

Extraction of Major Soluble Impurities from Fly Ash in Open and Closed Leaching Systems

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Major impurities in fly ashes are iron and calcium oxides, sulphate and hazardous leachable elements such as As, B, Cd, Cr, Mn, Pb, Se and V¹. These impurities have a negative impact on the fly ash utilisation due to technical (free lime, iron oxide, sulphate) or environmental restrictions²⁻⁶.

This study focuses on the development of decontamination tests for extraction of major water soluble impurities from fly ash in open and heated closed systems in order to increase the extraction yields obtained from previous investigations based on room-temperature closed systems⁷. The aim of these experiments is the enrichment of Al and Si and the depletion of the content of undesirable species in coal combustion by-products using experimental conditions with a potential industrial application.

Prior studies evidenced that the leachable fraction of heavy metals was strongly influenced by pH levels attained during the extraction tests^{8,9}. The high pH levels attained in closed leaching systems due to the presence of free-lime in many Spanish fly ashes¹⁰ accounted in some cases for the lower extraction yields of soluble heavy metals⁷. This study identified two types of leaching trends according to the ionic, the anhydrite- and the free-lime-dominated leaching. From the results of this previous study the Compostilla, Narcea and Puertollano ashes were selected as representative samples from the first group (anhydrite dissolution), and the La Robla, Teruel and Los Barrios as representative samples from the second group (free-lime dissolution) for further research on decontamination of fly ash by open-leaching system. These two groups also represent the low conductivity and low alkalinity leachates (first group, Narcea, Puertollano and Compostilla, 8.2-9.4 pH and 60-150 $\mu\text{S}\cdot\text{cm}^{-1}$) and the high conductivity and high alkalinity leachates (second group, La Robla, Teruel and Los Barrios, 11.6-12.1 pH and 1080-1100 $\mu\text{S}\cdot\text{cm}^{-1}$). In addition, the Puertollano and the Teruel fly ashes were selected for the high heavy metal and iron oxide contents, respectively. The open leaching system is tested in the present study to reach higher extraction ratios for those fly ash with high free lime content, since the leaching will take place without pH equilibrium due to continuous $\text{Ca}(\text{OH})_2$ dissolution. In addition, the continuous leaching with low mineralised waters in the open system may increase the extraction efficiencies. Also, heated closed extraction experiments are tested to compare the extraction yields with the other extraction procedures.

EXPERIMENTAL SECTION

The six previously mentioned fly ashes were selected for the leaching experiments carried out in this study. Detailed physical, chemical and mineralogical characterisation of the fly ashes selected are reported in prior studies¹⁰.

Given that the mobility of many heavy metals may be reduced by the high alkalinity induced by free lime in fly ashes, one may expect that the open leaching system will lead to higher extraction ratios with respect to the room-temperature closed leaching tests, specially for the high lime fly ashes. In order to check this hypothesis, open leaching reactors were designed and constructed. The method is based on a continuous upward water flow through a fly ash column. The experiments were developed with pH and conductivity measurements for the 6 previously fly ashes in order to obtain leaching final conditions which reached relatively low pH and low conductivity values (30-50 $\mu\text{S}\cdot\text{cm}$) for the last leachates of each experiment. From these four fly ashes; the Compostilla, Los Barrios, Puertollano and Teruel fly ashes were selected for chemical analysis of leachates.

Low conductivity solutions were attained at different time intervals for the different fly ashes using a water flow rate of $50\text{ ml}\cdot\text{h}^{-1}$ and 2 g of fly ash in each column, but in all cases, samples were collected at 10 ml rates. After the analysis of selected 10 ml leachates, leaching curves for pH, conductivity and concentrations of the different elements considered were obtained.

For the heated closed test, the six fly ashes selected were mixed individually with MilliQ®-grade water (18.2 $\text{M}\Omega\cdot\text{cm}$) at 95 °C using a water/fly ash ratio of $50\text{ ml}\cdot\text{g}^{-1}$ as previously done in the room temperature closed extraction tests¹³. The mixtures were introduced in PFA reactors and subsequently submitted to continuous stirring during 24 hours. The pH and the conductivity were measured and the end of each run.

The concentration of major and trace elements in the leachates from both, open and heated-closed leaching were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Rb, Se, Sn, Sr, U, V and Zn; Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for Al, Ca, Fe, K, Mg, Mn, Na, Si, B, Ba and Li. Sulphate contents were determined by ionic chromatography (IC).

