**STUDY OF BORON BEHAVIOUR IN TWO SPANISH COAL COMBUSTION
POWER PLANTS**

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Abstract

A full-scale field study was carried out at two Spanish coal-fired power plants equipped with electrostatic precipitator (ESP) and wet flue gas desulfurization (FGD) systems to investigate the distribution of boron in coals, solid by-products, wastewater streams and flue gases. The results were obtained from the simultaneous sampling of solid, liquid and gaseous streams and their subsequent analysis in two different laboratories for purposes of comparison. Although the final aim of this study was to evaluate the partitioning of boron in a (co-)combustion power plant, special attention was paid to the analytical procedure for boron determination. A sample preparation procedure was optimised for coal and combustion by-products to overcome some specific shortcomings of the currently used acid digestion methods. In addition boron mass balances and removal efficiencies in ESP and FGD devices were calculated. Mass balance closures between 83 and 149 % were obtained. During coal combustion, 95 % of the incoming boron was collected in the fly ashes. The use of petroleum coke as co-combustible produced a decrease in the removal efficiency of the ESP (87 %). Nevertheless, more than 90 % of the remaining gaseous boron was eliminated via the FGD in the wastewater discharged from the scrubber, thereby causing environmental problems.

1. Introduction

Boron is an essential micronutrient for certain plants. However, this element can also be toxic to aquatic species, plants and micro-organisms at high concentrations. In Europe the release of boron is covered by EC Directive 2006/11 *Pollution caused by certain dangerous substances discharged into the aquatic environment of the Community* and EC Directive 84/360 *Combating of air pollution from industrial plants*. Moreover, boron is considered to be matter of concern in coal utilisation by the United States Environmental Protection Agency (US-EPA) and the Australian National Pollution Inventory, and it is included under Annex 3

of the European Union Directive 2008/1/EC concerning Integrated Pollution Prevention and Control (IPCC).

Boron is present in coals in concentrations ranging from 5 to 400 ppm (Swain, 1994; Swain et al., 1995). Three modes of occurrence have been identified for this element in coals: i) bound to the organic fraction, ii) locked inside clay minerals (mainly illite), and iii) bound within the crystal lattice of tourmaline. The organically bound mode is generally considered to be the most common (Swain et al., 1995). Boron easily volatilizes during combustion and condenses on the surface of fly ashes in the exhaust gas (Swain et al., 1995; Clark et al., 1992). In accordance with its behaviour during coal combustion, boron has been classified in between class II (elements volatilised and later condensed on and becoming adsorbed onto the fly ash) and class III (elements that remain mainly in gas phase) (Clark et al., 1992, Meij et al, 1983). Boron partitioning depends on the temperature of the combustion system, the combustion technology, its modes of occurrence in coal and the chemistry of the ashes (Clemens et al., 2000). In addition, the growing use of co-fuels in combustion processes may modify the partitioning of elements when compared with coals or coal blends. The application of emission control technologies can also affect the redistribution behaviours of coal trace elements and alter the concentrations of these metals in certain coal combustion by-products (CCBs). As a result, the disposal (i.e., landfilling and impoundment) and utilization (e.g., construction and agricultural applications) of fly ash and FGD solid waste, as well as the discharge of FGD wastewater, have given rise to considerable environmental, operational, and regulatory concerns. All of these actions may result in more restrictive waste disposal and wastewater discharge regulations and have the potential to impact the design and operation of coal-fired power plants (US EPA, 2008). There is therefore a clear need for the coal-fired power industry to acquire a better understanding of the behaviours of trace elements (i.e., partitioning profile of trace elements) in the coal combustion process.

Concerning partitioning in coal power plants, a number of problems have made it difficult to achieve a good closure for the boron mass balance. The determination of the boron content in coal involves a significant degree of uncertainty. The major problem in determining boron at trace levels is the loss of boron due to volatilization during sample digestion owing to the high volatility of BF_3 (US EPA, 2008; Pougnet et al., 1986a; Pougnet et al., 1986b; Zarcinas et al., 1987).

