gypsum (76-100 %)	<b>P</b> , Ca, Nd, Ti, Ce, <b>Zr</b> , La, Y, <b>Al</b> , Nb, Fe, Pb, <b>Li</b> , Sr, <b>Ga</b> , Rb, Ba, V, <b>Sn</b> , Cr, Cu, K, U, and <b>Ni</b>
PM (60-100 % emitted)	REEs, Hf, Ta, W, Bi, Th, Cs, Ge, Sb and Be
Water soluble (>60 % in the effluent)	Mg, Na, Mn, Co, Sc, Cd, Zn, and Mo
<b>PP2</b>	
Partially volatile (0.1-17 % volatile OUT-FGD %)	S, Cl, F, Hg, B, As and Se
Retained in FGD Gypsum (85-99 %)	Ca, Sr, Y, Nd, La, Ce, Fe, Pb, Ti, Ba, Cu, V, Cr
PM (46-100 % emitted)	REEs, Hf, Cs, Bi, W, Rb, Th, Sb, Ta, Ge, Be, <b>Nb</b> , <b>Zr</b> , <b>Sn</b> , <b>P</b> , <b>Ga</b> ,
Water soluble (44-94 % in the effluent)	Na, K, Zn, Li, Sc, Co, Cd, U, Mn, Mg, <b>Al</b> and, <b>Ni</b>

The partitioning of the partially volatile elements is of high relevance in view of the potential emissions. These elements are the highly volatile elements during co-combustion. A discussion and comparison of their behavior in the FGD facilities studied are reported below.

### *Sulphur*

In PP1 most of the S incomes the FGD as gaseous species (95 %) and is retained as gypsum (87 and 90 % for sampling days 1 and 2, respectively). Only 9.1 % (day 1) and 6.6 % (day 2) of the incoming S is emitted as gaseous SO<sub>2</sub>.

In the PP2, most of the S incomes the FGD facility as gaseous species (76-80 %). The bulk incoming S is mainly retained in gypsum (69 and 76 % for sampling days 1 and 2, respectively), being partially emitted as gaseous SO<sub>2</sub> (12 %, day 1 and 17 %, day 2). The rest of S is retained as water soluble sulfates.

### *Mercury*

In the PP1 most of the Hg enters the FGD in gaseous form (98 % day 1 and 97 % day 2) being the element with the highest proportion (39 %, day 1 and 37 %, day 2) emitted in gaseous form. However significant proportions (44 % day 1 and 61 % day 2) of this metal are retained in gypsum. The differences on Hg retention within gypsum between the 2 sampling days are related to the occurrence of water soluble Hg species (HgCl<sub>2</sub>), which are high (17 %) in day 1 (the Hg content in gypsum slurry was one order of magnitude higher in the day 1 than in day 2). Most of the Hg emitted is Hg<sup>0</sup> while most of the Hg<sup>2+</sup> is retained in gypsum and in the effluent. The high retention of Hg in FGD gypsum suggests a major occurrence of insoluble Hg species in the scrubber, such as Hg-sulfate [9] or insoluble Hg<sup>0</sup> species. Oxidized Hg may be partially reduced to insoluble Hg<sup>0</sup> in the scrubber liquids [8-11] by a number of redox elements such as I or Mn (Ruud Meij, personal communication). However the speciation of Hg in the FGD streams should be investigated in more detail.

In the PP2 high fractions of this metal occurs a water soluble species in the re-circulated water streams incoming FGD (62-73 % in the mixture of limestone slurry and filtered water) and relatively high fractions (27-38 %) incomes FGD as volatile Hg. The unexpected high proportion of Hg in the incoming water stream was indicative that high proportions of Hg were dissolved in the effluent OUT-FGD. Indeed, the prevalent output of Hg from FGD is the effluent (78-81 %), with relatively high fractions of Hg (14 and 15 %) leave the scrubber as volatile species being potentially emitted and only 6-7 % is retained in gypsum. The high fraction of Hg in the water streams indicates that this metal occurs in high proportions as high water soluble Hg species, most probably  $\text{HgCl}_2$ .

