Enrichment and Speciation of Elements in Re-circulated Waters from Desulphurisation at Two Spanish Power Plants

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ABSTRACT
The enrichment of Al, F, B, Se, Hg, and U and other elements in water streams is the most important consequence of the flue gas desulphurisation (FGD) systems with water re-circulation at two Spanish power plants. The knowledge of the speciation of these elements in FGD waters and in gypsum is of paramount importance should the re-circulation system be interrupted since the waters would require a decontamination treatment. The PHREEQC code 2.0 was used for calculation of the aqueous speciation of these elements and for the saturation index (SI) in the re-circulated waters. The preliminary calculations of PHREEQC reveal that, at pH 7.6 of the re-circulated water at PP1, $Al(OH)_4^-$ is the main specie of Al; MgF^+ of F; $Hg^{(0)}$ of Hg; SeO_3^{-2} of Se, and $(UO_2)_3(OH)_5^+$ of U. At PP2, at pH~5.0 of the re-circulated water, AlF_3 is the main specie of Al and F, $Hg^{(0)}$ of Hg, SeO_3^{-2} Se, H_3BO_3 of B, and $UO_2(SO_4)_2^{-2}$ and $UO_2(SO_4)$ of U. A relationship between water enrichment and gaseous Hg retention may explain the differential Hg speciation OUT-FGD between power plants observed in previous studies. The different speciation of Hg OUT-FGD may be attributable to: a) the high soluble salt concentrations of the FGD water streams at PP2 which reduce the gaseous solubility and probably, the gas retention efficiencies; b) the entraining of $HgCl_2$ droplets by the gas OUT-FGD; and c) the operational such as, limestone purity, use of additives, fluoride and/or sulphate complexes, and the S/F and S/Cl ratios in the scrubber. The potential parameters controlling Hg speciation and partitioning are currently investigated.

1. INTRODUCTION

The enrichment of trace inorganic pollutants in water streams is the most important consequence of FGD systems with re-circulation of water to the scrubber at two Spanish power plants (PP1 and PP2) [1]. This enrichment could result in a reduction of the gaseous retention efficiencies and pollution of soil and groundwater; and technical problems such as the fouling of scrubber and pipes of the FGD. Furthermore, the leaching of fly ash (FA) particles reaching FGD system given their trace element content, and the continuous re-circulation of filtered water to the scrubber determines the subsequent occurrence and concentration in the FGD gypsum sludge.

As result of the analysis of water streams collected in the sampling campaigns carried out at PP1 and PP2, an element enrichment study in FGD waters was performed. The elements enriched at PP1 are: Na, Mg, Cl, B, Mn, Se, Cd, Mo, and U. At PP2, the elements enriched are: Na, Cl, K, Mg, F, Hg, Li, B, Mn, Sc, Co, Ni, Cu, Ge, Zn, Se, Cd, and U [1]. Given the importance of the environmental and technical problems derived of this enrichment, a comprehensive study of the aqueous speciation of elements and those of the main environmental concern in FGD waters is proposed.

This paper seeks to (i) study the speciation of trace inorganic elements enriched in FGD waters from the two Spanish power plants equipped with forced-oxidation wet limestone FGD with water re-circulation, and those of the main environmental concern; (ii) study the different Hg speciation in the water and gaseous streams OUT-FGD between the two power plants; iii) determine trace inorganic pollutants requiring future application of preventive and/or corrective measures for their removal in FGD water streams.

2. MATERIALS AND METHODS

2.1 Characteristics of the FGD systems at PP1 and PP2

The FGD waters can be divided into 2 categories: (i) water streams not involved directly in FGD (process and slag water); and (ii) FGD water streams (treated and added water, limestone and gypsum slurry waters, and filtered water). At PP1, the process water comes from a nearby lake located over sedimentary rocks rich in sulphate species with a high content of Sr, whereas at PP2, the process water is located over metamorphic and igneous rocks. In both power plants, the process water is used in slag quenching and drainage giving rise to slag water. At PP1, a fraction of process water is treated before its use to reduce the high content of salts. The resulting water (treated water) is used for limestone slurry preparation, and is then considered as FGD water stream. The added water is similar in composition to the treated water and is used to offset the water loss because of moisture in the gypsum and evaporation of gypsum slurry water. The gypsum slurry water is the liquid fraction from gypsum slurry produced in the scrubber. The filtered water is the water that results from the gypsum slurry filtration after a purge process. The most distinctive feature of these FGD systems is the re-circulation of water from gypsum slurry to the scrubber (Figure 1).

