1 **STUDY OF BORON BEHAVIOUR IN TWO SPANISH COAL COMBUSTION**

2 **POWER PLANTS**

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16   **Abstract**

17   A full-scale field study was carried out at two Spanish coal-fired power plants equipped with

18   electrostatic precipitator (ESP) and wet flue gas desulfurization (FGD) systems to investigate

19   the distribution of boron in coals, solid by-products, wastewater streams and flue gases. The

20   results were obtained from the simultaneous sampling of solid, liquid and gaseous streams

21   and their subsequent analysis in two different laboratories for purposes of comparison.

22   Although the final aim of this study was to evaluate the partitioning of boron in a

23   (co-)combustion power plant, special attention was paid to the analytical procedure for boron

24   determination. A sample preparation procedure was optimised for coal and combustion by-

25   products to overcome some specific shortcomings of the currently used acid digestion

26   methods. In addition boron mass balances and removal efficiencies in ESP and FGD devices

27   were calculated. Mass balance closures between 83 and 149 % were obtained. During coal

28   combustion, 95 % of the incoming boron was collected in the fly ashes. The use of petroleum

29   coke as co-combustible produced a decrease in the removal efficiency of the ESP (87 %).

30   Nevertheless, more than 90 % of the remaining gaseous boron was eliminated via the FGD in

31   the wastewater discharged from the scrubber, thereby causing environmental problems.

32

33   **1. Introduction**

34   Boron is an essential micronutrient for certain plants. However, this element can also be toxic

35   to aquatic species, plants and micro-organisms at high concentrations. In Europe the release

36   of boron is covered by EC Directive 2006/11 *Pollution caused by certain dangerous*

37   *substances discharged into the aquatic environment of the Community* and EC Directive

38   84/360 *Combating of air pollution from industrial plants*. Moreover, boron is considered to be

39   matter of concern in coal utilisation by the United States Environmental Protection Agency

40   (US-EPA) and the Australian National Pollution Inventory, and it is included under Annex 3

41 of the European Union Directive 2008/1/EC concerning Integrated Pollution Prevention and

42 Control (IPCC).

43 Boron is present in coals in concentrations ranging from 5 to 400 ppm (Swain, 1994; Swain et

44 al., 1995). Three modes of occurrence have been identified for this element in coals: i) bound

45 to the organic fraction, ii) locked inside clay minerals (mainly illite), and iii) bound within the

46 crystal lattice of tourmaline. The organically bound mode is generally considered to be the

47 most common (Swain et al., 1995). Boron easily volatilizes during combustion and condenses

48 on the surface of fly ashes in the exhaust gas (Swain et al., 1995; Clark et al., 1992). In

49 accordance with its behaviour during coal combustion, boron has been classified in between

50 class II (elements volatilised and later condensed on and becoming adsorbed onto the fly ash)

51 and class III (elements that remain mainly in gas phase) (Clark et al., 1992, Meij et al, 1983).

52 Boron partitioning depends on the temperature of the combustion system, the combustion

53 technology, its modes of occurrence in coal and the chemistry of the ashes (Clemens et al.,

54 2000). In addition, the growing use of co-fuels in combustion processes may modify the

55 partitioning of elements when compared with coals or coal blends. The application of

56 emission control technologies can also affect the redistribution behaviours of coal trace

57 elements and alter the concentrations of these metals in certain coal combustion by-products

58 (CCBs). As a result, the disposal (i.e., landfilling and impoundment) and utilization (e.g.,

59 construction and agricultural applications) of fly ash and FGD solid waste, as well as the

60 discharge of FGD wastewater, have given rise to considerable environmental, operational, and

61 regulatory concerns. All of these actions may result in more restrictive waste disposal and

62 wastewater discharge regulations and have the potential to impact the design and operation of

63 coal-fired power plants (US EPA, 2008). There is therefore a clear need for the coal-fired

64 power industry to acquire a better understanding of the behaviours of trace elements (i.e.,

65 partitioning profile of trace elements) in the coal combustion process.

66 Concerning partitioning in coal power plants, a number of problems have made it difficult to

67 achieve a good closure for the boron mass balance. The determination of the boron content in

68 coal involves a significant degree of uncertainty. The major problem in determining boron at

69 trace levels is the loss of boron due to volatilization during sample digestion owing to the high

70 volatility of BF_3 (US EPA, 2008; Pougnet et al., 1986a; Pougnet et al., 1986b; Zarcinas et al.,

71 1987).