The partitioning of Hg in the PP2 plant is then different from that founded at the FGD system of the PP1 power plant. In the PP1 power station most of Hg was retained in the FGD gypsum as insoluble Hg species. The causes for this different partitioning and speciation of Hg are currently being investigated, but both the high Hg input from coal and the addition of Al may accounts for this.

#### *Fluorine*

In The PP1 limestone is an important source of F (over 16 %) but the highest fraction of this element (77 and 76 % for day 1 and 2, respectively) income the scrubber in gaseous form from coal combustion. Low proportions (2.2, day 1 and 0.5 %, day 2) are emitted as gaseous species being highly retained in gypsum (92 and 94 %) mainly as fluorite ( $\text{CaF}_2$ ).

In the PP2, a high fraction of F (79 %) escapes the ESP as volatile species. Nevertheless, the gaseous F incoming the FGD is reduced to 37 %, due to the high occurrence of soluble F species in the FGD of the PP2 plant (63 and around 67 % in the water streams IN and OUT-FGD, respectively). Relatively high proportions of this element (31-34 %) are also trapped in the FGD gypsum, most probably as low acid soluble rastonite ( $\text{NaMgAlF}_6 \cdot \text{H}_2\text{O}$ ), as found in samples from FGD deposits from this power plant. The high retention of F in the effluent gypsum the FGD of the PP2 plant (>99 % of incoming F is trapped), accounts for reducing the F emissions down to 0.2-0.3 %.

The above results revealed that the partitioning of F is completely different between PP1 and PP2 power plants. The addition of Al accounts for modifying the partitioning of F in FGD facilities. The analysis of blank samples (collected prior the addition of Al) demonstrate that the contents of F in the effluent (liquid fraction of the gypsum slurry) are lower 351 mg/L) and the contents in FGD gypsum higher (1239 mg/kg), than that produced after the addition of Al (around 1000 mg/l and 900 mg/kg, respectively). Although gas measurements were not carried out during the collection of blank samples it may be thought that similar values of gaseous F entered the FGD facility. The resulting partitioning of F without Al addition is the opposite that founded when Al was added to the scrubber, being F highly retained in FGD gypsum (around 65 %) and in the effluent (around 33 %). From these results it may be deduced that besides the high



occurrence of low acid soluble ralstonite ( $\text{NaMgAlF}_6 \cdot \text{H}_2\text{O}$ ) which is retained in gypsum, the addition of Al accounts for favoring the occurrence of highly soluble F complexes being retained in the effluent.

Furthermore, without Al addition the fractions of F retained in the FGD gypsum produced in PP2 still lower than that in the PP1 power plant. This may be attributed to the higher occurrence of Al in the water streams of the scrubber of the PP2. The contents of F (353 mg/L) and Al (10 mg/L) in the PP2 effluents are lower than that with Al addition (around 1000 and 537 mg/L for F and Al, respectively) but still one order of magnitude higher than the contents of F (27-60 mg/L) and Al (below detection limits) in the PP1 effluents. The Al most probably arises from the dissolution of fly ash particles, favoring the formation of the above mentioned soluble F complexes and ralstonite.

It can be stated that the occurrence of higher contents of soluble Al in the scrubbers is then a critical factor controlling the partitioning and speciation of F in wet FGD facilities.

#### *Boron and Chlorine*

The volatile fraction of B and Cl before ESP is highly reduced after FGD. Only 0.8-0.5 % of B and 0.2-0.7 and 0.1 % of Cl are potentially emitted in PP1 and PP2, respectively. This is due to the high water solubility of most of the B and Cl species (95-97 % for B and 91 % for Cl in the effluent. Both, the high occurrence of B and Cl soluble phases and the re-circulation of the effluent to the scrubber accounts for the highest FGD input of these elements (94-95 % for B and 90-92 % for Cl) in the water stream IN-FGD.

