

Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products

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Abstract

The fate of trace elements in a combustion power plant equipped with a wet limestone flue gas desulphurisation (FGD) installation was studied in order to evaluate its emission abatement capacity. With this aim representative samples of feed coal, boiler slag, fly ash, limestone, FGD gypsum and FGD process water and wastewater were analysed for major and trace elements using the following techniques: inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), ion chromatography (IC), ion selective electrode (ISE) and atomic absorption spectroscopy (AAS). Mass balances were established allowing to determine the element partitioning behaviour. It was found that, together with S, Hg, Cl, F, Se and As were those elements entering in the FGD plant primarily as gaseous species. The abatement capacity of the FGD plant for such elements offered values ranged from 96% to 100% for As, Cl, F, S and Se, and about 60% for Hg. The environmental characterisation of combustion by-products (boiler slag, fly ash and FGD gypsum) were also established according to the Council Decision 2003/33/EC on waste disposal. To this end, water leaching tests (EN-12457-4) were performed, analysing the elements with environmental concern by means of the aforementioned techniques. According to the leaching behaviour of combustion by-products studied, these could be disposed of in landfills for non-hazardous wastes.

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1. Introduction

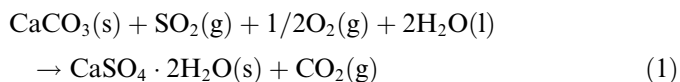
Sulphur emissions from coal combustion have been the focus of great concern during the last decades due to their relation to the formation of acid rain, accelerated soil acidification and forest degradation. In order to comply with the air quality regulations established accordingly in this regard, and so to protect the environment, in many countries coal-combustion electricity-generating plants have switched from

high- to low-sulphur coal or blending, together, or not, with the installation of flue gas desulphurisation (FGD) plants. Although not everywhere applied, the latter measure has been necessary in several countries for many years to fulfill regulations on sulphur emission abatement. In the near future it is also expected to increase worldwide implementation of FGD systems as regulations are becoming stricter.

Many types of FGD systems have been developed. These can be classified in two major groups, wet and dry processes, which are subdivided in several types depending on the specific chemical reactions taking place and the flow conditions employed. Among them, the wet limestone FGD process is by far the most widely used because of

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its high desulphurisation performance, reliability and low utility consumption (Kikkawa et al., 2002). In this system SO_2 is removed from the flue gas by absorption into limestone slurry as sulphate which in turn is extracted from the absorber as gypsum slurry and finally dewatered. The chemical reaction occurring in a wet limestone FGD process can be summarised as follows:



The so-called FGD gypsum produced in this manner has found commercial application in the wallboard manufacture, besides it is also employed as a landfill material in mine reclamation. Other uses such as agricultural lime substitute, amendment for improving soil properties, construction material for roads, and waste stabilisation product have been suggested (Solem-Tishmack et al., 1995; Stehouwer et al., 1995; Payette et al., 1997; Chen et al., 2005; Chou et al., 2005). In spite of the proposed applications, most of this by-product ends up in landfills. Up to now, the FGD gypsum is regarded as environmentally friendly, but with increasing landfill closures and regulatory pressures on operating facilities to improve environmental conditions (Council Directive 1999/31/EC; Council Decision 2003/33/EC) its characterisation could change and therefore this by-product could come out as a new environmental issue to be faced by the coal combustion plants. It is worth noting that the limestone slurry used in the aforementioned desulphurisation technique acts as an scavenging system not only for sulphur but for other high volatile elements such as fluorine, chlorine, mercury, arsenic, selenium and boron present either in the gas emissions or condensed on the small particles escaping to the electrostatic precipitators (ESPs) (typically <1%) before entering in the FGD installation, and for trace elements (Cd, Cr, Cu, Ni, Pb, Zn, Ba, Mo) enriched also in these particles. Therefore, it is relevant to know the fate of trace elements in the coal-combustion power plants in order to assess the effectiveness of the wet limestone FGD process as well as the environmental characteristics of the coal combustion by-products, namely FGD gypsum, fly ash and boiler slag. Fly ash and boiler slag, likewise FGD gypsum, are usually disposed of, especially in the case of slag. As regards fly ashes, although their application in the concrete manufacture is clearly established, their destination to this use greatly depends on the producer country; thus in some countries, e.g. The Netherlands, most ashes find their way to such application as the cost of using them this manner is much lower than the cost of their landfilling (Reijnders, 2005), but in many others, e.g. Greece, disposal is still the main mode of dealing with them (Antiohos and Tsimas, 2004). This fact is sometimes caused by the special characteristics (high free lime and sulphur contents) of some fly ashes (class C fly ashes) that make them not so suitable for cementitious systems, but generally the reason lies in the high fly ash production that greatly surpasses the amounts required by the construction industry. Several

other uses have been proposed for this by-product, including the synthesis of zeolites (Querol et al., 1997a,b), geopolymers (Swanepoel and Strydom, 2002; Bakharev, 2005) and fire-proof products (Vilches et al., 2002), but their commercial application is still very limited.

