

# Influence of Coal Geochemistry on the Leaching of Lignite-fired By-products

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## INTRODUCTION

The power generation sector in Greece is heavily reliant on lignite-fired stations that cover 60% of the domestic power supply<sup>1</sup>. The main deposit of lignite is in Western Macedonia (Ptolemaida, Amynteo and Florina areas) with a total of 1.9 billion tonnes; while in Peloponissos (Megalopolis area, Southern Greece) lignite resources reach 240 million tonnes. The lignite-based electricity generation in Greece produces around 12 Mt/year of fly ash but only 15% is recycled. Current research efforts increasingly focus on added-value applications based on lignite fly ash. Alkaline-rich lignite fly ash has proven to be successful in soil remediation<sup>2</sup>, road construction<sup>3</sup>, synthesis of geopolymers<sup>4</sup>, zeolites<sup>5</sup> and metal matrix composites<sup>6</sup>. All these alternatives are expected to utilise large amounts of ash as long as ash-based products do not pose risks to the environment. This calls for a better understanding of the underlying factors controlling the mobility of trace pollutants contained in of lignite-derived by-products.

The mineralogy and geochemistry of lignites and lignite fly ash have been extensively studied over the last decades<sup>7-10</sup>. However, little attention has been paid to the leaching of Ca-rich fly ash worldwide and a number of elements of environmental relevance have been overlooked. Moreover, there is a substantial lack of data on bottom ash. The present study is therefore aimed at determining the role that the geochemical features of lignite, the partitioning of elements and the ash composition play in leaching of by-products.

## METHODOLOGY

Three sampling campaigns were undertaken at three Power Stations in Greece, fired with local lignites extracted from open cast mines in the near vicinity. Power Station 1 (PS1), located in the centre of Peloponissos (Southern Greece), is equipped with a wet flue gas desulphurisation (FGD) and fed with high ash and high moisture lignite. Power Station 2 (PS2) and 3 (PS3) are located in Western Macedonia (Northern Greece). PS2 is also equipped with wet FGD and fired with xylite (coalified wood). Due to the very

high Ca contents in the lignite fired in PS3, none of the units of this Power Station is equipped with an FGD unit.

The fuel streams i.e. lignite/xylite, fly ash, and bottom ash were sampled on an hourly basis. Subsamples were combined and homogenised to obtain representative samples for further analyses. The samples were acid-digested by using a special two-step digestion method devised for the analysis of trace elements in coal and combustion wastes<sup>11</sup>. The EU compliance leaching test EN 12457-2<sup>12</sup> was applied. This is a single batch leaching test performed at a liquid to solid ratio (L/S) of 10 L/kg with 24 hours of agitation time and deionised water as the leachant. Element concentrations in acid-digested samples and leachates were determined by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

## RESULTS AND DISCUSSION

### ASH COMPOSITION

#### *Influence of the lignite inputs*

The concentrations of elements in ash samples trace the geological setting of lignite basins feeding the power stations. Thus, the xylite deposits (PS2) were developed in a fluvial environment, which enhanced the accumulation of detrital silicates (13). PS2 ash is therefore enriched in  $Al_2O_3$  (Figure 1).