#### *Selenium*

In the PP1, the gas escaping ESP (31 and 52 %) and the water streams (61 and 45 %) are the prevalent sources of Se in the FGD unit. Relatively high fractions of the incoming Se are retained in FGD gypsum (28 and 41 %) most probably as Ca selenate. Gypsum and calcium selenate dihydrate ( $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ ) are isomorphous and their lattice constants are very similar [12-13] having been shown that selenate can substitute for sulphate in the gypsum structure [14-15]. However, the major output of this pollutant is as fly dust (28 and 29 for day 1 and 2, respectively). Selenium is the element with the highest enrichment factor in PM OUT-FGD (287 as a mean). Low proportions (2.2 and 2.8 %) of Se are emitted as gaseous species.

The input of Se in the FGD of the PP2 power plant is made in relatively similar proportions as PM (fly ash, 33-48 %), water stream IN-FGD (28-38 %), limestone (0.1-24 %) and gas IN-FGD (14-15 %). It has to be noted the high input of Se by limestone in Day 1, while <0.1 % of Se was measured in limestone for sampling Day 2. Most of the incoming Se is retained in the FGD gypsum (42-28 %) and in the effluent (23 %), reducing the gaseous emissions of Se down to 0.7-9.9 %. Nevertheless, the incoming fraction of Se as PM (33-48 %, most probably as condensate Ca selenate during co-combustion) is not significantly reduced being PM (fly dust) the major FGD output of Se (35-38 %). As revealed by the EFs, Se is the element with the highest  $\text{EF}_{\text{fly dust}}$  (287 as a mean). The low abatement of particulate Se may be attributed to a combination of the following causes: a) a reduced trapping capacity by FGD of Ca-selenate condensed on

fly ash particles b) Ca seleniate particles formed in the FGD from gaseous  $\text{SeO}_2$  and entrained by the gas OUT-FGD and c) evaporation of dissolved Se subsequently condensate in the filters.

### *Arsenic*

Most of As incoming the FGD system of PP1 is supplied by limestone (78 and 88 % for day 1 and 2, respectively) due to the aforementioned As content in limestone (2mg/kg) coupled with a high and continuous limestone flow (32.5 tn/h). Arsenic also enters the scrubber as fly ash (15 and 6 %). High fractions (89 and 87 %) of this element are retained in gypsum, most probably as Ca arsenate ( $\text{Ca}_3(\text{AsO}_4)_2$ ), [6]. The emission of As occurs predominantly as PM (5 and 7 %) while only very low proportions are emitted as gaseous As-bearing species (0.3 %).

In the PP2 power plant, As escapes the ESP mainly as PM than as volatile species (1.7-0.6 %). Therefore PM is the prevalent source (90-93 %) of As in the FGD facility of this power plant. Most of the gaseous As and high fractions of particulate As, are trapped in gypsum, most probably as Ca arsenate. Only very low proportions of this element are emitted as gaseous As-bearing species (0.3 %), but the high incoming fraction of As as PM is not successfully reduced and an important fraction (40-46 %) of this element escapes the FGD as fly dust being potentially emitted as PM. Likely to Se, most of the particulate As incoming FGD occurs as Ca arsenate condensate on fly ash particles during co-combustion. Due to the low solubility of Ca arsenate species at the pH (4.5-5) of the scrubber and the low residence time, most of the particulate As escapes the FGD being potentially emitted as PM.

The comparison of the above partitioning and behavior of As between PP1 and PP2 power plants revealed significant differences. Due to the high ESP temperature and the relatively high contents of As of limestone of the PP1 plant most of the As incoming the FGD arises from limestone being easily retained in FGD gypsum than particulate As. Since only around 5 % enters FGD as PM, the As fraction escaping as fly dust the FGD of PP1 is reduced to 4 %, reducing the fraction potentially emitted of particulate As.