Whereas numerous researches have been devoted to evaluate the partitioning behaviour of trace element between the by-products arising from coal combustion in power plants, using different coal types as well as different combustion conditions (Querol et al., 1995a; Martinez-Tarazona and Spears, 1996; Yan et al., 1999; Vassilev et al., 2001, 2005; Pires and Querol, 2004; Spears and Martinez-Tarazona, 2004; Li et al., 2005; among others), the studies concerning the final fate of trace elements in coal-combustion power plants equipped with a FGD facility are much more scarce (Meij, 1994; Yokoyama et al., 2000; Sandelin and Backman, 2001; Meij et al., 2002; Lee et al., 2006), besides most of these studies are either theoretical approaches or are mainly focused on the behaviour of mercury.

The objective of the present work is twofold: (a) to study the fate of trace elements in a combustion coal plant equipped with a wet limestone FGD installation, and so to evaluate its abatement capacity for hazardous element emissions, and (b) to assess the environmental characteristics of arisen by-products (FGD gypsum, fly ash and boiler slag) according to the Council Decision 2003/33/EC on waste disposal recently put in force.

2. Materials and methods

2.1. Sample collection and preparation

Samples of feed coal were collected from a Spanish coal-combustion power plant equipped with a wet limestone FGD installation for 7 days during which a 69 900 t stockpile of constant coal quality (H_2O , S, ash (wt.%): 18.01, 4.66 and 23.3, respectively) was consumed by the boiler. Collection was performed every two days, obtaining three different samples that were mixed and homogenised to give a single sample. The coal was a mixture of four local sub-bituminous coals and one imported sub-bituminous coal (<27%). The combustion by-products from the coal combustion plant-FGD installation were also collected simultaneously with feed coal. Thus, three different samples of the slag (composition: glass, quartz, mullite, magnetite, hematite and albite; C (wt.%): 0.35; LOI (wt.%): <1) from the ashers of the boiler and of the fly ash (composition: glass, quartz, mullite and magnetite; C (wt.%): 1.0; LOI (wt.%): 1.4) from the hoppers of the ESPs were collected, then mixed and homogenised. Likewise, different samples of the FGD gypsum together with the limestone and process water used in the desulphurisation process were collected. Moreover, the wastewater derived from the gypsum slurry filtration was sampled as well.

Representative splits of the coal, slag, fly ash and limestone were separated by riffing, splitting and then grinding

to <250 µm particle size (fly ash was already <250 µm in particle size, and, therefore, did not need to be ground). Subsamples of coal, slag, fly ash and limestone were dried at 105 °C (with exception of samples for Hg analysis), and used in subsequent characterisation analysis. A representative split of FGD gypsum was also separated and subsamples dried at 45 °C were used in their chemical characterisation because at this temperature moisture is eliminated from such samples while keeping crystalline water. Gypsum transforms into bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) by losing 1.5 molecules of crystalline water when heating, the onset of the dehydration temperature of gypsum to bassanite is generally accepted to be about 100 °C (Sarma et al., 1998). X-ray diffraction analysis of gypsum subsamples dried at 105 °C confirmed that at this temperature gypsum was completely transformed into bassanite (data not shown).

2.2. Chemical analysis

The coal, slag, fly ash, limestone and gypsum samples were digested for most major and trace element analyses following the method described by Querol et al. (1995b). This is a two-step method involving a first step for the digestion of volatile elements using nitric acid in closed PFA bombs heated at 90 °C for 2 h, and a second one for the digestion of non-volatile elements using hydrofluoric acid in closed PFA bombs heated at 90 °C, followed by a perchloric and nitric acid treatment in open PFA bombs heated until dryness. After digestion major elements were analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Thermo Jarrell-Ash iris Advantage radial ER/S unit, and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Electron Corporation ICP-MS X Series II apparatus.

Different extraction procedures and/or analytical methods were employed for the determination of boron, chlorine, fluorine and mercury. The determination of B was performed using the method described by Pougnet and Orren (1986). Following such a method the samples were acid-digested ($\text{HNO}_3 + \text{HF}$) in PP closed reactors under stirring at 70 °C during 15 h. The resulting extracts were analysed by ICP-AES. The determination of Cl was carried out using the Eschka method (Chakrabarti, 1978; Gent and Wilson, 1985). The procedure utilizes a sample decomposition in covered porcelain crucibles using the Eschka mixture (two parts of MgO and one part of Na_2CO_3) at 800 °C during 2 h, followed by ion chromatography (IC) analysis of the water-leached residues performed using a KONTRON-WATERS unit. The determination of F was carried out following the method described by Sager (1987). This method uses a sample fusion with NaOH at 550 °C during 1 h, followed by a residue dissolution by means of tiron (pyrocatechol-3,5-disulfonic acid, disodium salt) and further analysis by fluoride selective electrode performed using a Thermo Orion ISE-meter (model 710). An

