Speciation of Cr and its leachability in coal by-products from Spanish coal combustion plants

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Abstract

This study evaluates the behaviour of total Cr and Cr (VI) during coal combustion in two Spanish power stations. The content and distribution of Cr in the feed coal and combustion wastes was determined and the Cr contents were normalized using enrichment factor indexes. The speciation of Cr in the fly ash fractions from the different hoppers of the electrostatic precipitators was established and the possibility that the Cr (VI) might leach when ashes are disposed of at landfill sites was assessed. Differences in the distribution and behavior of Cr in the two power stations were observed. According to European directive 1999/31/CEE, soluble Cr(VI) in the fly ashes studied would be unlikely to pose an environmental or health risk when the ash is disposed of.

Keywords: chromium; fly ash; bottom ash; coal combustion

1. Introduction

Cr occurs in the environment primarily in two valence states, as Cr (III), which is essential for metabolic processes and as Cr (VI), which is toxic and carcinogenic. Emission sources of Cr can be direct or indirect. The direct sources include those that produce or consume Cr when a product is manufactured, whereas the indirect sources are those that emit Cr because it is present as an impurity in the primary activity¹. This is the case of coal combustion plants². In the year 2004, 25% of all the Cr emitted to the air in Europe originated from combustion installations³. The US Environmental Protection Agency estimates the emissions of Cr for the year 2010 at 87 tons/year⁴.

Cr concentrations in coal commonly range between 0.5 and 60 $\mu\text{g g}^{-1}$ ⁵. Cr may be associated with clays or with other fine-grained minerals and it is also reasonable to expect some organically associated Cr in many coals⁵⁻⁸. Upon coal combustion, a large amount of trace elements leaves the coal matrix and is distributed between the vapor and particulate phases in proportions that depend on the initial Cr concentration in the coal, the design and operating conditions of the combustion facility and the particulate control devices. Elements such as chromium are apparently not totally volatilized during the coal combustion process and exhibit a tendency to be deposited in bottom ash or fly ash⁹⁻¹². The quantity of toxic Cr species in these subproducts is important because it might lixiviate when the ashes are disposed of at landfill sites. According to European directive 1999/31/CEE on the admission of wastes at disposal sites, the limit value of total leachable Cr per liquid/solid proportion of 10 l/Kg is: i) 0.5 $\mu\text{g g}^{-1}$ as inert waste, ii) 10 $\mu\text{g g}^{-1}$ as a non-dangerous waste and iii) 70 $\mu\text{g g}^{-1}$ as dangerous waste.

The objective of this study was to provide a detailed content and distribution assessment of the total Cr and Cr (VI) present in the feed coal and ashes. However, our attention mainly directed to the Cr speciation in fly ash fractions from different hoppers of electrostatic

precipitators, with the aim of determining the proportions of Cr that may lixiviate from the ashes and its possible toxicity.

2. Experimental Section

Samples from two power plants (A and B) were used. Power station A (550 MW) consumed a bituminous coal, while power station B (350 MW) used a blend of bituminous coals. A representative sample of bottom ash from each power station was studied (BAA, BAB). Seven fly ashes (FA) were sampled from the hoppers of the electrostatic precipitators of A and nine from B. In each case the fly ashes were retained by two parallel rows of hoppers. The gas stream with the whole fly ash was channelled into the two rows. In the case of A each electrostatic precipitator is formed by a row of hoppers. Four were sampled in the first (FAaA-FAdA) whereas only three were sampled in the second (FAeA-FAgA) as the fourth did not capture a sufficient amount of sample. In the case of power station B the two rows belong to one precipitator. Five hoppers were sampled in the first row (FAhB-FAIB) and four in the second (FAmB-FApB). Again, in the last hopper of the second row no significant quantities of ashes were captured.

The results of the work were assessed on the basis of i) the content of total Cr and Cr(VI) and its relationship with the particle size of the fly ashes, ii) the values of the Cr enrichment factor calculated by means of two different methods and iii) Cr leachability.

For the analysis of total Cr in the solid samples a digestion method in a microwave oven¹³ was used. The total Cr in solution was determined by ICP-MS. Two standard samples (coal sample SARM19 and fly ash sample 1633 b) were employed to ensure the quality of the data. The Standard 3060A¹⁴ method was used to extract Cr (VI) from each solid sample.