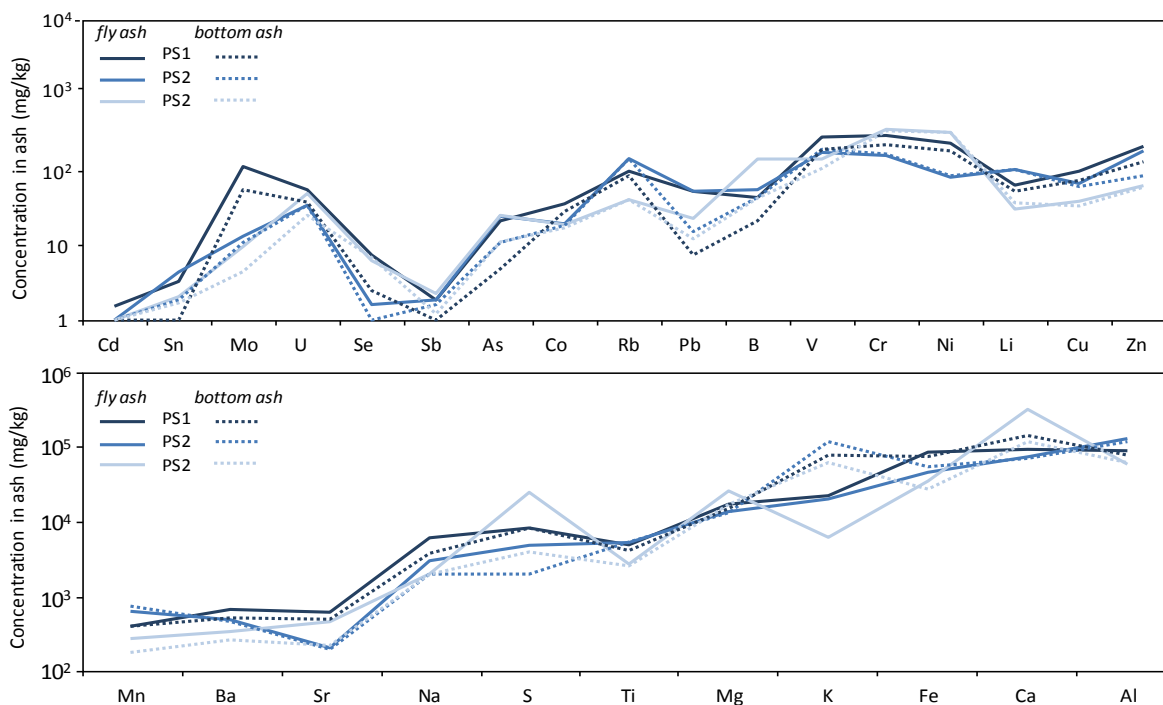


Figure 1. Concentration of a number of elements in the studied ash samples. The logarithmic scale of Y-axis should be noted.

PS1 ash also revealed a clastic influence in the depositional environment of the lignite fired, as the high Fe, Al and Ti concentrations suggested. This association points to mafic/ultramafic rocks as a possible source. By contrast, lignite deposits in the PS3 area were developed in a lacustrine environment where the deposition of calcareous sediments<sup>13</sup> prevailed over detrital inputs. This resulted in fly ash and bottom ash depleted in aluminosilicates, Ti, K and Fe in relation to other samples and the typical contents in coal ash<sup>14</sup>.

Lignite, fly ash and bottom ash contain a broad array of trace elements in concentrations >1 mg/kg (Figures 1 and 2). With the exception of elements displaying a highly volatile behaviour, the differences in the concentration of elements can be attributed to variations in the feed fuel.

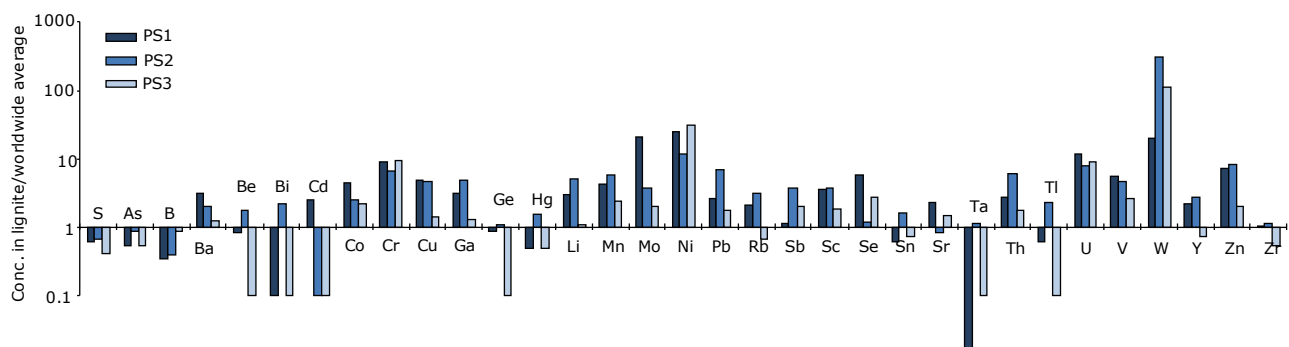


Figure 2. Relative concentrations of a number of trace elements in lignites fired in the studied power stations in comparison with the worldwide average contents<sup>15</sup>. The logarithmic scale should be noted.