72 In this work a full-scale field investigation was carried out at two Spanish power plants

73 equipped with electrostatic precipitator (ESP) and flue gas desulfurization (FGD) systems to

74 evaluate boron partitioning during a (co-)combustion process. Special attention was paid to

75 the analytical procedure for boron analysis in coal, and CCBs by means of the optimization of

76 a sample preparation procedure prior to the analysis of boron in solution. The specific

77 objectives of this study were: (1) to develop a preparation method for boron determination in

78 solid coal combustion by-products in which specific shortcomings of the currently used acid

79 digestion methods are solved; (2) to develop a procedure to collect representative samples

80 from all the solid, liquid and gaseous streams in two Spanish power plants; (3) to acquire an

81 understanding of the partitioning of boron in the combustion process by means of mass

82 balances and enrichment factors among co-combustion by-products (slag and fly ash).

83

84 **2. Materials and Methods**

85 *2.1. Boron analysis*

86 Two different procedures for complete dissolution of the samples were compared in this

87 study: i) method 1 involves acid digestion in closed Teflon vessels (Querol et al., 1992)

88 whereas ii) method 2 involves alkaline fusion with Na_2CO_3 which was optimized in this study

89 on the basis of previous experiments (Smith et al., 1991; Hofstetter et al., 1991). Method 1 is

90 a two-step digestion procedure which consists of the wet oxidation of the organic matter using

91   HNO_3 followed by acid digestion using $HF + HNO_3 + HClO_4$. In method 2, before the

92   alkaline fusion, the organic matter is eliminated by ashing at 500 ºC. The fused sample is

93   dissolved in HCl. In both cases, after the dissolution of the sample, the determination of boron

94   was performed by means of a quadrupole ICP-MS (HP 4500) equipment using Be as internal

95   standard.

96   *2.2. Power stations and sampling procedures*

97   The sampling campaigns were undertaken in two large (1050 and 1200 MW) Spanish

98   Pulverised Coal (co) Combustion (PCC) power stations (labelled PP1 and PP2, respectively)

99   equipped with ESP and wet-limestone based FGD facilities with forced-oxidation. The

100 sampling campaigns were carried out at 100% maximum capacity and 100% desulphurisation

101 over 2 consecutive days at PP1 in September 2007 and at PP2 in November of 2007 (PP2-1)

102 and 2008 (PP2-2). Power plant PP1 was fed with 100 % of coal (a 60:40 blend of local sub-

103 bituminous with bituminous coal). The PP2 co-combustion power plant was fed with a coal

104 and coke blend (84:16 in 2007 and 88:12 in 2008). At PP1 water derived from the filtration of

105 the gypsum slurry was mixed with process water to prepare the limestone slurry and the rest

106 of the filtered water was re-circulated to the scrubber system while at PP2 all of the filtered

107 water was directly re-circulated to the FGD system. A total of 11 streams, 7 solid (raw coals

108 and petroleum coke, coal blend, slag, pulverised fly ash (PFA), limestone and FGD gypsum)

109 and 4 liquid (process water, water filtered from gypsum slurry, and the limestone and gypsum

110 slurries) were sampled. The flue gas was sampled at the same time at the solid and liquid

111 streams. The gas measurements were carried out at two different sampling points, upstream,

112 (IN)-FGD, and downstream, (OUT)-FGD, inside the FGD unit. A sample of approx 1 m^3 was

113 extracted from the flue gas stream through a filter system collected by a series of impingers

114 and placed in an ice bath according to standard UNE-EN 14385, (UNE 2004). Particle-bound

115 boron was collected at the front half of the sampling train using Teflon micro filters. The solid

116   samples were mixed, crushed, milled and then rafted and representative samples of each

117   sampling day were analyzed. The water streams and gas trapping solution samples were

118   filtered in situ. All the samples were divided for comparative analysis between two

119   independent laboratories.