### CONCLUSIONS

The partitioning of most of the trace pollutants in the PCC, FGD and whole installation is highly similar in both power plants with the exception of Hg, F and As in the FGD system. The use of additives seems to be the major parameter affecting the partitioning of trace pollutants in the FGD systems. The addition of Al in the scrubber accounts for modifying the partitioning of F in the FGD facilities, and it can be stated that the occurrence of higher contents of soluble Al in the scrubbers is a critical factor controlling the partitioning and speciation of F in wet FGD facilities. Fluorine is highly retained in gypsum as fluorite when no Al is added in the scrubbers. The addition of Al results in the occurrence of high soluble Al complexes being this element mainly partitioned in the FGD effluent, while low fraction are retained in FGD gypsum as low acid soluble ralstonite ( $\text{NaMgAlF}_6 \cdot \text{H}_2\text{O}$ ). The partitioning and speciation of Hg is also different in FGD facilities with Al addition, being water soluble Hg species the major Hg species in the scrubber. Regarding As and Se, the ESP temperature and the composition (purity) and

flow of limestone are controlling the partitioning and abatement capacity of these gaseous-condensate elements. Furthermore, from the results it may be deduced a relatively low abatement capacity of FGD facilities for reducing incoming PM fractions when combining low soluble species (such as Al-Si fly ash, or relatively low soluble salts) at slightly acidic pH and short residence time in the scrubber.

Although the different partitioning of the above trace pollutants very high retention efficiencies (>95 %) were obtained for the gaseous components S, Cl, F, I and B in the power plants studied. The gaseous As shows very high retention potential in the PP1 (78-87 %) and PP2 (>90 %). High retention potential was also found for Se (generally from 67 to 100 %) but the efficiencies may vary between samplings in a given power plant Regarding the retention efficiency for PM, about 50% of the particulates in the flue gases were removed in the power plants.

#### AKNOWLEDGEMENTS

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

#### REFERENCES

- [1]. O.Font, M, Izquierdo, E. Alvarez, N. Moreno, S. Diez, X. Querol, P. Otero, A. Giménez, F.E. Huggins. World of coal Ash 2007, Cincinnati May 7-10, paper #77.
- [2] Izquierdo, M; Font, O; Moreno, N; Querol, X; Huggins, FE; Alvarez, E; Diez, S; Otero, P; Ballesteros, JC; Gimenez, A. *Env.Sc & tech.* (2007), vol. 41, pp. 5330-5335.
- [3] Aunela-Tapola L., Hatanpää E., Hoffren H., Laitinen T., Larjava K., Rasila P. and Tolvanen M. (1998). *Fuel Processing Technology*, Volume 55, 1, 13-34
- [4] Heebink L.V., Hassett D.J.. 2003 International Ash Utilization Symposium, CAER, University of Kentucky, paper 75, 1-11.
- [5] Schroeder K. and Kairies C. (2005). World of Coal Ash Conference, CAER, University of Kentucky, April 11-15, 2005.
- [6] Alvarez-Ayuso, E., Querol, X., Tomás, A. (2006), *Chemosphere*, 65, 2009-2017.
- [7] Querol, X., Fernandez-Turiel. J.L., Lopez-Soler, A., (1995). *Fuel*, v. 74, 3, pp331-343.
- [8] Díaz-Somoano, M., Unterberger S, Hein R.G. *Fuel processing technology*, 88 (2007) 259–263.
- [9] C.L. Senior. Proceedings of 21st Century: Impacts of Fuel Quality and Operations, Engineering Foundation Conference, 2001.
- [10] G.T. Amrhein, M.J. Holmes, R.T. Bailey, G.A. Kudlac, W. Downs, D.A. Madden, Advanced Emissions Control Development Program, Phase III-Approved Final Report, 1999 DOE Contract DEFC22-94PC94251.
- [11] H. Gutberlet, Report No ENV-492-D (B), Commission of the European Communities, Luxembourg, 1984.
- [12] Pedersen, B.F., Semmingsen, D., 1982. *Acta Crystallogr. B* 38, 1074–1077.
- [13] Kruger, R.R., Abriel, W., 1991. *Acta Crystallogr. C* 47, 1958-1959.
- [14] Freyer, D., Voigt, W., 2003. *Monatsh. Chem.* 134, 693–719.

[15] Fernández-González, A., Andara, A., Alí'a, J.M., Prieto, M., 2006. Chem. Geol. 225, 256–265.