advanced mercury analyser (AMA-254) equipped for thermal decomposition of the sample, amalgam formation and atomic absorption measurement was used for the Hg determination. Unlike the other processes where samples previously dried to eliminate their moisture content were used, in this latter determination non-dried samples were those employed to avoid mercury losses by volatilisation before its analysis. The moisture content was obtained in parallel in replicate samples to give Hg concentration values on a dry basis. Three replicates of each sample subject of study were subjected to the aforementioned extraction treatments and analytical determinations. To check the accuracy of the digestion or fusion procedures and/or analytical methods standard reference materials (SARM 19, NIST 1633b and 031 MRG-1) also underwent the whole processes. Analytical accuracy checked with the aforementioned reference materials yielded analytical errors <10%.

The process water used in the desulphurisation stage as well as the wastewater resulting from the gypsum slurry filtration were also analysed by ICP-AES and ICP-MS to determine the concentration of most elements there present. The F, Hg and Cl concentrations were determined by fluoride selective electrode, mercury analyser and IC, respectively. All analyses were also performed by triplicate.

2.3. Leaching tests

Combustion by-products (fly ash, slag and FGD gypsum) were investigated concerning their leaching behaviour. Leaching tests were performed using the European standard EN-12457-4 as established the Council Decision 2003/33/EC. According to this European standard the leachant to use is deionised water in liquid to solid ratio of 10 l kg⁻¹ dry matter. The solid must be used in the leaching test without being dried unless its moisture content does not allow its crushing to reach the required sample grain size (<10 mm). Nevertheless, the amount of constituent leached from the material from the agitation step (24 h) must be referred on the dry mass of the material. Three replicates of each sample underwent the leaching test using a rotary shaker (10 rpm) following strictly the specifications of the EN-12457-4 standard mentioned before. Leached liquids were analysed for As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Se, Zn by ICP-MS, F by fluoride selective electrode, Cl and sulphate by IC and Hg using a Hg analyser. The moisture content of samples was determined at 105 °C according to ISO 11465 as is established in the EN-12457-4 standard.

3. Results and discussion

3.1. Chemical characterisation

3.1.1. Enrichment factors and mass balances

Table 1 shows the concentration of major and trace elements in the feed coal, slag and fly ash samples (the reported concentrations represent mean values). Table 1

Table 1

Major and trace element contents of coal, fly ash and slag, element content ratios in fly ash and slag (FA/S) and enrichment factors ($EF_{\text{fly ash}}$, EF_{slag} and EF_t)