The amount of leachable total Cr in the fly ash and bottom ash samples was determined according to the standard UNE-EN-12457/2 method and the Standard 7195 method¹⁵ was used to

determine the concentration of leachable Cr (VI). In all cases Cr in solution was analyzed by ICP-MS. The particle sizes of the samples were measured with a Beckman Coulter LS 13 320. The aluminium content was determined by atomic absorption spectrometry.

3. Results and discussion

3.1 Total Cr and Cr (VI) content and relationship with the particle size of the fly ashes

The concentrations of Cr in the feed coal (CA and CB) of the two power stations were similar: $19.9 \mu\text{g g}^{-1}$ and $18.8 \mu\text{g g}^{-1}$ respectively. The average Cr contents in the bottom ashes were also similar ($\sim 170 \mu\text{g g}^{-1}$) (Table 1). However, the content and speciation of Cr in the fly ash fractions taken from the hoppers were found to differ considerably in the two power stations (Table 1). In the fly ashes from the hoppers of power station B, the distribution of the total Cr is more homogeneous ($129\text{-}173 \mu\text{g g}^{-1}$) than in the fractions from A ($219\text{-}777 \mu\text{g g}^{-1}$). The concentrations of Cr (VI) range between $6.8\text{--}11 \mu\text{g g}^{-1}$ in A and $4.6\text{-}14 \mu\text{g g}^{-1}$ in B (Table 1). Consequently the highest percentages of Cr (VI) were found in the fly ashes from plant B, between 4 and 9%.

The dependency of Cr concentration on the fly ash particle size observed in previous works¹⁶ could not be confirmed (Table 1). Although the particle size range of the fly ash samples from plant A is narrow, the particle sizes of the fly ashes from plant B vary considerably. However the total Cr content is similar. Thus, at least in this size range, Cr concentration in fly ashes is not dependent on particle size.

3.2 Behaviour of elements during combustion; enrichment factors

The element content in the ashes can be normalized by correlating it with a non-volatile element in the coal using the enrichment factor (EF) defined by Gordon and Zoller¹⁷ as:

$$\text{EF} = ([\text{X}]_s/[\text{Al}]_s)/([\text{X}]_c/[\text{Al}]_c)$$

where $[X]_s$ and $[X]_c$ are the contents of element X in the fly ash or bottom ash and in the coal respectively, and $[Al]_s$ and $[Al]_c$ are the aluminium contents. The volatile elements will give $EF < 1$ and may give $EF_{\text{fly ash}} > EF_{\text{bottom ash}}$. Elements which are enriched by fractionation into bottom ash or fly ash may show an EF slightly > 1 .

Other enrichment factors have been formulated. The term “relative enrichment” (RE) was defined by Meij et al.¹⁸ as

$$RE = (\text{conc. in ash} / \text{conc. in coal}) \cdot (\% \text{ ash content in coal} / 100)$$

Based on the RE factor, elements can be grouped into three classes:

Class I: elements that do not vaporize ($RE \sim 1$).

Class II: elements that volatilize in the boiler and afterward condense on the ash particles. ($RE > 1$ in the fly ashes).

Class III: very volatile elements ($RE \ll 1$)

The values of the two enrichment factors (EF and RE) calculated in this work were found to be comparable (Table 2). Different tendencies for the behaviour of Cr species in the two power stations were observed. In power station B the distribution of total Cr in the bottom ashes and fly ash fractions was similar ($RE \sim 1$). The Cr in these fly ashes should be assigned to Class I (non-volatile element)¹⁸. In power station A, the total Cr in the fly ash fractions showed enrichment factors of up to 2 and 7.3 in one case (FAdA). Therefore, in the fly ashes from A, the Cr can be considered volatile (Class II), even though condensation occurs on the ash particles captured in the electrostatic precipitators. The enrichment of Cr (VI) in fly and bottom ashes cannot be discussed in this work because with the available data it was not possible to verify whether Cr(III) is oxidized to Cr(VI) during coal combustion.

3.3 Results of leachable total Cr and Cr (VI) in fly ashes and bottom ash

In Fig. 1 and Fig. 2 the relative proportions of Cr species leached are compared and are related to the pH values. The Cr concentrations in the lixiviates from the different fly ash samples vary from sample to sample and range from 18.7 ng g^{-1} to 1277 ng g^{-1} . The leachable Cr was lower in the bottom ashes (4.5 ng g^{-1} for BAB and 20.8 ng g^{-1} for BAA). The pHs of the lixiviates of the fly ashes range between 8 and 13. According to European directive 1999/31/CEE, these fly ashes may be admitted to disposal sites as inert or non dangerous wastes. In general, the lowest particle sizes show a higher concentration of Cr in solution that may reach values as high as $1 \mu\text{g g}^{-1}$ for the particle sizes between $3\text{-}17 \mu\text{m}$ (Table 1, Fig. 2). The leachates of these samples have the lowest pH values (Fig. 2). These fly ashes would not be permitted to be deposited at landfill sites as inert waste, but would be accepted as non dangerous wastes.