At PP1, a fraction of filtered water is re-circulated to the scrubber after a purge process, which reduces the concentrations of some elements (especially Cl), while

the remaining filtered water fraction is used for limestone slurry preparation. This result in a 0.55/0.45 mixture of limestone slurry water and filtered water in the scrubber (named mixture water). At PP2, all filtered water is directly re-circulated to the scrubber and the limestone slurry is only prepared with process water which results in limestone slurry water/filtered water ratio of 0.47/0.53 (mixture water). Furthermore, an aluminium additive is injected into the scrubber at PP2 to boost the reaction of F with Al in order to improve SO_2 sorption by Ca.

2.2 Chemical analysis

Isokinetic measurements of gaseous streams were performed at two sampling points (Figure 1), IN-FGD (1) and OUT-FGD (2), simultaneously. Each sampling run lasted about 2.5h. At each sampling point, two trains of sampling system were assembled with specific trapping solutions, one for the capture of anions and metals, and other for the capture and speciation of Hg. The sampling and speciation of gaseous Hg (Hg^0 and Hg^{2+}) was devised according to EN 13211 and Meij and Winkel [2].

Water streams and trapping solutions from flue gas sampling were directly analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for major and minor elements and by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for most trace elements. Chloride contents were measured by HPLC, and fluorides were determined by ion selective electrode.
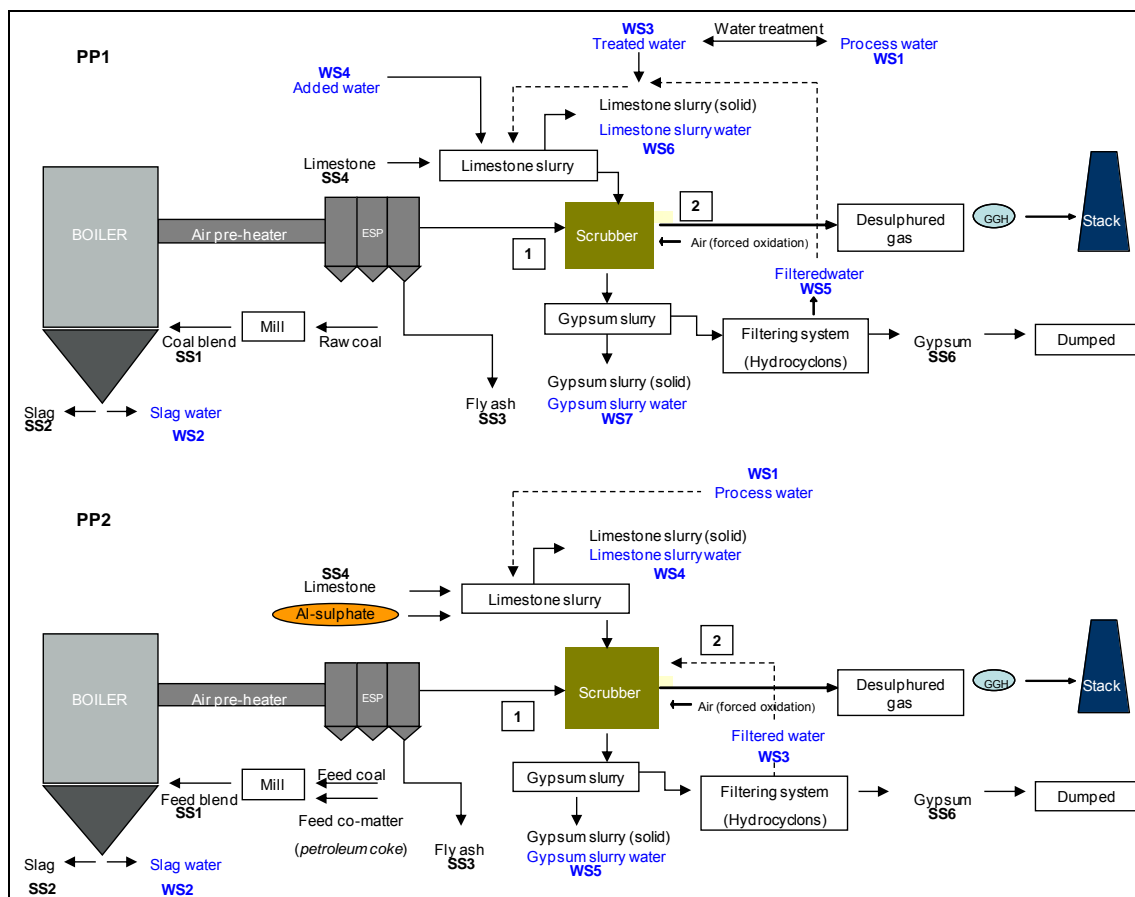

Figure 1. Sampling scheme of PP1 and PP2 and the corresponding samples.