	Coal	Fly ash	Slag	FA/S	$EF_{\text{fly ash}}$	EF_{slag}	EF_t
	wt. %						
Al	3.5	12.5	12.0	1.0	1.0	1.0	1.0
Ca	0.96	3.5	3.3	1.1	1.0	1.0	1.0
Fe	3.7	12.5	19.1	0.7	0.9	1.5	1.0
K	0.28	1.0	0.90	1.1	1.0	0.9	1.0
Mg	0.20	0.8	0.7	1.1	1.1	1.0	1.1
Mn	0.007	0.027	0.030	0.9	1.0	1.2	1.1
Na	0.03	0.13	0.10	1.3	1.2	1.0	1.1
P	0.05	0.20	0.13	1.5	1.1	0.7	1.0
S	5.7	0.32	0.1	3.2	0.0	0.0	0.01
Ti	0.13	0.5	0.4	1.3	1.0	0.9	1.0
	mg kg ⁻¹						
As	16.4	62.8	13.1	4.8	1.0	0.2	0.9
B	119	474	175	2.7	1.1	0.4	1.0
Ba	143	514	489	1.1	1.0	1.0	1.0
Be	3.7	13.9	10.7	1.3	1.0	0.8	1.0
Bi	1.4	6.0	1.6	3.8	1.2	0.3	1.0
Cd	0.3	1.2	0.4	3.0	1.1	0.4	1.0
Ce	36	134	126	1.1	1.0	1.0	1.0
Cl	460	89	57	1.6	0.1	0.0	0.05
Co	12	43	43	1.0	1.0	1.0	1.0
Cr	39	140	139	1.0	1.0	1.0	1.0
Cs	3.5	12.9	10.7	1.2	1.0	0.9	1.0
Cu	20	73	66	1.1	1.0	0.9	1.0
Dy	2.9	11	9.5	1.2	1.0	0.9	1.0
Er	1.4	5.0	4.6	1.1	1.0	0.9	1.0
Eu	0.6	2.2	1.8	1.2	1.0	0.9	1.0
F	237	113	10	11.3	0.1	0.0	0.1
Ga	12	47	27	1.7	1.1	0.6	1.0
Gd	3.0	11	9	1.2	1.0	0.9	1.0
Ge	2	9	3	3.0	1.2	0.4	1.1
Hf	5	18	20	0.9	1.0	1.1	1.0
Hg	0.12	0.02	<0.01	>2	0.04	0.0	0.04
Ho	0.5	1.9	1.6	1.2	1.0	0.9	1.0
La	15	56	51	1.1	1.0	1.0	1.0
Li	71	260	226	1.2	1.0	0.9	1.0
Lu	0.2	0.8	0.7	1.1	1.1	1.0	1.1
Mo	3	12	4	3.0	1.1	0.4	1.0
Nb	6	22	19	1.2	1.0	0.9	1.0
Nd	17	62	53	1.2	1.0	0.9	1.0
Ni	31	119	112	1.1	1.0	1.0	1.0
Pb	14	58	25	2.3	1.1	0.5	1.0
Pr	4	15	13	1.2	1.0	0.9	1.0
Rb	15	57	55	1.0	1.0	1.0	1.0
Sb	1	4	2	2.0	1.1	0.6	1.0
Sc	24	91	82	1.1	1.0	1.0	1.0
Se	1.9	4.3	2.6	1.7	0.6	0.4	0.6
Sm	2.5	9	8	1.1	1.0	0.9	1.0
Sn	2	9	3	3.0	1.2	0.4	1.1
Sr	214	809	754	1.1	1.0	1.0	1.0
Ta	0.7	2.6	2.5	1.0	1.0	1.0	1.0
Tb	0.5	1.8	1.5	1.2	1.0	0.9	1.0
Th	5	20	18	1.1	1.1	1.0	1.1
Tl	0.5	2.1	0.4	5.3	1.1	0.2	1.0
Tm	0.2	0.8	0.7	1.1	1.1	1.0	1.1
U	5	19	13	1.5	1.0	0.7	1.0
V	47	172	137	1.3	1.0	0.8	1.0
W	2	8	5	1.6	1.1	0.7	1.0
Y	19	69	56	1.2	1.0	0.8	1.0
Yb	1.3	5	4	1.3	1.0	0.9	1.0
Zn	109	433	205	2.1	1.1	0.5	1.0
Zr	43	158	168	0.9	1.0	1.1	1.0

also gives the element concentration ratios in fly ash and slag (FA/S) as well as the enrichment factors (EFs) including those of fly ash and slag ($EF_{\text{fly ash}}$ and EF_{slag}) and weighted enrichment factors (EF_t).

Enrichment factors are used to properly describe the behaviour of trace elements in coal combustion. The EF defined by Gordon and Zoller (1973) was employed with this aim:

$$EF = ([X]_s/[Y]_s)/([X]_c/[Y]_c) \quad (2)$$

where $[X]_s$ and $[X]_c$ are the concentrations of element X in the fly ash or slag and in the coal, respectively, and $[Y]_s$ and $[Y]_c$ are the concentrations of a non-volatile element taken as a reference in the fly ash or slag and in the coal, respectively. Thus, element concentrations in fly ash and slag are normalized with respect to a non-volatile element and to their concentrations in the coal, what allows to quantify element partitioning in the by-products arising from the coal combustion plant. The non-volatile elements most frequently employed for EF calculation are Al, Fe, Ti, Ce and La (Smith, 1987; Ratafia-Brown, 1994). Cerium was chosen as the reference element in the calculation of EF of elements because rare earth elements such as Ce and La present the additional advantage of being present in constant concentrations in all particle sizes of fly ashes (Pires and Querol, 2004). Taking into account the ratio of fly ash to slag production in the combustion power plant (0.85:0.15), the EF_t can be calculated as follows:

$$EF_t = (EF_{\text{fly ash}} \times 0.85 + EF_{\text{slag}} \times 0.15) \quad (3)$$

Upon combustion, elements in coal are retained in combustion by-products in different amounts depending firstly on their volatilisation behaviour under the operating conditions of the power plant. The analysis of FA/S values allows to classify the elements in different groups according to their segregation behaviour:

- Elements enriched in the fly ash ($FA/S > 1.5$): As, B, Bi, Cd, Cl, F, Ga, Ge, Hg, Mo, Pb, S, Sb, Se, Sn, Tl, W and Zn.
- Elements enriched in the boiler slag ($FA/S < 1$): Fe, Hf, Mn and Zr.
- Elements showing no segregation between fly ash and slag ($FA/S = 1.0$ – 1.5): Al, Ba, Be, Ca, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ho, K, La, Li, Lu, Mg, Na, Nb, Nd, Ni, P, Pr, Rb, Sc, Sm, Sr, Ta, Tb, Th, Ti, Tm, U, V, Y and Yb.

