

A three-step metal fractionation scheme for fly ashes collected in an Argentine thermal power plant

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Received 30 January 2007; received in revised form 4 July 2007; accepted 12 July 2007

Available online 7 August 2007

Abstract

A new three-step fractionation scheme was applied to study the distribution of Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Sb, Ti, V and Zn in fly ashes collected in the electrostatic precipitator of a thermal power plant in the city of San Nicolás (Argentina). Seven samples were collected during one week of operation in 2005. For the fractionation, the scheme applied consisted of extracting the elements in three fractions: (i) soluble and exchangeable elements, (ii) carbonates, oxides and reducible elements and (iii) residual elements. Metals and metalloids at $\mu\text{g g}^{-1}$ level were determined in each fraction by plasma based techniques namely, inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). For validation, a certified reference materials NIST SRM 2711 (Montana soil) was subject to the same chemical sequential extraction procedure. X-ray diffraction powder (XRD) analysis and scanning electron microscopy (SEM) were used to characterize the major minerals present in the matrix. The predominant phases found in the total samples were mullite, quartz, iron oxides and lime. Total analyte concentration varied (in $\mu\text{g g}^{-1}$) from 1.54 for Cd to 30600 for Al. The leachability of the 15 elements under study proved to be different. All the elements (except Cd and Pb) were detected in the soluble fraction in the order: Cu (0.10%) \sim Mn (0.13%) $<$ Ni (0.17%) \sim Ti (0.19%) \sim Fe (0.20%) \sim As (0.21%) $<$ Zn (0.86%) $<$ Al (1.3%) $<$ Cr (2.9%) $<$ V (3.9%) $<$ Sb (6.9%) $<$ Mo (45.1%) $<$ S (58.0%). Percentages higher than 20% of S (24.1%) $<$ V (27.5%) $<$ Mn (29.0%) were detected in the second fraction. Al, As, Cr, Cd, Cu, Fe, Ni, Pb, Sb and Zn were mostly associated to the residual fraction. Recoveries of the overall procedure varied between 106% (Mo) and 72% (Cr).

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Keywords: Coal fly ashes; Three-step fractionation scheme; Trace elements; Plasma-based techniques

1. Introduction

Coal combustion is recognized as one of the major anthropogenic sources of many metals and metalloids into the atmosphere [1]. As an example, a 1000 MW power

plant has a typical consumption of 12000 t day^{-1} of coal [2] generating significant amounts of by-products. The amount and nature of metals and metalloids released are related to the composition of the coal burned and the technology employed at the power station. Coal contains many elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn, etc.) and many of them have been reported to be human potentially carcinogens [3]. Electrostatic precipitators can remove more than 95% of the fly ashes but particles with aerodynamic diameters $<10 \mu\text{m}$ as well as any gaseous compounds will be emitted directly to the atmosphere.

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However, the possible fate of the different elements released during the combustion process requires proper understanding because those elements present on the surface of fly ashes particles will be mobile in the aqueous environment possibly representing a serious health risk.

The availability and mobility of elements present in fly ashes will depend on the physicochemical forms of the elements [4]. In this context, the knowledge of the chemical composition, physical characteristics and fractionation of the ashes are of prime importance to assess the environmental impact and health risks.

Chemical sequential extractions provide useful information about solubility, origin, mode of occurrence, biological and physicochemical availability, mobilization, fate and transport of trace metals in the environment [5]. These procedures are operationally defined. Their operationally defined nature may be considered a weakness. In spite of this, sequential extraction methods provide knowledge that can improve our understanding of the risks for human health and the environment. Recently, Smichowski et al. [5] have reviewed metal fractionation of atmospheric aerosols, via sequential chemical extraction procedures. The same authors also reviewed the role of atomic spectrometric techniques in the determination of chemical elements in atmospheric aerosol, including fractionation studies [6].