2.3 Characterisation of FGD waters

The limestone and gypsum slurry waters at PP1 had very high concentrations of S, Mg, Ca, and Cl, followed by B, Li, Se, Ba, Mo, and especially Ni, Zn, Co and U in the gypsum slurry water. In the case of the limestone slurry water, the high contents of the above elements are attributed to the re-circulation of a fraction of filtered water for limestone slurry preparation. Furthermore, U may form soluble uranyl complexes with carbonates that may promote presence of U bearing complexes in the gypsum slurry water [3]. The leaching of fly ash particles reaching FGD system may also account for the high concentration of abovementioned oxy-anionic species and U complexes in limestone and gypsum slurry waters.

At PP2, the limestone and gypsum slurry waters showed high concentrations of elements associated with soluble salts (Ca, K, Mg, Na, S, Sr, and Cl) and major and minor elements (B, Mn, Cu, Se, Cu Ba, and U), which give rise a high ionic strength in these water streams, specially the free Cl^-. The high concentration of these elements in the limestone and gypsum slurry water may be ascribed to the dissolution of limestone components and to the complete re-circulation of the filtered water to the scrubber, respectively. The re-circulation of the filtered water also accounts for the increase in B, Sr, Se, and Ba in the 2008 gypsum slurry water given the similar contribution of these elements by gaseous and PM streams in 2007 and 2008. Other differences between sampling campaigns are the higher contents of Mg, S, and Al in the 2007 gypsum slurry water than those in 2008 owing to the high dosages of the Al additive (68 and 14 kg/h, respectively) and to the addition of MgO during the operational period of 2006-2007. The addition of Al to the scrubber at the PP2 modifies the partitioning of these elements, promoting the presence of soluble Al-fluoride complexes and reducing the fraction in gypsum. In addition, a highly acid insoluble Al-fluoride ralstonite ($NaMgAlF_6.H_2O$) [4] is formed instead of fluorite (CaF_2), probably because ralstonite forms an iso-structural solid solution between hydrated Al-fluoride complexes rich in Na and Mg compounds [5].

Filtered water shows a composition similar to that of the corresponding gypsum slurry waters. However, the highly efficient purge at PP1 increases the differences between filtered water and gypsum slurry water in terms of element concentration. These differences are especially significant for Ni, Zn, and Cd with concentrations over 2 orders of magnitude higher in filtered water at PP2 than at PP1.

2.4 Geochemical modelling

The PHREEQC code (version 2.0) was used for calculation of the aqueous speciation of elements in the FGD waters, and for the saturation index (SI) with respect to selected minerals and solid phases of the elements enriched in the FGD waters at PP1 and PP2. The thermodynamic database of PHREEQC was enlarged with data from other geochemical codes (MINTEQA2) for the speciation of As and U.

3. RESULTS AND DISCUSSION

3.1 Aqueous speciation of trace inorganic pollutants at PP1 and PP2

The geochemical calculations performed with PHREEQC reveal that at 7.6 pH and 60ºC conditions of the gypsum slurry sampled at PP1, F, Na, and Cl are mainly present as MgF^+ and, Na^+ and Cl^- free aqueous ion, respectively. Calcium mostly occurs as divalent metal cation (Ca^{2+}), and secondarily associated to sulphate

(CaSO$_4$); while sulphur appears as metal-sulphate ionic complexes (MgSO$_4$) and oxidized S (VI) ionic specie (SO$_4^{2-}$)(Table 2).

Aluminium is primarily present in hydroxide form (Al (OH)$^-_4$), being the highly soluble AlF$_3$ complexes the secondary specie. Elemental Hg is the main specie, with HgCl(OH)$_2$ as secondary specie of Hg. The bi-selenite ion is the main specie of Se followed by HSeO$_3^-$. Arsenic and U also present as acid and hydroxide ion specie forms, whereas H$_3$BO$_3$ and H$_2$BO$_3^-$ are the main ion species of B.

Table 2. Speciation of selected elements in gypsum slurry waters at PP1.