RESULTS AND DISCUSSION

The results of the open leaching experiments using the six fly ashes selected show the three following types of pH leaching trends (Figure 1):

- a) The Narcea, Robla, Teruel and Los Barrios show a first pH increase from the first 10 ml leachates up to the 20-50 ml and a later alkalinity decrease from 30-60 ml up to the end of the experiments (1500 ml). An alkaline break-point is reached at different pH values depending on the fly ash (from pH 11.4 to 12.4). Usually, after 200 ml the pH values are stabilised around 10 pH.

- b) The Compostilla fly ash experiments a very narrow pH evolution, reaching pH values from 9.3. to 9.6 across the whole experiment (lower alkalinity values compared with the previously described pH trends).
- c) The Puertollano fly ash leachates reach neutral values in the initial leachates, which increase up to a maximum pH of 9.1 in the 60 ml. After this volume, the pH decreases progressively up to neutral values (7.0).

With respect to the conductivity evolution, the general trend is to decrease the conductivity of the leachates up to a break-point from which the conductivity remains constant. Major differences between the evolution of the ionic conductivity obtained for the different fly ashes are (Figure 1):

- a) Maximum conductivity values attained, which varied from 420 $\mu\text{S}\cdot\text{cm}$ for Puertollano up to 5200 $\mu\text{S}\cdot\text{cm}$ for Los Barrios.
- b) Water volume needed to stabilise the ionic conductivity of leachates at low ionic concentrations ($<100 \mu\text{S}\cdot\text{cm}$). This low conductivity values are attained between 30 and 60 ml for Puertollano and Compostilla fly ashes, at 200 ml for the Narcea fly ash and at 400 ml for Los Barrios, Robla and Teruel fly ashes.

Given that some of the six fly ashes studied showed very similar open leaching trends (Robla, Narcea, Teruel and Los Barrios fly ashes), as deduced from the pH and conductivity evolution, only four of the six fly ashes were selected for the study of the extraction yields under the open leaching conditions. The selected fly ashes were the Compostilla, Los Barrios, Puertollano and Teruel

With some exceptions (As and V), which will be discussed below, the evolution of the concentration of both major and trace elements show a sharp decrease during the first 50 ml of leaching volume, and tend to a steady concentration (Figure 2 and 3). This general trend is similar for the four ash samples analysed, regardless the pH values.

This evolution trend may be attributed to the volatile trace element enrichment in the external rim of the fly ash particles¹¹. However, the same evolution pattern could be obtained from the faster dissolution of finer particles, which are usually enriched in most of the trace elements^{12,13}. Both alternatives may take place at the same time and result indistinguishable. We have modelled the dissolution trend of the free-CaO for the experimental conditions used following the calculation procedure of Ayora et al.¹⁴ and Saaltink¹⁵ and assuming that the grain size of free-CaO is homogeneously distributed in four equal groups of 0.1, 1, 10 and 100 μm sized¹⁶. The Ca concentration trend resulting from the leaching simulation of CaO and the experimental data are easily comparable and similar to the trend shown by the rest of elements. Due to their faster dissolution kinetics (higher $\kappa\sigma$ value), the smaller particles give rise to higher amount of solute and are exhausted earlier. Therefore, differences in the size distribution of the particles may be responsible for the variation in shape observed in the leaching evolution patterns.

Differently from the rest of trace elements, As and V concentration in the effluent show minimum values at the beginning of the leaching experiments. Then, both elements may also experience a concentration peak along the extraction test (Figure 3). This is particularly evident for Los Barrios

and Teruel ashes, and is not observed in the Puertollano ash, where the leaching trend is similar to the rest of trace elements.