Extraction methods have been developed and applied to chemical fractionation of fly ashes both for research and regulatory. Bódog et al. [7] reported a five-stage leaching procedure applied to fly ash samples collected at several emission sources in Europe. The analysis of the extracts by atomic absorption spectrometry (AAS) and graphite furnace atomic absorption spectrometry (GFAAS) showed different leachabilities and distribution patterns of Cd, Cr, Cu, Pb, V and Zn. Smeda and Zyrnicki [8] used a modified BCR extraction scheme [9] for studying the distribution of metals in fly ashes.

Recently, Gómez and coworkers [10] reported a four-step fractionation scheme for metals and metalloids by chemical bonding for particles accumulated by electrostatic precipitation in a thermal power plant. This fractionation procedure was based on a sequential extraction scheme reported by Fernández et al. [11] that was optimized for the analysis of fine atmospheric aerosols.

Continuous exposure to airborne particulate matter and fly ashes can have harmful effects on human health and the environment. In this context, a new three-step scheme was specifically adapted for the extraction of the more bioavailable elements present in fly ashes. Our previous studies applied to the fractionation of urban airborne particulate matter samples and fly ashes [10–14] demonstrated that the first two fractions contained the most bioavailable elements. Therefore, the third fraction constituted by metals bound to organic matter and sulphides was combined with the residual fraction. Commonly, very low proportion of trace elements are bound to the oxidizable fraction in pulverized coal combustor (PCC) fly ash because this fraction refers only to unburned coal particles and no sulphide spe-

cies occur in combustion of coal. Summarizing, the new scheme is constituted by two fractions of elements with different mobility plus the last fraction, which unifies practically all non-bioavailable elements.

In the present study, the fractionation of ashes by chemical bonding was performed using a three-step chemical sequential leaching scheme focused to gain information on the most mobile fractions. It was carried out by assessing the distribution of 15 elements in seven samples, between (i) soluble and exchangeable elements, (ii) elements bound to carbonates, oxides and sulphides (reducible elements), (iii) environmentally immobile elements.

2. Experimental

2.1. Instrumentation and reagents

A Fisons-ARL (Accuris, Switzerland) sequential ICP OES Model 3410 inductively coupled plasma optical emission spectrometer was employed for major and minor element determination. Instrumental details and operating conditions are summarized in Table 1.

An Agilent Technologies (Santa Clara, CA, USA) inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) Model 7500ce was used for trace elements determination. This instrument has an Octopole Reaction System (ORS) for elimination of polyatomic interferences arising from the plasma and sample matrix. Instrumental details and operating conditions are summarized in Table 2.

Welding Ar from Air Liquide (Paris, France) was used for ICP OES and ICP-MS determinations. Deionized distilled water (DDW) of Milli-Q grade was from Waters-Millipore (Billerica, MA, USA). All reagents were of analytical grade. Hydrochloric, hydrofluoric and nitric acids, and hydroxylamine chloride (Merck, Darmstadt, Germany) were used for sample treatment and preparation of the standards. Commercially available 1000 mg l⁻¹ standard solutions for ICP determinations (Merck) of the elements analyzed were used. All glassware and Teflon® vessels were treated in a solution 10% v/v nitric acid for 24 h and then washed with deionized water. All treated samples were stored in polyethylene tubes of 15 ml (Sterilin®).

A MLS-model Ethos 900 (Milestone-FKW, Sorisole, Bergamo, Italy) microwave apparatus equipped with six Teflon-PFA (perfluoroalkoxy) vessels was used to digest the samples.

X-ray powder diffraction patterns were taken at room temperature using a Philips PW 3710 diffractometer with Cu graphite monochromatized radiation. X-ray measurements were performed using the step mode using 0.02° per step with a 2 s counting time per step, over the range 10° ≤ 2θ ≤ 70°. For phase identification, the diffraction patterns obtained were analyzed using PC-Identify and ICDD database.

Morphological and compositional identification was performed by scanning electron microscopy (SEM), with a Philips 515 microscope (Philips Export B.V., Eindhoven,

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