The proportion of leachable Cr (VI) with regard to leachable total Cr ranges from 35 to 100%, these proportions being usually higher in the fly ash samples from B (Fig. 1-2). The proportion of Cr (VI) in the solid samples was lower (Table 1). Although the chromium concentrations are in the order of ng g^{-1} , the largest proportion of soluble chromium is the toxic species of chromium, Cr (VI). No relationship between pH and the amount of Cr leached was observed in the samples from A power station (Fig. 1). However, in the samples from B the greatest proportion of Cr was found in the leachates with the lowest pHs (Fig. 2).

From the results it can be inferred that the fly ash samples must be considered as inert wastes, with a few exceptions which may be considered as non dangerous. What must also be taken into account is the different behavior of Cr in each power station. According to the RE values, Cr may be considered as a non volatile element (Class I) in power station B, whereas in power station A it is a semi-volatile element (Class II)

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Table 1 Concentrations of Cr in the feed coals, fly ashes and bottom ashes and particle sizes for the fly ash samples

Power station	Product	Sample	Cr total $\mu\text{g g}^{-1}$	Cr (VI) $\mu\text{g g}^{-1}$	Cr (VI) %	Particle size μm
A	Feed coal	CA	19.9 ± 0.5^a	0.39 ± 0.02	2	
	Fly ashes	FAaA	219 ± 27^b	6.75 ± 0.18	3	56.3
		FAbA	284 ± 50^b	11.1 ± 0.2	4	28.0
		FAcA	352 ± 26^b	8.64 ± 0.17	3	21.5
		FAdA	777 ± 53^b	9.53 ± 0.31	1	17.1
		FAeA	277 ± 35^b	9.99 ± 0.61	4	50.8
		FAfA	437 ± 21^b	10.6 ± 0.3	2	27.4
		FAgA	289 ± 23^b	7.65 ± 0.11	3	13.3
	Bottom ash	BAA	170 ± 11^b	0.75 ± 0.05	0.4	
B	Feed coal	CB	18.8 ± 1.1^c	0.44 ± 0.03	2	
	Fly ashes	FAhB	138 ± 4^b	6.55 ± 0.06	5	114
		FAiB	142 ± 12^b	7.39 ± 0.01	5	107
		FAjB	164 ± 1^b	11.4 ± 0.2	7	17.2
		FAkB	163 ± 15^b	14.2 ± 0.2	9	5.11
		FAlB	173 ± 12^b	15.1 ± 0.2	9	2.98
		FAmB	146 ± 15^b	7.33 ± 0.04	5	32.5
		FAnB	129 ± 16^b	4.63 ± 0.06	4	13.8
		FAoB	131 ± 2^b	9.36 ± 0.18	7	11.1
		FApB	159 ± 12^b	12.4 ± 0.1	8	4.16
	Bottom ash	BAB	179 ± 5^b	1.11 ± 0.10	0.6	

^a Standard deviation (SD) of five coal samples

^b Standard deviation (SD) of replicated measurements (n=2)

^c Standard deviation (SD) of four coal samples

Table 2 Enrichment factors correlated with a non-volatile element in coal (EF) and with the ash content in coal (RE) in fly ashes and bottom ashes.

Power station	Product	Sample	Cr total	
			EF	RE
A	Fly ashes	FAaA	1.6	1.6
		FAbA	2.2	2.1
		FAcA	2.9	2.6
		FAdA	7.3	5.6
		FAeA	2.1	2.0
		FAfA	3.5	3.2
		FAgA	2.5	2.1
	Bottom ash	BAA	1.3	1.2
B	Fly ashes	FAhB	1.1	1.0
		FAiB	1.1	1.1
		FAjB	1.3	1.2
		FAkB	1.2	1.2
		FAlB	1.4	1.3
		FAmB	0.99	1.1
		FAnB	0.96	0.96
		FAoB	0.98	0.98
		FApB	1.3	1.2
	Bottom ash	BAB	1.4	1.3

Fig. 1 Concentrations and pH of leachable Cr in fly ashes from power station A

Fig. 2 Concentrations and pH of leachable Cr in fly ashes from power station B