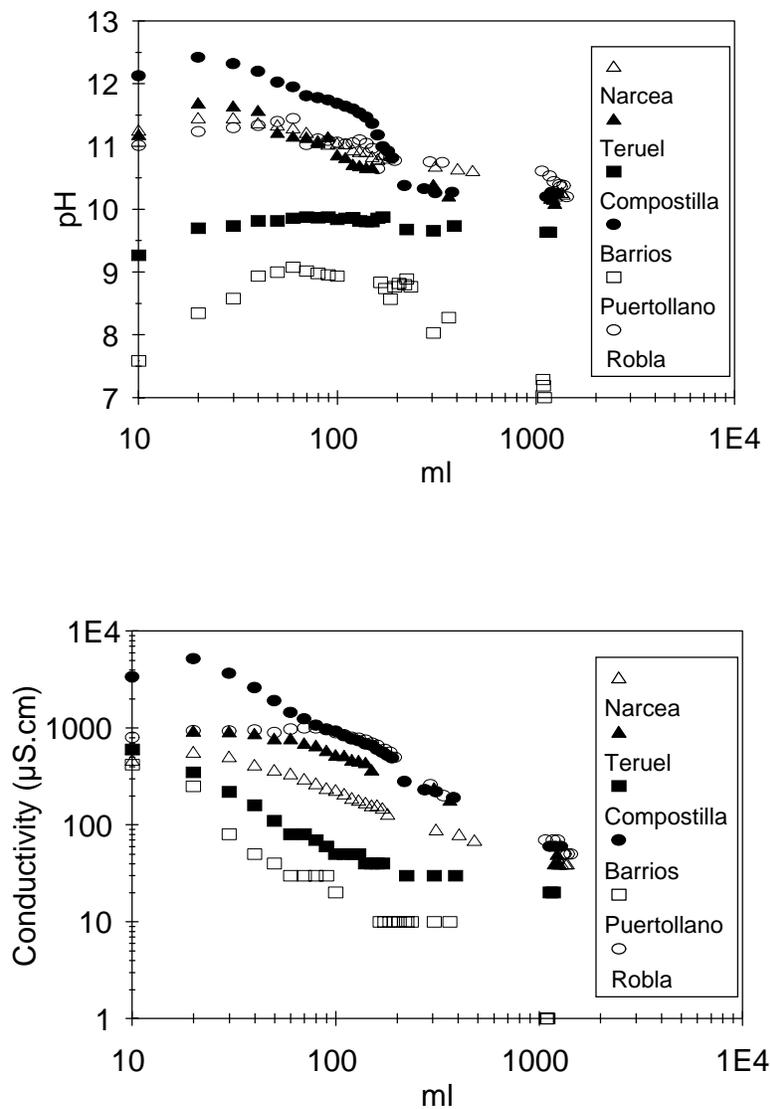


Figure 1. Time evolution of pH and ionic conductivity values in the open-leaching tests using the fly ash from Compostilla, Los Barrios, Narcea, Puertollano, Robla and Teruel power plants.

The low As and V concentration found at the beginning of the experiment is coincident with high pH and Ca concentration values due to the free-CaO dissolution. At such high pH values, AsO_4^{3-} and $\text{V}_2\text{O}_7^{4-}$ play a significant role in the aqueous speciation. As a result of the high Ca concentration in solution, the precipitation of the stable phases $\text{Ca}_3(\text{AsO}_4)_2\cdot 6\text{H}_2\text{O}$ and $\text{Ca}_2\text{V}_2\text{O}_7$ may take place. The low As and V concentration is coincident with the supersaturation of the solution with respect to the above mentioned solid phases. The low As and V concentration with high supersaturation values suggests that their precipitation rate is a function of supersaturation.

This fact has also been described for several minerals¹⁷. As pH and Ca concentration values decrease the solution becomes subsaturated, precipitation no longer takes place and the As and V follow the patterns described for the rest of trace elements.

Differential leaching behaviour of the elements

The normalised leaching rate of the different trace elements with respect their theoretical content in the glass varies from one to other, but it is always several orders of magnitude higher than those of Si and Al. This patterns is not consistent with a homogeneous distribution of the trace element within the glass, but rather their accumulation whether in the external rim and/or in discrete non aluminium-silicate fine particles.

The normalised leaching rate of a particular trace element may vary up to one order of magnitude from one ash sample to other. However, a fairly constant sorting in the leaching rates has been observed in the four samples analysed. From higher to lower, the rates are: $B \geq Se \geq Mo > As > V > Cr \geq Cu > Rb \geq Pb > Mn$. As the majority of trace elements are concentrated within the same range of particle size¹⁶, the differences observed in the leaching rate (up to orders of magnitude) are probably due to the dissolution constant (κ) of the solid compounds present in the ash. This could also explain the sorting of the leaching rate of the different trace elements consistently found in the four samples studied.

The comparison between the extraction yields obtained from the open and closed leaching systems demonstrated that, for the same water/fly ash ratio, the closed system showed relatively high extraction yields for major and trace impurities (i.e. Ca, S, Mg, B, Mo, Se, Ni, Pb and Zn) using a simple and inexpensive extraction method. Higher extraction yields for calcium, and specially for some impurities (As, Cr and V) can be reached by using the open leaching system with higher water volumes, specially for lime-bearing ashes. However, the high water volume consumed may limit the industrial application of these decontamination procedures.