	GS PP1	Activity
Al (III)	Al(OH)$_4^-$	2.530e-005
	AlF$_3$	2.845e-009
	AlF$_4^-$	7.042e-010
	Al(OH)$_3$	3.273e-010
F	MgF$^+$	2.620e-003
	F$^-$	4.939e-004
	CaF$^+$	3.410e-005
	NaF$_+$	4.752e-006
Cl	Cl$^-$	1.718e-002
	MnCl$^+$	1.954e-006
	CuCl$_2^-$	1.595e-007
	NiCl$^+$	7.390e-008
Se (IV)	SeO$_3^{-2}$	1.987e-007
	HSeO$_3^-$	1.013e-006
Se (VI)	SeO$_4^{2-}$ (VI)	1.579e-008
	MnSeO$_4$ (VI)	6.948e-010
Na	Na$^+$	9.170e-003
	NaSO$_4^-$	2.752e-004
	NaF	4.752e-006
	NaH$_2$BO$_3$	1.410e-006
Hg	Hg$^{(0)}$	5.044e-008
	HgCl(OH)	2.891e-011
	Hg(OH)$_2$	1.465e-011
	HgCl$_2$	8.586e-012
SO$_4^{-2}$	MgSO$_4$	3.370e-002
	SO$_4^{-2}$	5.30e-003
	CaSO$_4$	5.744e-003
	NaSO$_4^-$	2.725e-004
U (VI)	(UO$_2$)$_3$(OH)$_5^+$	2.068e-007
	UO$_2$H$_3$SiO$_4^+$	2.407e-008
	UO$_2$OH$^+$	1.667e-008
	UO$_2$F$^+$	3.114e-009
B	H$_3$BO$_3$	4.208e-003
	H$_2$BO$_3^-$	1.688e-004
	MgH$_2$BO$_3^+$	1.598e-004
	CaH$_2$BO$_3^+$	4.026e-005
As (V)	HAsO$_4^{2-}$	3.520e-008
	H$_2$AsO$_4^{2-}$	7.102e-009
	AsO$_4^{3-}$	9.109e-012
	H$_3$AsO$_4$	4.188e-014

At PP2, the PHREEQC calculations reveal that at ~5.0 and 60ºC conditions of the gypsum slurries, the speciation of the selected elements for the study is equal with respect to primary species in the two gypsum slurries (2007-2008, Table 3).Thus, Al and F are appear as AlF_3 complexes as primary specie, and AlF_4^- and F^- as secondary species, respectively. Sodium and Cl are mainly present as Na^+ and Cl^- free aqueous ion, while H_3BO_3 and $HSeO_3^-$ are the main species of B and Se, respectively. Sulphur appears as metal-sulphate ionic complexes ($MgSO_4$) and oxidized S (VI) ionic specie (SO_4^{2-}). Uranium is mainly present in sulphate form.

Table 3. Speciation of selected elements in gypsum slurry waters at PP2.

	GS PP2 2007	Activity	GS PP2 2008	Activity
Al (III)	AlF_3	1.427e-002	AlF_3	8.162e-004
	AlF_4^-	1.436e-003	AlF_4^-	3.512e-004
	AlF_2^+	5.553e-003	AlF_2^+	7.424e-005
	$AlSO_4^+$	2.851e-005	$AlSO_4^+$	2.363e-008
F	AlF_3	1.427e-002	AlF_3	8.162e-004
	F^-	2.008e-004	F^-	8.586e-004
	AlF_4^-	1.436e-003	AlF_4^-	3.512e-004
	MgF^+	1.309e-003	MgF^+	2.543e-003
Cl	Cl^-	8.498e-002	Cl^-	7.354e-002
	$CuCl_2^-$	2.597e-006	$CuCl_2^-$	1.590e-006
	$NiCl^+$	1.062e-006	$NiCl^+$	5.389e-007
	$MnCl^+$	8.066e-006	$MnCl^+$	1.137e-005
Se (IV)	$HSeO_3^-$	1.649e-006	$HSeO_3^-$	7.386e-006
	H_2SeO_3	9.146e-009	H_2SeO_3	1.029e-007
	SeO_3^{-2}	8.119e-010	SeO_3^{-2}	1.448e-009
Se (VI)	SeO_4^{2-} (VI)	3.993e-016	SeO_4^{2-} (VI)	1.144e-016
Na	Na^+	4.648e-004	Na^+	1.986e-003
	$NaSO_4^-$	1.199e-004	$NaSO_4^-$	5.810e-004
	NaF	9.790e-008	NaF	1.789e-006
	NaH_2BO_3	6.601e-010	NaH_2BO_3	1.180e-009
Hg	$Hg^{(0)}$	9.648e-006	$Hg^{(0)}$	1.015e-005
	$HgCl_2$	4.017e-008	$HgCl_2$	3.163e-008
	$HgCl_3^-$	3.190e-008	$HgCl_3^-$	2.174e-008
	$HgCl_4^{2-}$	8.124e-009	$HgCl_4^{2-}$	4.791e-009
SO_4^{-2}	$MgSO_4$	3.589e-001	$MgSO_4$	1.849e-001
	SO_4^{-2}	4.605e-002	SO_4^{-2}	5.223e-002
	$CaSO_4$	1.444e-002	$CaSO_4$	1.990e-002
	$MnSO_4$	8.927e-004	$MnSO_4$	1.649e-003
U (VI)	$UO_2(SO_4)_2^{2-}$	2.500e-008	$UO_2(SO_4)_2^{2-}$	5.370e-008
	UO_2SO_4	1.921e-008	UO_2SO_4	3.638e-008
	UO_2F^+	3.413e-009	UO_2F^+	2.438e-008
	UO_2F_2	2.062e-009	UO_2F_2	6.299e-008
B	H_3BO_3	1.543e-002	H_3BO_3	1.621e-002
	$BF_2(OH)_2^-$	3.634e-007	$BF_2(OH)_2^-$	1.732e-005
	$BF(OH)_3^-$	1.716e-006	$BF(OH)_3^-$	7.712e-006
	$H_2BO_3^-$	1.555e-006	$H_2BO_3^-$	6.504e-007
As (V)	$H_2AsO_4^-$	2.029e-007	$H_2AsO_4^-$	2.536e-007
	$HAsO_4^{2-}$	2.526e-009	$HAsO_4^{2-}$	1.257e-009
	H_3AsO_4	4.764e-010	H_3AsO_4	1.496e-009
	H_3AsO_3	1.884e-011	H_3AsO_3	3.684e-010