Element enrichment in the fly ash points out high element volatilisation during the combustion process and subsequent condensation, whereas enrichment in the boiler slag is indicative of non-volatile behaviour and formation of heavier mineral phases. Slight or no segregation between combustion by-products is typical of low-volatile elements. In addition to element volatilisation characteristics, element retention processes on fly ash (mostly condensation processes) determine the final fate of elements that volatilise.

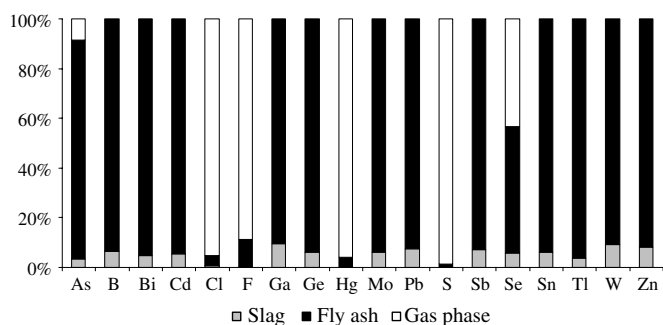


Fig. 1. Partitioning behaviour of high volatile elements between the effluents (slag, fly ash and flue gas) arising from the coal combustion power plant.

The evaluation of the whole process is possible considering the EFs that allow to establish element mass balances. Understanding the element partitioning between the three different effluents arising from the combustion power plant (slag, fly ash and flue gas) and their further characterisation makes possible an assessment of combustion power plant environmental impact. Thus, for elements not showing volatilisation ($FA/S < 1$) mass balance calculations indicate that element partitioning in fly ash attained values about 80% in spite of displaying lower fly ash concentrations; this is due to the much higher fly ash production. Partitioning values in fly ash rise slightly up to about 85% for low volatile elements ($FA/S = 1.0\text{--}1.5$). The rest remained partitioned in the slag fraction for both groups of elements. For those displaying high volatilisation their partitioning behaviour (Fig. 1) varied greatly between elements. The EF_t corresponding to B, Bi, Cd, Ga, Ge, Mo, Pb, Sb, Sn, Tl, W and Zn gave values very close to 1 indicating that these elements, although initially volatilised, subsequently condensate remaining retained on the fly ash and not emitted with flue gas. Moderately high partitioning in the gas phase was shown by As and Se with values about 10% and 45%, respectively; most of the As remaining retained by the fly ash (close to 90%) while a lower value was found for Se (about 50%) due to its lower retention on this fraction. Most of the S, Hg, Cl and F initially present in coal were partitioned in the gas phase with values about 99%, 96%, 95% and 89%, respectively.

The different partitioning behaviour of high volatile elements is mainly related to their condensation temperatures and to their affinity to calcium oxide that acts as a scavenging system for them in fly ash (Querol et al., 1995a). The relatively high partitioning in the fly ash fraction of Se, As and B, three typical high volatile elements, can be explained bearing in mind this latter factor. Thus, the formation of $CaSeO_4$ (Clemens et al., 1999) and $Ca_3(AsO_4)_2$ and $CaAsO_4$ (Clemens et al., 1999; Furimsky, 2000; Yudovich and Ketris, 2005a) has been proposed as the responsible for the retention of these two elements in the fly ash fraction arising from coal combustion processes, the formation of the latter compound taking place only through slow cooling of the flue gas (Yudovich and Ketris, 2005a). Concerning

B, its high inclusion affinity for more complex calcium compounds, namely calcium aluminosilicate matrices ($CaO \cdot Al_2O_3 \cdot SiO_2$ or $2CaO \cdot Al_2O_3 \cdot SiO_2$), could be responsible in great extent for its retention in fly ash; Clemens et al. (1999, 2000) have proven the formation of the $Ca_{11}Si_4B_2O_{22}$ phase in the combustion by-products of a sub-bituminous coal. Anyway, the occurrence of B in coal in minerals (such as tourmaline) may contribute to reduce the volatile B fraction (Boyd, 2002). In addition to the factors just exposed defining the different partitioning behaviour of high volatile elements, other aspects such as the chlorine content of coal being combusted and the presence of unburned carbon in the arisen fly ash are decisive in the Hg partitioning. Low chlorine content, as is the case of the coal subject of study, supposes a decrease in the Hg oxidation extent (Cl^- is known as effective Hg oxidant) and therefore a decrease in the Hg capture by fly ash (Meij, 1991; Meij et al., 2002; Yudovich and Ketris, 2005b). Furthermore, sub-bituminous coals produce fly ash poor in char (unburned carbon) lowering strongly the Hg fly ash retention capacity (Yudovich and Ketris, 2005b; Meij and te Winkel, in press). Finally, the role of post-combustion systems is crucial in determining the fate of Hg leaving the combustion plant. It has been proven that only cold-side electrostatic precipitators (CS-ESPs) are those really effective in the capture of Hg. The power plant subject of study is not equipped with these kind of ESPs, so this latter aspect also contributes to the low Hg partitioning in fly ash, nevertheless this aspect is more determinant when combusting bituminous coals for which retention values of 35–50% have been reported (Meij et al., 2002; Yudovich and Ketris, 2005b; Lee et al., 2006; Meij and te Winkel, in press). The relatively wide range of values is explained by the difference in the flue gas temperature in the ash hopper system, the higher the temperature, the less Hg condensation and retention in fly ash ($HgCl_2$ can condense on fly ash particles as the temperature declines to $140^\circ C$, furthermore at this temperature or lower $HgCl_2$ directly sorbs from the vapour phase; Yudovich and Ketris, 2005b). Thus, temperatures about $120^\circ C$ are reported for the most effective CS-ESP systems, and $\geq 140^\circ C$ for those showing the lowest retention levels. The relatively high temperature of the flue gas in the ash hopper system of the coal combustion plant subject of study ($180^\circ C$) represents another reason contributing to the low Hg retention in the fly ash fraction. As regards F and Cl, their low partitioning in this fraction is mostly related to their low condensation temperatures.