Concerning the comparison of the results obtained from the heated and ambient closed leaching system, for the Teruel and Narcea fly ashes there was not large differences between the salinity of the leachates obtained from both extraction methods. However, the heated leaching of the other fly ashes (Puertollano, Los Barrios, La Robla and Compostilla) gave rise to increased ionic conductivity, from 35 to 56 % with respect the leachates obtained at room temperature⁷. As inferred from the chemical analysis of leachates, this higher salinity is mainly attributed to the higher dissolution rates of S, Al, Si, K and Na for these fly ashes in the heated leaching experiments with respect ambient extractions. No major changes were observed in the pH measurements.

The improvement of the extraction ratios in the heated leaching with respect the ambient extraction affected mainly to the elements from the aluminium-silicate fraction, mainly Al, Si, K, Na, Ba, Cr, Rb, Sr and V. However, the major impurities (Ca, S and Fe) and heavy metals did not increased considerably the mobility (generally <30%) in the heated extraction with respect the ambient extraction. Consequently this heated leaching procedure has not important advantages with respect the closed extraction at room temperature.

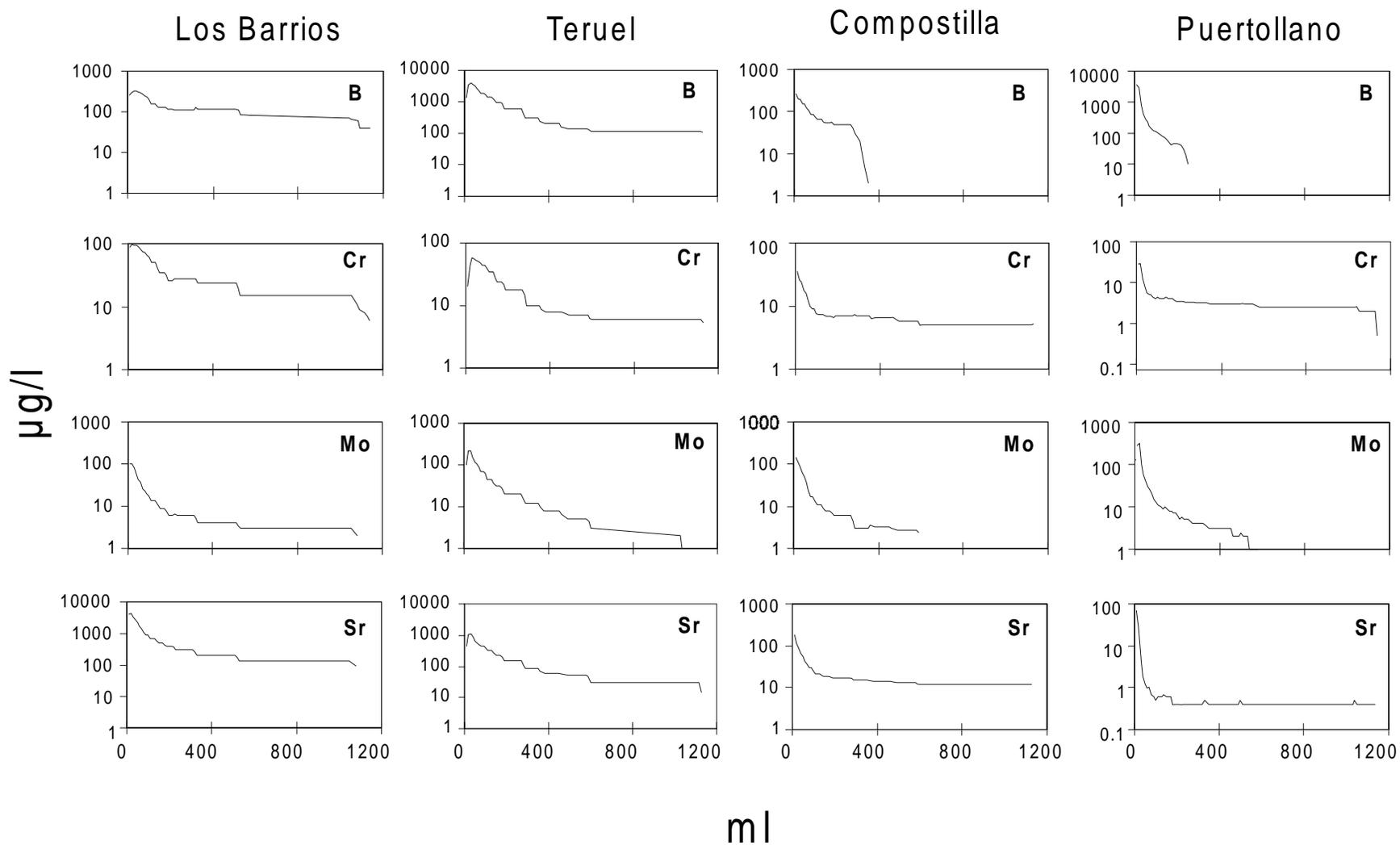


Figure 2. Time evolution of concentrations of B, Cr, Mo and Sr in leachates from the open leaching tests using the Los Barrios, Teruel, Compostilla and Puertollano fly ashes. Concentration in $\mu\text{g.l}^{-1}$ vs. ml of water used.

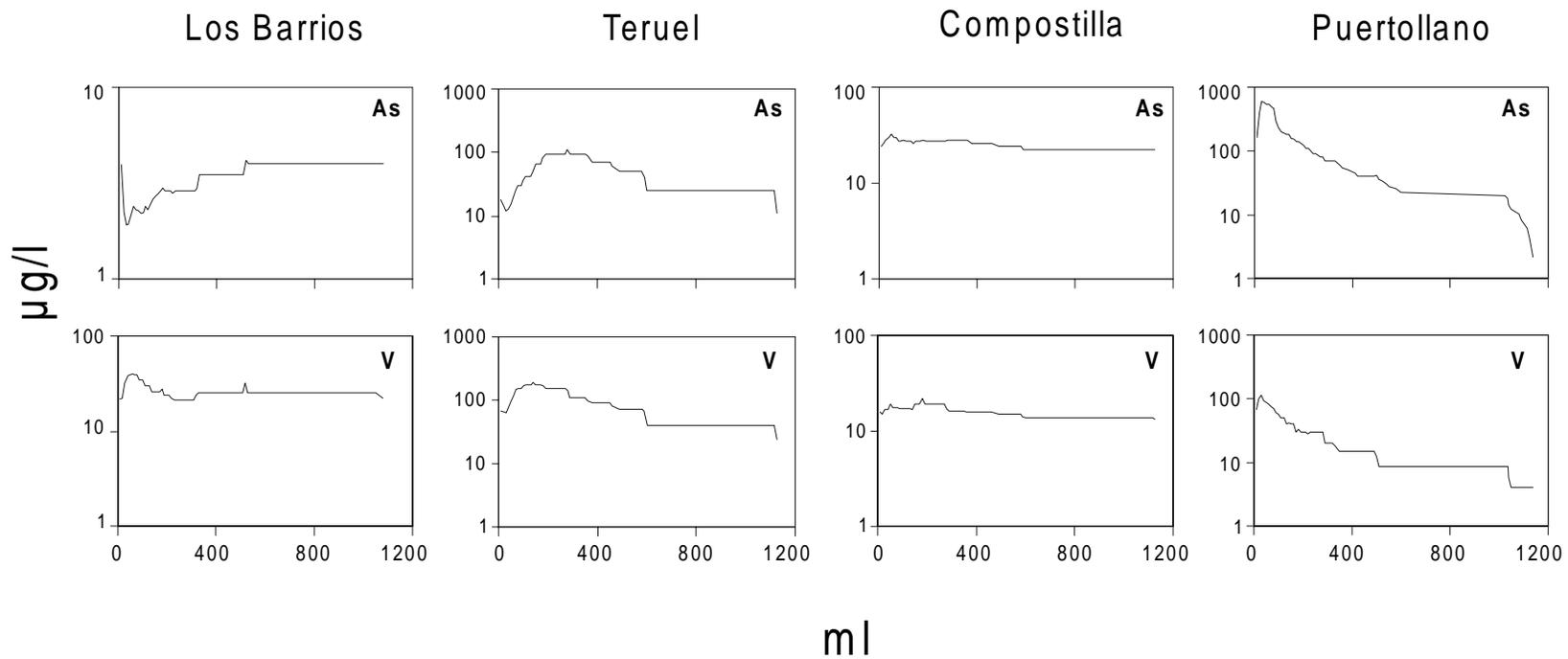


Figure 3. Time evolution of concentrations of As and V in leachates from the open leaching tests using the Los Barrios, Teruel, Compostilla and Puertollano fly ashes. Concentration in $\mu\text{g.l}^{-1}$ vs. ml of water used.

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