120   *2.3. Mass Balances*

121   In order to validate the design of the sampling campaign and to ensure the validity of the

122   sampled streams different mass balance calculations were performed: i) whole installation

123   (total) ii) Boiler + ESP and iii) FGD. The input and output streams used for mass balance

124   calculations are summarised in Table 1. The stream flows used for the mass balance

125   calculations are based on the monitored data and on historical data recorded by the power

126   plant.

127   *2.4. Relative Enrichment factors (REs)*

128   Boron partitioning among ashes was comparatively evaluated by using its relative enrichment

129   (REs) factors as defined by Meij (Meij et al., 1983, 2002; Meij, 1994). The term "relative

130   enrichment" was adopted in order to describe the behaviour of a particular trace element

131   during coal combustion. This parameter is defined as: RE = (conc. in ash / conc. in coal) (%

132   ash content in coal / 100). Based on this RE factor, Meij grouped trace elements into three

133   classes denoted as: Class I, II and III (Meij et al., 2002; Meij et al., 2007). Class I elements

134   are defined as elements that do not vaporise during combustion and their RE factor is around

135   1.0. All elements that volatilise in the boiler but condense in the ESPs are grouped in Class II.

136   For these elements the RE factor of the furnace bottom ash (FBA) is less than 0.7 because,

137   these elements in gas phase have no chance of condensing on the bottom ash particles. The

138   RE factor of the pulverised fly ash (PFA) is close to 1. Class III elements have a very low RE

139   factor, especially in the furnace bottom ash and to a lesser extent, in the pulverized fly ash. In

6

140   other words, most of these elements are volatilized and, in the absence of an FGD plant, they

141   are totally emitted into the atmosphere in the gaseous phase.

142

143   **3. Results and discussion**

144   *3.1. Boron analysis*

145   In order to validate the alkaline fusion procedure (method 2) reference materials were used for

146   the determination of accuracy and precision. Due to the lack of certified reference material for

147   the determination of boron, two coal standards (SARM 20 and NIST-1632c) and one

148   reference soil (CRM026) were analysed by this procedure. The results obtained by the

149   proposed digestion method (Table 2) are statistically accurate and precise.

150   The results obtained using the two different dissolution procedures were compared. Table 3

151   shows the concentrations of boron obtained by both methods in the coal and CCBs (slag and

152   fly ashes). The results reveal that a significant boron volatilization occurred when the two-

153   step digestion method was used for the coal, the petroleum coke and the fuel blend feed, while

154   a good agreement between both digestion procedures was obtained for the slag and fly ash

155   samples. These results corroborate that boron losses can occur when the sample is

156   decomposed by wet oxidation methods using an acid mixture containing HF (Pougnet et al.,

157   1986a; Pougnet et al., 1986b; Zarcinas et al., 1987), due to the high volatility of BF_3. The

158   difficulty of boron determination in coal and fly ash samples is mainly due to the low

159   concentrations found in some coals and the complex nature of the sample. The results appoint

160   to the volatilization of organically-bound boron during the acid digestion procedure (method

161   1).

162   *3.2. Boron behaviour*

163   After determining the content of boron in the samples collected from the power plants, mass

164   balance calculations were carried out. As already mentioned, in addition to the total mass

165   balance (total), other mass balances were also calculated i.e., around the boiler plus the

166   electrostatic precipitator (Boiler + ESP) and in the flue gas desulfurization unit (FGD). Boron

167   mass balances were closed with good Out/In ratios when method 2 was used to decompose

168   the sample. Total mass balance closure were slightly greater than 100 % in both power plants,

169   while the Boiler + ESP balance in PP2 was slightly lower, 80-90 % (Table 4). Closure for the

170   mass balance around the FGD deviated more than 20% in both power plants because of the

171   uncertainty related to the water flows, as much of the water employed in the plant is filtered,

172   mixed and re-circulated. As expected, coal is the main source of boron (8000 and 5000 g/h at

173   PP1 and PP2, respectively) while the FGD input water, which is re-circulated, provides a

174   relatively high proportion of this element (1000 and 1700 g/h in PP1 and PP2, respectively).

175   Total mass balances and mass balances around the boiler + ESP are dominated by the fuel

176   input, whereas the FGD balance is dominated by the recovered water and gas inputs.