3.1.2. Abatement capacity of the FGD plant

The elements escaping the ESP system in the coal combustion power plant are emitted in the flue gas phase mainly as gaseous species but also retained in the finest fly ash particles not removed by the particulate control systems. The different gaseous species corresponding to those elements present in the flue gas phase have been reported to be: SO_2 , SeO_2 , As_2O_3 , AsO , HF , HCl , Hg , $HgCl_2$ and HgO (Bolten, 1987; Germani and Zoller, 1988; Clarke and Sloss,

Table 2

Element contents in limestone, FGD gypsum, process water and filtered wastewater involved in the desulphurisation step following the coal combustion process

	Limestone	FGD gypsum	Process water	Filtered wastewater
	mg kg ⁻¹		mg l ⁻¹	
As	1.0	2.6	0.003	0.024
Cl	148	307	98.6	1137
F	152	778	0.536	26.4
Hg	0.001	0.212	<0.001	0.007
S	509	175 379	332	7120
Se	2.3	4.0	0.003	0.030
Ba	15.4	9.21	0.089	0.164
Cd	0.05	0.04	<0.001	0.001
Cr	5.8	4.0	<0.001	0.076
Cu	2.6	2.8	0.032	0.043
Mo	0.14	0.11	0.002	0.004
Ni	8.7	5.7	0.008	0.047
Pb	0.88	0.64	<0.001	0.002
Sb	0.09	0.06	<0.001	0.001
Zn	9.9	7.9	0.029	0.134

1993; Yudovich and Ketris, 2005a,b). Therefore, these species are those entering in the FGD installation, together with the different elements present in the fly ash escaping the ESP system, and interacting with the limestone slurry present in the FGD scrubber.

Mass balances have been performed taking into account the amounts of flows in the FGD installation as well as the element concentrations of such flows; in doing so the abatement capacity of the FGD plant for hazardous emissions arising from the coal-combustion power plant can be assessed. Likewise, considering all the flows, the whole element partitioning between the different outlets of the coal combustion-desulphurisation plant can be established. The coal stockpile combusted during the sampling period produced 13844 and 2443 t of fly ash and boiler slag, respectively, being necessary 10994 t of limestone to perform the desulphurisation process that generated 17 508 t of FGD gypsum. A flow rate of 360 m³ h⁻¹ of process water was employed during the 112 working hours involved in the desulphurisation process. A wastewater volume equivalent to 55% of that of the process water was generated from the filtration of gypsum slurry. Table 2 shows the concentration in limestone, FGD gypsum, process water and filtered wastewater for those elements present in the gaseous emission arising from the coal-combustion power plant and entering in the FGD plant as well as for those others considered in the Council Decision 2003/33/EC (the reported concentrations represent mean values).

Fig. 2 shows the abatement capacity of the FGD plant. Such abatement attained values ranged from 96% to 100% for As, Cl, F, S and Se while for Hg an abatement capacity about 60% was shown (it is important to note that an analytical error about 10% must be assumed in the determinations derived from the method employed). The efficiency of SO₂ removal is that typically found (>90%) for desulphurisation systems using the wet limestone process. The

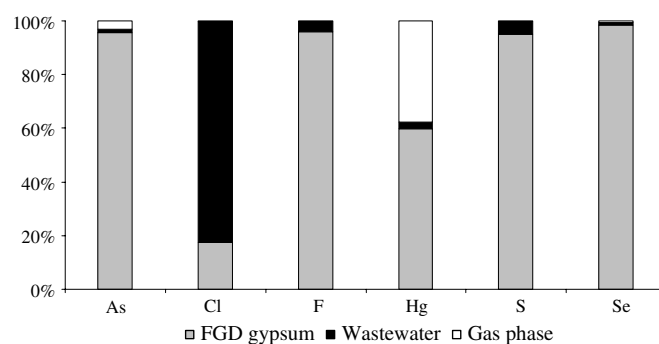


Fig. 2. Abatement capacity of the FGD plant for hazardous emissions arising from the coal-combustion power plant.