3.2 Saturation indices

The gypsum slurry water from the PP1 is saturated with respect to a number of Fe minerals such as ferrihydrite and goethite, and Al minerals (gibbsite, Table 4). As regards F minerals, gypsum slurry is saturated with respect to fluorite; whereas ralstonite is considerably below saturation. The species of the enriched elements because of the water re-circulation at this power plant are clearly below saturation, as deduced by their high negative SI value with the exception of U species. PHREEQC predicts the saturation of $UO_2(OH)$ in the gypsum slurry water at PP1. Thus, it is may be expected the subsequent precipitation of U in the gypsum sludge after a number of water re-circulations. Most species of the elements enriched at PP1 remain in the solution of the gypsum slurry. However, it could also result in a subsequent equilibrium and/or saturation as consequence of the water re-circulation.

The species close to the equilibrium are $CaSO_4.2H_2O$ and $CaSO_4$ given their role as main components of the gypsum slurry. Other species close to the equilibrium are MgF_2 (0.10), SiO_2 (chalcedony, 0.24), and $Cu(OH)_2$ (0.09).

Table 4. Saturation indices of mineral phases in gypsum slurry from the PP1.

GS PP1 2007			
Phases			**SI**
Al minerals	$AlSO_4OH$	Jurbanite	-6.93
	$Al(OH)_3$	Gibbsite	0.77
	$KAl_3(SO_4)_2(OH)_6$	Alunite	-2.86
	$Al_4SO_4(OH)_{10}$	Basaluminite	-10.95
Fe minerals	$FeOOH$	Goehtite	0.77
	$Fe(OH)_3$	Ferrihydrite	2.05
	$NaFe_3(SO_4)_2(OH)_6$	Na-jarosite	-3.73
F	CaF_2	Fluorite	1.28
	$NaMgAlF_6.H_2O$	Ralstonite	-7.07

Table 5. Saturation indices of solid phases in gypsum slurry from the PP1.

Solid phases		
		SI
Se (IV)	$CaSeO_3.2H_2O$	-3.31
	$CaSeO_4.H_2O$	-7.09
Se (II)	$HgSe$	6.54
Mg	MgF_2	0.10
Mn	$MnSO_4$	-7.71
Hg	Hg_2Cl_2	-5.36
	$HgCl_2$	-10.28
	Hg_2SO_4	-14.29
	$HgSO_4$	-19.16
SO$_4^{-2}$	$CaSO_4.H_2O$	-0.14
	$CaSO_4$	-0.24
	$BaSO_4$	0.80
Cd	$CdMoO_4$	-0.66
U (VI)	UO_2	-5.69
	UO_3	-1.37

	$UO_2(OH)$	0.27
As	$Ca_3(AsO_4)_2.4H_2O$	-10.83

At PP2, the 2007 gypsum slurry water is saturated with respect to Fe minerals such as goethite and especially hematite, and Al minerals such as gibbsite and alunite (Table 6). As regards the main species of F, fluorite is practically in equilibrium and ralstonite is slightly below saturation, showing an opposite behaviour with respect to 2008 speciation. This different behaviour is also especially patent with respect to other Al and F species due to the aforementioned use of additives at this power plant during 2007 sampling campaign. The high Al dosage added in 2007 enhances the formation of water soluble AlF complexes leading to F-rich FGD waters, and also modifying the speciation of other elements. Thus, when the Al-additive is used (2007), jurbanite and k-jarosite (sulphate minerals), gibbsite and boehmite (hydroxide minerals), and fluorite and ralstonite are in equilibrium or are slightly satured; whereas in 2008, with a lower dosage of additives, these species are below saturation. With lower dosage of Al-additives, the reaction of Ca and HF give rise to the CaF_2 formation which is highly retained in the FGD gypsum. This explains the higher SI of fluorite in the gypsum slurry in 2008 than in 2007.