177   The total output of boron for the plants sampled in this study is shown in Figure 1. This boron

178   was partially distributed between the fly ashes (40-65%) and FGD by-products *i.e.* effluent

179   and gypsum, (31-53 %). A very low proportion (< 0.5 %) reached the stack in gas phase.

180   Some differences were observed in boron behaviour between the two power plants. At PP1 65

181   % was retained on the fly ash and 31 % of the boron was removed with the FGD by-products.

182   However, at PP2 more than 50 % was discharged with the FGD effluent and a lower

183   proportion (40-45%) was retained on the fly ash. This can be attributed to the higher

184   proportion of organically bound boron in the pet-coke that was used as co-fuel. This

185   behaviour can be clearly seen by comparing the boiler+ESP outputs (Figure 2). A higher

186   amount of boron remains in gas phase at the output of the ESP in PP2 (7-8 %) while boron is

187   retained to a lesser extent in the fly ashes. This result confirms that boron behaviour, during

188   combustion, is controlled by the mode of occurrence of the element in the coal (Clemens et

189   al., 2000).

190   Moreover, as revealed by the boron partitioning at the FGD output (Figure 3), the gaseous

191   boron and fly ash particles that escape from the ESP are retained in high proportions in the

192   FGD effluent and partially in the FGD gypsum, confirming the high capacity of this device

193   for retaining boron. The FGD system allowed the abatement of 90-95 % of the incoming

194   boron, most of which remained in aqueous phase (>85 %) while the rest was removed with

195   the FGD gypsum. The high water solubility of B coupled with the re-circulation of a

196   considerable amount of the effluent stream makes the boron being concentrated in water

197   producing a waste of increasing environmental concern.

198   The calculated enrichment factors are shown in Table 5. Boron can be classified in class II

199   (RE~1 for PFA; RE<0.7 for FBA) which means that it is volatilised and mostly condensed on

200   fly ash. Therefore, in the combustion power plant configuration, most of the boron volatilised

201   during combustion is mostly removed with the fly ashes collected from the ESP, the rest

202   being removed via the FGD system. The most remarkable finding was that the boron

203   collected in the FGD is mostly in the aqueous stream which is very often re-circulated to the

204   scrubber, resulting in an increase in boron concentration in the scrubber by-products, with the

205   consequent environmental and technological risks that this implies. This suggests the need for

206   additional wastewater control before it is discharged.

207

208   **4. Conclusions**

209   Boron content in coal and coal combustion by-products can be determined with good results

210   by applying an alkaline fusion method to ashes obtained at 500ºC, and by analysing the

211   resulting dissolution by means of ICP-MS using Be as internal standard.

212   During coal combustion in a power station, boron is volatilised and then mostly condensed

213   onto the fly ashes collected by the electrostatic precipitator. However different boron

214   behaviour was observed when pet coke was used as co-fuel. In this case, a higher proportion

215 of boron remained in gas phase confirming that organically bound boron is volatilised to a

216 greater extent and can remain in gas phase after the ESP. Nevertheless, any boron remaining

217 in gas phase is eventually removed in the desulphurization plant. Most of the boron captured

218 in the FGD plant remains in the aqueous phase. Because many of the power plants are

219 designed to re-circulate the water stream that comes from the FGD plant, the boron is re-

220 circulated to the FGD plant, leading to a significant increase in the concentration of boron in

221 the FGD by-products with serious implications for the environment.

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229

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269   112:1107–1112.

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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272