removal of Se from the gaseous emission is expected to occur similarly to the process described before for S. Furthermore, selenate and sulphate have similar structural and chemical properties and they can play a similar geochemical role. Gypsum and calcium selenate dihydrate (CaSeO₄·2H₂O) are isomorphous and their lattice constants are very similar (Pedersen and Semmingsen, 1982; Kruger and Abriel, 1991), having been shown that selenate can substitute for sulphate in the gypsum structure (Freyer and Voigt, 2003; Fernández-González et al., 2006). As regards As, its retention by means of the limestone slurry is consistent with the formation of Ca₃(AsO₄)₂. The high removal of F is known to occur by the precipitation of CaF₂, nevertheless, due to the limestone Al content (0.40 wt.%), together with that present in the finest fly ash particles entering in the FGD installation, some contribution of aluminium–fluorine-containing compounds (CaAlF₃(OH)₂CaF₂) cannot be neglected. Limestone with similar Al content has been proven to be a source of AlF_x complexes responsible for the formation of the mentioned Al-F-containing compounds (Ukawa et al., 1992). The amount of Hg captured by the wet scrubber system is consistent with data reported by Meij et al. (2002) who found, on average, Hg removal of 54.4 ± 24% when studying the behaviour of Hg in coal-combustion power plants in The Netherlands. It is known that oxidised Hg species (HgCl₂ and HgO) are the forms of Hg that are predominately captured in wet scrubbers by means of Hg²⁺ sorption on sulphate (such retention is considered to be weak; Yudovich and Ketris, 2005b), whereas Hg⁰ is not captured by them. Concerning Cl, its relatively small amount present in the FGD gypsum must be related to its original presence in the limestone used in the FGD process and to the precipitation of chloride salts reaching their solubility limits at the process conditions. The final fate of Hg and Cl is quite different; thus, whereas an important fraction of Hg, not removed by the formation of FGD gypsum, is emitted to the atmosphere through the FGD plant stack, most Cl remains in the wastewater arising from the gypsum slurry filtration. Due to internal recirculation of this filtered water in the FGD installation subject of study the Cl emissions to the environment are greatly minimised.

Fig. 3 shows the partitioning behaviour of the different elements considered in the Council Decision 2003/33/EC

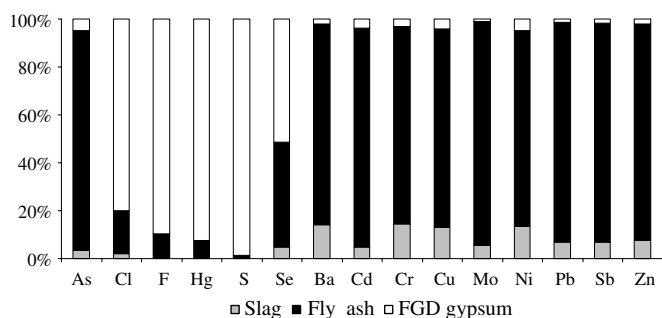


Fig. 3. Partitioning behaviour of the different elements considered in the Council Decision 2003/33/EC between the different solid combustion by-products arising from the coal combustion-desulphurisation plant.

between the different solid combustion by-products arising from the coal combustion-desulphurisation plant (slag, fly ash and FGD gypsum). Regarding elements being essentially present as gaseous species in the flue gas emission entering in the FGD plant, S, Hg and F are mostly partitioned in the FGD gypsum with values comprised in the range 90–99% (values decreasing in the cited order), while Cl, Se and As only attained levels about of 80%, 52% and 5% respectively, showing therefore important partitioning in the fly ash fraction with values about 18%, 44% and 92%, respectively. Concerning the elements not entering in the FGD plant as gaseous species, fly ash is the solid combustion by-product displaying higher partitioning with values in the range 80–94%, the rest remaining mostly in the slag fraction. The presence of these elements in the FGD gypsum has limestone as its main origin.