In this work a full-scale field investigation was carried out at two Spanish power plants equipped with electrostatic precipitator (ESP) and flue gas desulfurization (FGD) systems to evaluate boron partitioning during a (co-)combustion process. Special attention was paid to the analytical procedure for boron analysis in coal, and CCBs by means of the optimization of a sample preparation procedure prior to the analysis of boron in solution. The specific objectives of this study were: (1) to develop a preparation method for boron determination in solid coal combustion by-products in which specific shortcomings of the currently used acid digestion methods are solved; (2) to develop a procedure to collect representative samples from all the solid, liquid and gaseous streams in two Spanish power plants; (3) to acquire an understanding of the partitioning of boron in the combustion process by means of mass balances and enrichment factors among co-combustion by-products (slag and fly ash).

2. Materials and Methods

2.1. Boron analysis

Two different procedures for complete dissolution of the samples were compared in this study: i) method 1 involves acid digestion in closed Teflon vessels (Querol et al., 1992) whereas ii) method 2 involves alkaline fusion with Na_2CO_3 which was optimized in this study on the basis of previous experiments (Smith et al., 1991; Hofstetter et al., 1991). Method 1 is a two-step digestion procedure which consists of the wet oxidation of the organic matter using

HNO₃ followed by acid digestion using HF + HNO₃ + HClO₄. In method 2, before the alkaline fusion, the organic matter is eliminated by ashing at 500 °C. The fused sample is dissolved in HCl. In both cases, after the dissolution of the sample, the determination of boron was performed by means of a quadrupole ICP-MS (HP 4500) equipment using Be as internal standard.

2.2. Power stations and sampling procedures

The sampling campaigns were undertaken in two large (1050 and 1200 MW) Spanish Pulverised Coal (co) Combustion (PCC) power stations (labelled PP1 and PP2, respectively) equipped with ESP and wet-limestone based FGD facilities with forced-oxidation. The sampling campaigns were carried out at 100% maximum capacity and 100% desulphurisation over 2 consecutive days at PP1 in September 2007 and at PP2 in November of 2007 (PP2-1) and 2008 (PP2-2). Power plant PP1 was fed with 100 % of coal (a 60:40 blend of local sub-bituminous with bituminous coal). The PP2 co-combustion power plant was fed with a coal and coke blend (84:16 in 2007 and 88:12 in 2008). At PP1 water derived from the filtration of the gypsum slurry was mixed with process water to prepare the limestone slurry and the rest of the filtered water was re-circulated to the scrubber system while at PP2 all of the filtered water was directly re-circulated to the FGD system. A total of 11 streams, 7 solid (raw coals and petroleum coke, coal blend, slag, pulverised fly ash (PFA), limestone and FGD gypsum) and 4 liquid (process water, water filtered from gypsum slurry, and the limestone and gypsum slurries) were sampled. The flue gas was sampled at the same time at the solid and liquid streams. The gas measurements were carried out at two different sampling points, upstream, (IN)-FGD, and downstream, (OUT)-FGD, inside the FGD unit. A sample of approx 1 m³ was extracted from the flue gas stream through a filter system collected by a series of impingers and placed in an ice bath according to standard UNE-EN 14385, (UNE 2004). Particle-bound boron was collected at the front half of the sampling train using Teflon micro filters. The solid

samples were mixed, crushed, milled and then rafted and representative samples of each sampling day were analyzed. The water streams and gas trapping solution samples were filtered in situ. All the samples were divided for comparative analysis between two independent laboratories.

2.3. Mass Balances

In order to validate the design of the sampling campaign and to ensure the validity of the sampled streams different mass balance calculations were performed: i) whole installation (total) ii) Boiler + ESP and iii) FGD. The input and output streams used for mass balance calculations are summarised in Table 1. The stream flows used for the mass balance calculations are based on the monitored data and on historical data recorded by the power plant.