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

277   Table 3. Results obtained for boron determination in the coal and coal combustion by-

278   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

279   db; dry basis

280

281   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

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283

284   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

285   [1] Furnace Bottom Ash; [2] Pulverised Fuel Ash
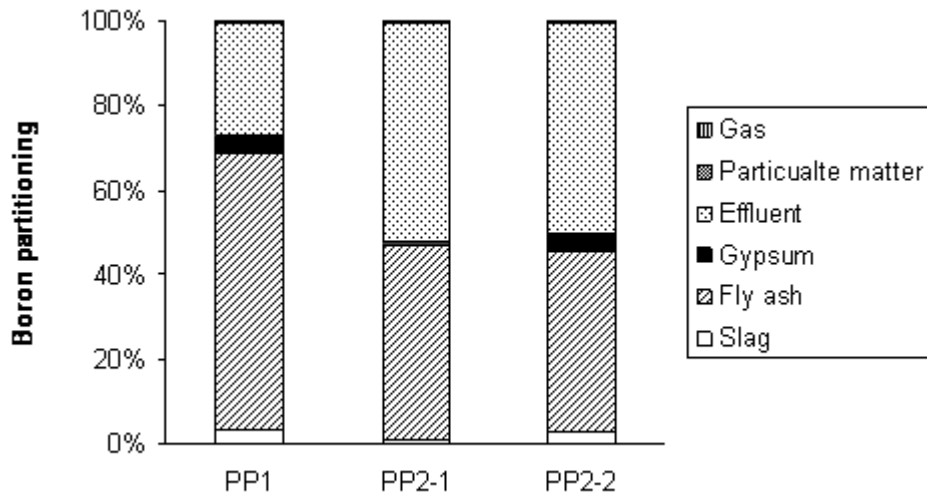
286   **Figure Captions**

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

288

289   Figure 2. Boron partitioning at the boiler+ESP output.
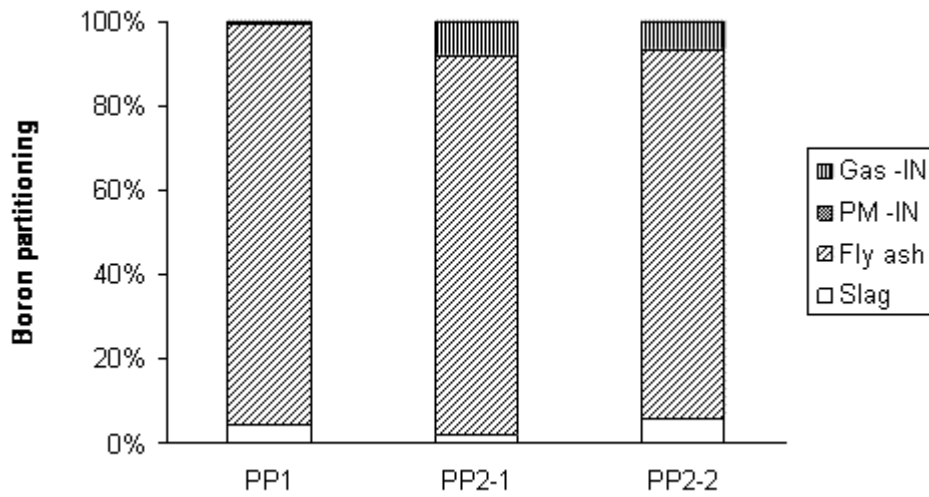
290

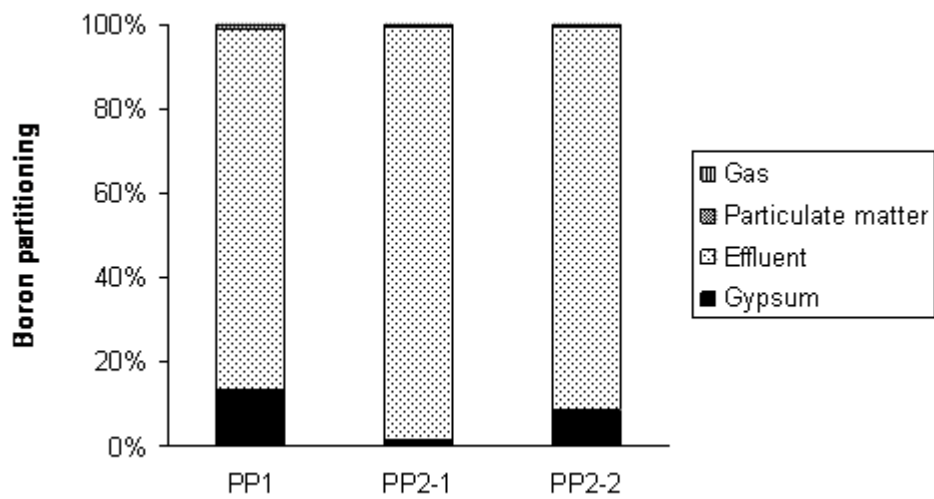291   Figure 3. Boron partitioning in FGD by products and flue gas.

292

293   Figure 1

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295

296   Figure 2

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298   Figure 3