3.2. Leaching tests

Table 3 shows the leachable contents for the elements considered as elements of environmental concern in the Council Decision 2003/33/EC for the different solid by-

products arising from the coal combustion-desulphurisation plant (the reported contents represent mean values). All the leachable contents of the inorganic components established to be evaluated in the aforementioned Council Decision remained below the required limit values for wastes being accepted at landfills for non-hazardous wastes for all the combustion by-products (slag, fly ash and FGD gypsum). Therefore, according to these leaching values, combustion by-products arising from the coal combustion-desulphurisation plant subject of study could be disposed of in landfills for non-hazardous wastes, following the additional stated dispositions (e.g.: non-hazardous gypsum-based materials should be disposed of only in landfills for non-hazardous wastes in cells where no biodegradable waste is accepted). Anyway, it is important to note that, in the case of FGD gypsum the concentrations of some components, namely F and sulphate, were very close to the mentioned limit values. Regarding F, care should be taken in controlling changes in feed coal to avoid higher F inlets. Concerning sulphate, their leaching behaviour is related to the gypsum solubility, and therefore no preventing measures are possible. Nevertheless, the Council Decision 2003/33/EC allows the use of the TDS (total dissolved solids) value (60000 mg kg^{-1}) alternatively to those for sulphate and chloride, which could allow higher sulphate leaching concentrations.

The highest percentages of leaching in the slag fraction are shown for Cl and S with values about 85% and 40%, respectively. Sulphur and Cl, together with Mo, were also the elements most leached from fly ash with leaching percentage values about 75%, 60% and 50%, respectively. The rest of the elements in these two combustion by-products displayed low mobility, always with leaching percentage values $<10\%$ (even $<1\%$ for most of them). For elements with higher contents in the FGD gypsum, Cl and F were those attained the highest leachable proportions (about 75% and 15%, respectively). The relatively high leaching of these elements suggests that their presence in the combustion by-products where they leached from is associated in the case of Cl, S and F with their occurrence as highly soluble salts in the form of chloride, sulphate and fluoride, and in the case of Mo with its occurrence as highly mobile molybdate salts or oxides under neutral or alkaline pH (Querol et al., 1995a).

4. Conclusions

The study of the element partitioning behaviour in a sub-bituminous coal combustion plant showed that elements can be classified in three groups according to their segregation between fly ash and slag, these are: (a) elements enriched in the fly ash (As, B, Bi, Cd, Cl, F, Ga, Ge, Hg, Mo, Pb, S, Sb, Se, Sn, Tl, W and Zn), (b) elements enriched in the boiler slag (Fe, Hf, Mn and Zr), and (c) elements showing no segregation between fly ash and slag (Al, Ba, Be, Ca, Co, Cr, Cs, Cu, K, La, Li, Mg, Na, Nb, Ni, P, Rb, Sc, Sr, Ta, Ti, V, Y and most rare earth elements).

Table 3

Leachable contents in the solid by-products arising from the coal combustion-desulphurisation plant (slag, fly ash and FGD gypsum) and limit values for these wastes to be accepted at landfills for non-hazardous wastes

Component	Slag	Fly ash	FGD gypsum	Limit value
	mg leachable kg^{-1} dry substance			
As	0.166	0.026	<0.001	2
Ba	0.605	1.70	0.301	100
Cd	0.001	0.017	0.006	1
Cr	0.129	0.708	0.001	10
Cu	0.017	0.046	0.031	50
Hg	<0.001	<0.001	<0.001	0.2
Mo	0.264	5.62	0.045	10
Ni	0.015	0.053	0.072	10
Pb	0.003	0.002	0.001	10
Sb	0.008	0.058	0.002	0.7
Se	0.016	0.381	0.381	0.5
Zn	0.046	0.055	0.094	50
Chloride	50.5	53.4	261	15000
Fluoride	0.816	4.44	133	150
Sulphate	1065	7285	19787	20000

Mass balances of high volatile elements displayed a moderately high partitioning in the gas phase for As and Se showing, respectively, values about 10% and 45% with respect to their bulk coal content, while S, Hg, Cl and F were partitioned primarily in the gas phase with values about 99%, 96%, 95% and 89%, respectively. The abatement capacity of the FGD plant for such elements offered values ranged from 96% to 100% for As, Cl, F, S and Se while for Hg an abatement capacity about 60% was shown (not captured Hg was emitted to the atmosphere through the FGD plant stack). Cl mainly remained in the wastewater arising from the gypsum slurry filtration, its emission to the environment being greatly minimised as a result of the filtered water internal recirculation. According to the [Council Decision 2003/33/EC](#) on waste disposal, the leaching behaviour of all the solid combustion by-products arising from the coal combustion-desulphurisation plant (slag, fly ash and FGD gypsum) allowed to classify them as wastes admissible at landfills for non-hazardous wastes. Nevertheless, in the case of FGD gypsum the concentrations of some components, namely F and sulphate, were very close to their corresponding limit values. Care should be taken in controlling changes in feed coal to avoid high F inlets. Concerning sulphate, their leaching behaviour is related to the gypsum solubility, and therefore no preventing measures are possible, nevertheless the use of the TDS value alternatively to those for sulphate and chloride, as is established in the [Council Decision 2003/33/EC](#), could allow higher sulphate leaching concentrations.

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