2.4. Relative Enrichment factors (REs)

Boron partitioning among ashes was comparatively evaluated by using its relative enrichment (REs) factors as defined by Meij (Meij et al., 1983, 2002; Meij, 1994). The term “relative enrichment” was adopted in order to describe the behaviour of a particular trace element during coal combustion. This parameter is defined as: $RE = (\text{conc. in ash} / \text{conc. in coal}) (\% \text{ ash content in coal} / 100)$. Based on this RE factor, Meij grouped trace elements into three classes denoted as: Class I, II and III (Meij et al., 2002; Meij et al., 2007). Class I elements are defined as elements that do not vaporise during combustion and their RE factor is around 1.0. All elements that volatilise in the boiler but condense in the ESPs are grouped in Class II. For these elements the RE factor of the furnace bottom ash (FBA) is less than 0.7 because, these elements in gas phase have no chance of condensing on the bottom ash particles. The RE factor of the pulverised fly ash (PFA) is close to 1. Class III elements have a very low RE factor, especially in the furnace bottom ash and to a lesser extent, in the pulverized fly ash. In

other words, most of these elements are volatilized and, in the absence of an FGD plant, they are totally emitted into the atmosphere in the gaseous phase.

3. Results and discussion

3.1. Boron analysis

In order to validate the alkaline fusion procedure (method 2) reference materials were used for the determination of accuracy and precision. Due to the lack of certified reference material for the determination of boron, two coal standards (SARM 20 and NIST-1632c) and one reference soil (CRM026) were analysed by this procedure. The results obtained by the proposed digestion method (Table 2) are statistically accurate and precise.

The results obtained using the two different dissolution procedures were compared. Table 3 shows the concentrations of boron obtained by both methods in the coal and CCBs (slag and fly ashes). The results reveal that a significant boron volatilization occurred when the two-step digestion method was used for the coal, the petroleum coke and the fuel blend feed, while a good agreement between both digestion procedures was obtained for the slag and fly ash samples. These results corroborate that boron losses can occur when the sample is decomposed by wet oxidation methods using an acid mixture containing HF (Pouget et al., 1986a; Pouget et al., 1986b; Zarcinas et al., 1987), due to the high volatility of BF_3 . The difficulty of boron determination in coal and fly ash samples is mainly due to the low concentrations found in some coals and the complex nature of the sample. The results appoint to the volatilization of organically-bound boron during the acid digestion procedure (method 1).

3.2. Boron behaviour

After determining the content of boron in the samples collected from the power plants, mass balance calculations were carried out. As already mentioned, in addition to the total mass

balance (total), other mass balances were also calculated i.e., around the boiler plus the electrostatic precipitator (Boiler + ESP) and in the flue gas desulfurization unit (FGD). Boron mass balances were closed with good Out/In ratios when method 2 was used to decompose the sample. Total mass balance closure were slightly greater than 100 % in both power plants, while the Boiler + ESP balance in PP2 was slightly lower, 80-90 % (Table 4). Closure for the mass balance around the FGD deviated more than 20% in both power plants because of the uncertainty related to the water flows, as much of the water employed in the plant is filtered, mixed and re-circulated. As expected, coal is the main source of boron (8000 and 5000 g/h at PP1 and PP2, respectively) while the FGD input water, which is re-circulated, provides a relatively high proportion of this element (1000 and 1700 g/h in PP1 and PP2, respectively). Total mass balances and mass balances around the boiler + ESP are dominated by the fuel input, whereas the FGD balance is dominated by the recovered water and gas inputs. The total output of boron for the plants sampled in this study is shown in Figure 1. This boron was partially distributed between the fly ashes (40-65%) and FGD by-products *i.e.* effluent and gypsum, (31-53 %). A very low proportion (< 0.5 %) reached the stack in gas phase. Some differences were observed in boron behaviour between the two power plants. At PP1 65 % was retained on the fly ash and 31 % of the boron was removed with the FGD by-products. However, at PP2 more than 50 % was discharged with the FGD effluent and a lower proportion (40-45%) was retained on the fly ash. This can be attributed to the higher proportion of organically bound boron in the pet-coke that was used as co-fuel. This behaviour can be clearly seen by comparing the boiler+ESP outputs (Figure 2). A higher amount of boron remains in gas phase at the output of the ESP in PP2 (7-8 %) while boron is retained to a lesser extent in the fly ashes. This result confirms that boron behaviour, during combustion, is controlled by the mode of occurrence of the element in the coal (Clemens et al., 2000).