The MgF_2 response between sampling campaigns should be pointed out. The MgO tests during the 2006-2007 periods, in conjunction with the Al-additive added in 2007, which increases the F and Mg in FGD water, respectively, promote the MgF_2 formation in gypsum slurry in 2007, and the subsequent enrichment in 2008 because of filtered water re-circulation. This is supported by the SI showed by this specie in 2008 (Table 6).

The species $CaSO_4.2H_2O$, $CaSO_4$, and Hg_2Cl_2 are slightly saturated in 2007 and 2008 (Table 7).The rest remaining species of the elements enriched at this power plant are far below saturation. However, as aforementioned for PP1, it could give rise a subsequent equilibrium and/or saturation in gypsum slurry after a number of water re-circulations. The Hg speciation will be discussed in subsequent sections.

Table 6. Saturation indices of mineral phases in gypsum slurry in 2007 and 2008 at PP2.

Mineral phases				
			SI PP2 2007	**SI PP2 2008**
Al minerals	$AlSO_4OH$	Jurbanite	-0.73	-4.21
	$Al(OH)_3$	Gibbsite	0.82	-3.50
	$KAl_3(SO_4)_2(OH)_6$	Alunite	6.83	-4.85
	$AlOOH$	Boehmite	0.95	-3.37
	$Al_4SO_4(OH)_{10}$	Basaluminite	-4.60	-21.03
Fe minerals	Goehtite	$FeOOH$	1.66	0.21
	Hematite	Fe_2O_3	5.88	2.96
	K-jarosite	$KFe_3(SO_4)_2(OH)_6$	-0.20	-3.28
F	CaF_2	Fluorite	-0.04	1.31
	$NaMgAlF_6.H_2O$	Ralstonite	-0.37	-1.61

Table 7. Saturation indices of solid phases in gypsum slurry in 2007 and 2008 at PP2.

Solid phases		SI	SI
Se (IV)	$CaSeO_3.2H_2O$	-6.25	-5.91
Se (VI)	$CaSeO_4.H_2O$	-15.24	-15.69
Mg	MgF_2	-0.59	0.33
Mn	$MnSO_4$	-6.85	-6.58
Hg	Hg_2Cl_2	0.59	0.51
	$HgCl_2$	-6.61	-6.72
	Hg_2SO_4	-8.79	-8.69
	$HgSO_4$	-15.94	-15.86
SO_4^{-2}	$CaSO_4.H_2O$	0.24	0.39
	$CaSO_4$	0.16	0.30
Cd	$CdSe$	0.18	3.14
U (VI)	UO_2	-5.26	-5.04
	U_3O_8	-10.26	-11.18
	$UO_2(OH)_2$	-4.52	-5.08
As	$Ca_3(AsO_4)_2.4H_2O$	-19.97	-21.10

As for the differences between PP1 and PP2, the main distinctions are those related with:

a) Al and Fe minerals. Most of the Al and Fe minerals are sub-saturated in the gypsum slurry at PP1, while the opposite trend is showed at PP2 given the higher concentration of these elements in gypsum slurry at PP2 than at PP1.

b) The different behaviour of fluorite and ralstonite, and other Al and F minerals in the gypsum slurry between PP1 and PP2 due to the use of Al-additive at PP2.

c) The different U speciation. At PP1, the U species appear in oxide and hydroxide form while at PP2, U is mainly present in sulphate form ($UO_2(SO_4)_2^{2-}$ and UO_2SO_4) which is probably due to the Al-additive used at PP2 and the different pH in the scrubber in PP2 (4.6-5.0) and in PP1 (7.6). At PP1, $UO_2(OH)_2$ is slightly satured which is in line with the U enrichment observed in the gypsum slurry water at PP1. By contrast, at PP2 the uranium sulphates are below saturation.

d) The differences in the water speciation are those related to the elements affected by the use of Al-additives and also related with those affected by the operational conditions of the power plants.

3.3 Relationship between water enrichment and gaseous Hg retention

As result of sampling campaigns carried out at PP1 and PP2, a differential speciation of Hg in the gas stream OUT-FGD is revealed. At PP1 and PP2 a high proportion (86-88%) of Hg escapes the ESP in a gaseous form, being Hg^{2+} (75-86%) specie incoming the FGD at the two power plants. By contrast, the speciation of the Hg species OUT-FGD is the opposite between PP1 and PP2. At PP2, Hg^{2+} is the prevalent Hg specie OUT-FGD in 2007 (66%) and 2008 (87%), while Hg^0 (71%) is the major Hg specie OUT-FGD at PP1. The differential speciation of Hg in the FGD system at PP1 and PP2 may attributable to: a) the high soluble salt concentrations of the FGD water streams at PP2, which reduce the gaseous solubility and probably, the gas retention efficiencies; b) the entraining of $HgCl_2$ droplets by the gas OUT-FGD; and c) the operational conditions at PP2 such as, limestone purity, use of additives, fluoride and/or sulphate complexes, and the S/F and S/Cl ratios in the

scrubber.

a) Soluble salt concentrations of FGD Waters
As above discussed, a high concentration of soluble salts in FGD waters at PP2 may give rise to a high ionic strength which may reduce the activity of the water for the gaseous retention. High ionic strength avoids the interaction between the solid-water-gaseous phases in the scrubber. Thus at PP2, the Hg^{2+} may enter and leave FGD system without interaction and therefore being emitted OUT-FGD as Hg^{2+}. This could explain the differential Hg behaviour between PP1 and PP2.

b) Entraining of $HgCl_2$ droplets by the gas OUT-FGD.
At PP1, the geochemical modelling of the gypsum slurry reveals that $Hg^{(0)}$ is the primary specie of Hg in this water stream followed by $HgCl(OH)$, $Hg(OH)_2$, and $HgCl_2$ as $Hg^{(2+)}$. The negative SI values suggest that Hg species are far below saturation, remaining therefore in solution. Given the high efficiency to remove Hg^{2+} and the low elimination for Hg^0 of the scrubbers [7], and Hg^0 as the prevalent specie OUT-FGD; it could be stated that the $Hg^{(0)}$ emission OUT-FGD is due to a high gaseous retention of Hg^{2+} as $HgCl_2$ and $HgSO_4$ species in the scrubber and/or due to a reduction of Hg^{2+} to $Hg^{(0)}$ [7-10] by a number of redox elements such as I or Mn (Meij, personal communication), thus decreasing the $Hg^{(0)}$ retention by the FGD at PP1.

The relatively high retention of Hg in the gypsum sludge is in agreement with the major occurrence of low soluble Hg-sulphate (Hg^{2+}) in the FGD of this power plant [11], which is in line with the sub-saturation of $HgSO_4$ specie at PP1 (Table 8). This specie could precipitate in the gypsum sludge after a number of water re-circulations. Furthermore, insoluble and highly volatile Hg^0 species can be present in the FGD gypsum since 26% of elemental Hg is retained by FGD. These data are in line with earlier works carried out by Yudovich and Ketris [12], and by Meij [13] and Meij and Winkel [2].

Table 8. Speciation and SI of Hg species in gypsum slurry at PP1

PP1	Activity		SI	
$Hg^{(0)}$	$Hg^{(0)}$	5.044e-008	Hg_2Cl_2	-5.36
	$HgCl(OH)$	2.891e-011	$HgCl_2$	-10.28
$Hg^{(2+)}$	$Hg(OH)_2$	1.465e-011	Hg_2SO_4	-14.29
	$HgCl_2$	8.586e-012	$HgSO_4$	-19.16

At PP2, the geochemical modelling of the gypsum slurry reveals that $Hg^{(0)}$ is also the primary specie of Hg in this water stream, being the $HgCl_2$ the second specie of Hg in the gypsum slurry in the two sampling campaigns. The SI of Hg species show that Hg_2Cl_2 is slightly saturated in the gypsum slurry at PP2 in the two sampling campaigns, and the rest Hg species are below saturation (Table 9).

In this regard, $HgCl_2$ can react with Hg^0, which shows the main Hg activity, giving rise to the Hg_2Cl_2 formation. The formation of Hg_2Cl_2, in conjunction with the filtered water re-circulation may support the Hg_2Cl_2 saturation (Table 9) in the gypsum slurry in the two sampling campaigns. The low solubility of Hg_2Cl_2 (12 mg/L) [6] accounts for their

saturation in the gypsum slurry water and the subsequent precipitation in the gypsum sludge after water re-circulations. The reaction of $HgCl_2$ and Hg^0 is detailed below:

$$Hg^0 + HgCl_2 \longleftrightarrow Hg_2Cl_2 \tag{1}$$
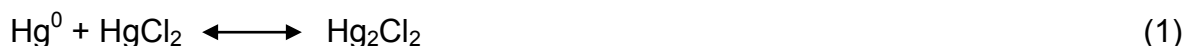
However the inverse process may also occurs. It is demonstrated that Hg_2Cl_2 decomposition in high temperatures releases Hg and $HgCl_2,$ which may promote the dissolution of the highly soluble $HgCl_2$ (71.5 mg/L) [6] in the gypsum slurry water. This could explain the occurrence of $HgCl_2$ in the solution of the gypsum slurry (Table 9). Given the Hg^{2+} is the prevalent gaseous specie OUT-FGD, the entraining of droplets of the $HgCl_2$ dissolved in the gypsum slurry by the gas OUT-FGD is the probable cause for the $Hg^{(2+)}$ emission.