Moreover, as revealed by the boron partitioning at the FGD output (Figure 3), the gaseous boron and fly ash particles that escape from the ESP are retained in high proportions in the FGD effluent and partially in the FGD gypsum, confirming the high capacity of this device for retaining boron. The FGD system allowed the abatement of 90-95 % of the incoming boron, most of which remained in aqueous phase (>85 %) while the rest was removed with the FGD gypsum. The high water solubility of B coupled with the re-circulation of a considerable amount of the effluent stream makes the boron being concentrated in water producing a waste of increasing environmental concern.

The calculated enrichment factors are shown in Table 5. Boron can be classified in class II (RE~1 for PFA; RE<0.7 for FBA) which means that it is volatilised and mostly condensed on fly ash. Therefore, in the combustion power plant configuration, most of the boron volatilised during combustion is mostly removed with the fly ashes collected from the ESP, the rest being removed via the FGD system. The most remarkable finding was that the boron collected in the FGD is mostly in the aqueous stream which is very often re-circulated to the scrubber, resulting in an increase in boron concentration in the scrubber by-products, with the consequent environmental and technological risks that this implies. This suggests the need for additional wastewater control before it is discharged.

4. Conclusions

Boron content in coal and coal combustion by-products can be determined with good results by applying an alkaline fusion method to ashes obtained at 500°C, and by analysing the resulting dissolution by means of ICP-MS using Be as internal standard.

During coal combustion in a power station, boron is volatilised and then mostly condensed onto the fly ashes collected by the electrostatic precipitator. However different boron behaviour was observed when pet coke was used as co-fuel. In this case, a higher proportion

of boron remained in gas phase confirming that organically bound boron is volatilised to a greater extent and can remain in gas phase after the ESP. Nevertheless, any boron remaining in gas phase is eventually removed in the desulphurization plant. Most of the boron captured in the FGD plant remains in the aqueous phase. Because many of the power plants are designed to re-circulate the water stream that comes from the FGD plant, the boron is re-circulated to the FGD plant, leading to a significant increase in the concentration of boron in the FGD by-products with serious implications for the environment.

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268 of boron by inductively coupled plasma atomic emission spectrometry. Analyst
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270 Table 1. Input and output streams used for the different mass balances.

	TOTAL	Boiler + ESP	FGD
Inputs	Feed Blend	Feed Blend	Limestone
	Limestone	Process water	Limestone slurry water
	Process water		(Process:Recovered)
	Recovered water		Fly dust (IN-FGD)
			Gas (IN-FGD)
Outputs	Slag	Slag	Gypsum
	PFA	PFA	Recovered water
	Recovered water	Fly dust (IN-FGD)	Fly dust (OUT-FGD)
	Gas (OUT-FGD)	Gas (IN-FGD)	Gas (OUT-FGD)
	Fly Dust (OUT-FGD)		
	Gypsum		

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273 Table 2. Results obtained for boron determination using certified reference materials and the
274 alkaline fusion digestion procedure (method 2).

Reference	Material	B (µg/g)		SD (%)*
		measured	Certified	
SARM20	Coal	94	90	4.4
NIST-1632c	Coal	63	62**	2.6
CRM026	Soil	26	25.4	1.2

275 * SD; standard deviation for 10 determinations

276 ** Reference value. Not certified

Table 3. Results obtained for boron determination in the coal and coal combustion by-products from PP2 by means of two different digestion procedures (method 1 and method 2).

Sample	B (µg/g) (db)	
	Method 1	Method 2
Coal	34.7	55.9
Pet-coke	0.10	6.91
Fuel blend	14.6	38.5
Slag	166	145
Fly ash	90.1	91.5

db; dry basis

Table 4. Boron mass balances at the different sampled power stations.

Power Station	Out/In (%)		
	Total	Boiler + ESP	FGD
PP1	133	114	119
PP2-1 (November 2007)	97	83	136
PP2-2 (November 2008)	106	92	149

Table 5. RE factors for the different collected solid by-products.

	FBA ¹	PFA ²
PP1	0.4	1.4
PP2 -1	0.1	0.6
PP2 -2	0.4	0.7

¹ Furnace Bottom Ash; ² Pulverised Fuel Ash

286 **Figure Captions**

287 Figure 1. Global output of boron during the different sampling campaigns.

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289 Figure 2. Boron partitioning at the boiler+ESP output.

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291 Figure 3. Boron partitioning in FGD by products and flue gas.

Figure 1

Figure 2

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298 Figure 3