The aforementioned thermal decomposition of $Hg_2Cl_2,$ in conjunction with the slight decreasing of the SI for Hg_2Cl_2 from 2007 to 2008 (Table 9) could entail a partial dissolution of Hg_2Cl_2 in 2008, giving rise to a higher proportion of Hg^{2+} entrained by the gas OUT-FGD in 2008 than in 2007 owing to the $HgCl_2$ liberation by the thermal decomposition.

However, these processes are strongly depend on the pH, temperature, redox potential, and the Hg and Cl concentrations in the scrubber and are currently studied in detail.

Table 9. Speciation and SI of Hg species in gypsum slurry at PP2.

PP2	Activity 2007		Activity 2008			SI 2007	SI 2008
Hg$^{(0)}$	Hg$^{(0)}$	9.648e-006	1.015e-005	Hg$_2$Cl$_2$		0.59	0.51
	HgCl$_2$	4.017e-008	3.163e-008	HgCl$_2$		-6.61	-6.72
Hg$^{(2+)}$	HgCl$_3^-$	3.190e-008	2.174e-008	Hg$_2$SO$_4$		-8.79	-8.69
	HgCl$_4^{2-}$	8.124e-009	4.791e-009	HgSO$_4$		-15.94	-15.86

c) Operational conditions of the power plants.
The different gaseous Hg speciation is also probably due to the higher Cl content in the FGD waters and the lower S/Cl ratio at PP2 than those at PP1. The higher Cl content and the lower S/Cl ratio promote the occurrence of highly soluble $HgCl_2$ complexes in the scrubber at PP2 favouring the $HgCl_2$ entrained by the gas OUT-FGD.

A greater occurrence of fluoride and/or sulphate complexes and the lower S/F (52-140) and S/Cl (28-37) ratios in the scrubber at PP2 than at PP1 (251 and 137 for S/F and S/Cl ratios, respectively) give rise to these enrichment factors for the elements enriched in the scrubber at PP2 than at PP1. The rapid dissolution of these elements as soluble sulphate and fluoride complexes promotes their enrichment after water re-circulations at PP2.

The higher PM contribution to the FGD system at PP2 [1] may increase the amount and the presence of metal chloride complexes in re-circulated waters. This together the lower acidic pH of the gypsum slurry (4.6-5.0) at PP2 than pH (7.6) at PP1 may also favour the presence of metal complexes at PP2.

The potential parameters controlling Hg speciation and partitioning at these power plants are currently investigated. However, it seems to be that the different ionic strength of the gypsum slurry waters account for a better understanding of the different behaviour of Hg in the FGD at PP1 and PP2.

4. Conclusions

The predominant species of the elements enriched at PP1 are those present in oxide, hydroxide, and ion form whereas at PP2, the species are mainly associated to sulphate, chloride, and fluoride ion forms. These species are mostly below saturation but they could reach the equilibrium and/or saturation in the gypsum slurry water after a number of water re-circulations.

The use of additives used at PP2 during the 2007 sampling campaign modifies the F and other elements speciation. The high Al dosage added in 2007 enhances the formation of water soluble AlF_3 complexes leading to F-rich FGD waters, whereas with a lower dosage of additives, HF reacts with Ca to form fluorite which is highly retained in the FGD gypsum. The F and Mg-rich FGD water promotes the MgF_2 formation in gypsum slurry in 2007, and the subsequent enrichment in 2008 because of filtered water re-circulation.

A relationship between water enrichment and gaseous Hg retention may explain the differential speciation of Hg OUT-FGD between PP1 and PP2. The differential speciation of Hg in the FGD system at PP1 and PP2 may attributable to: a) the high soluble salt concentrations of the FGD water streams at PP2, which reduce the gaseous solubility and probably, the gas retention efficiencies; b) the entraining of $HgCl_2$ droplets by the gas OUT-FGD; and c) the operational conditions such as, limestone purity, ESP gas temperature, use of additives, fluoride and/or sulphate complexes, and the S/F and S/Cl ratios in the scrubber. The potential parameters controlling Hg speciation and partitioning at these power plants are currently investigated.

The differences in the water speciation between PP1 and PP2 are those related to the elements affected by the use of Al-additives and also those affected by the operational conditions of the power plants.

Preventive and corrective measures are being studied for the enriched elements and those of main environmental concern (mainly F, U, Se, and As).

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6. Acknowledges