The lignites covered in this study were markedly enriched in a number of trace elements in comparison with the worldwide average in lignite<sup>15</sup> and coal<sup>16</sup>, most notably Cr, Ni, U, W, Zn and Mo (PS1) (Figure 2). This is in line with other lignite basins from Greece<sup>7</sup>, Anatolia<sup>17-18</sup> and Kosovo<sup>19</sup> and may reflect the regional geological setting of lignite deposits in the Eastern Mediterranean region. The anomalous enrichment in these coals is related to (i) the proximity to major East-West aligned belts of peridotitic bodies containing metal-bearing minerals<sup>17</sup> and (ii) the alkaline depositional environments in the circum-Mediterranean lignite/subbituminous basins that favoured the organic trapping of metals in peat<sup>20</sup>. The anomalously enriched metals contained in lignite are transferred to ash during combustion; with the result that lignite ash has substantial amounts of the Cr, Mo, Ni, U, W and Zn (Figure 1).

Alongside the general trends, the differences in the concentrations of trace elements in lignite and ash from different power stations (Figure 1 and 2) fingerprint the distinctive local features of every lignite basin.

#### *Influence of the alkalinity*

As for volatile elements, the likelihood of reacting with ash components during the combustion process plays a more important role than their inputs via lignite.

The studied lignites can be regarded as low-S fuels. However, fly ash is enriched in S and bottom ash is not as much depleted as one could expect bearing in mind the volatility of this element. The high ash and high Ca contents in lignite promoted the interaction of SO<sub>2</sub> with ash particles and S was thereby removed from flue gas in the ESP. Free CaO in excess revealed a large abatement potential for SO<sub>2</sub> and other entrained gaseous pollutants. The ability to naturally desulfurise flue gas increases with the ratio between free CaO in ash and SO<sub>2</sub> in the flue gas. This ratio is governed by the Ca/S inputs via lignite. The Ca/S ratio=24 in PS3 lignite allowed a fully naturally occurring desulphurisation, obtaining a Ca-sulphate-rich byproduct (31% Ca and 2.4% S in fly ash). This prevents the generation of another solid by-product to be managed (FGD gypsum) but may involve serious drawbacks to the use of such fly ash in construction, where S is regarded as a nuisance.

To a lesser extent S is also captured by bottom ash. Sulphate species are therefore distributed among solid by-products, which inevitably increases the overall ash solubility. These observations underline the fact that the fuel composition can substantially modify the volatile behaviour of a given element and plays a primary role in the leaching of by-products.

Enhanced contents of Se were found in PS1 lignite (Figure 2), but ash products do not reflect this anomaly (Figure 1). This needs to be explained in terms of partitioning and affinity for CaO. Because of its typical volatile behaviour, over 50% of total Se input leaves PS1 retained in the FGD gypsum<sup>21</sup>. However, in PS3, Se is mostly captured along with S by highly reactive CaO in excess, due to the strong affinity of Se for lime and sulphate during combustion. Selenate and arsenate oxyanions can form a partial solid solution with gypsum<sup>22</sup> and condense on the fly ash. This would explain why As levels in PS2 and PS3 ash were similar, while As inputs to the system were greater in PS2 (Figure 2). Sb displayed a similar trend and is highly captured in PS3 fly ash, although the lignite fired was depleted in this element. The natural desulphurisation is therefore effective for removal of elements sensitive to free lime and their subsequent retention primarily in fly ash.

### *LEACHING OF ELEMENTS*

The pH values of the leachates were markedly alkaline (10.8 to 12.2). With few exceptions noted, fly ash and bottom ash displayed similar leaching trends.

Ca releases varied widely, ranging from 1000 mg/kg (PS2) to 15000 mg/kg (PS3). The ion balance pointed sulphate as the major Ca-bearing soluble species in all bottom ash samples, Ca would be primarily in hydroxide form in PS3 fly ash while sulphates and CaO/Ca(OH)<sub>2</sub> would coexist in PS1 and PS2 fly ash. The leachable concentrations of Al, Fe, Mg, Si and Ti were very low and water extractable proportions were estimated at <0.05% of the total content. These elements are tightly bound within high temperature aluminosilicates or iron oxides and therefore they cannot be easily released to the environment.

K, Li, Na, Rb and Sr, presumably occurring in readily soluble chlorides and minor sulphates, were leached in variable and moderate amounts (1-200 mg/kg). The leachable concentrations of Ba were substantially lower due to precipitation as barium sulphate (Figure 3).

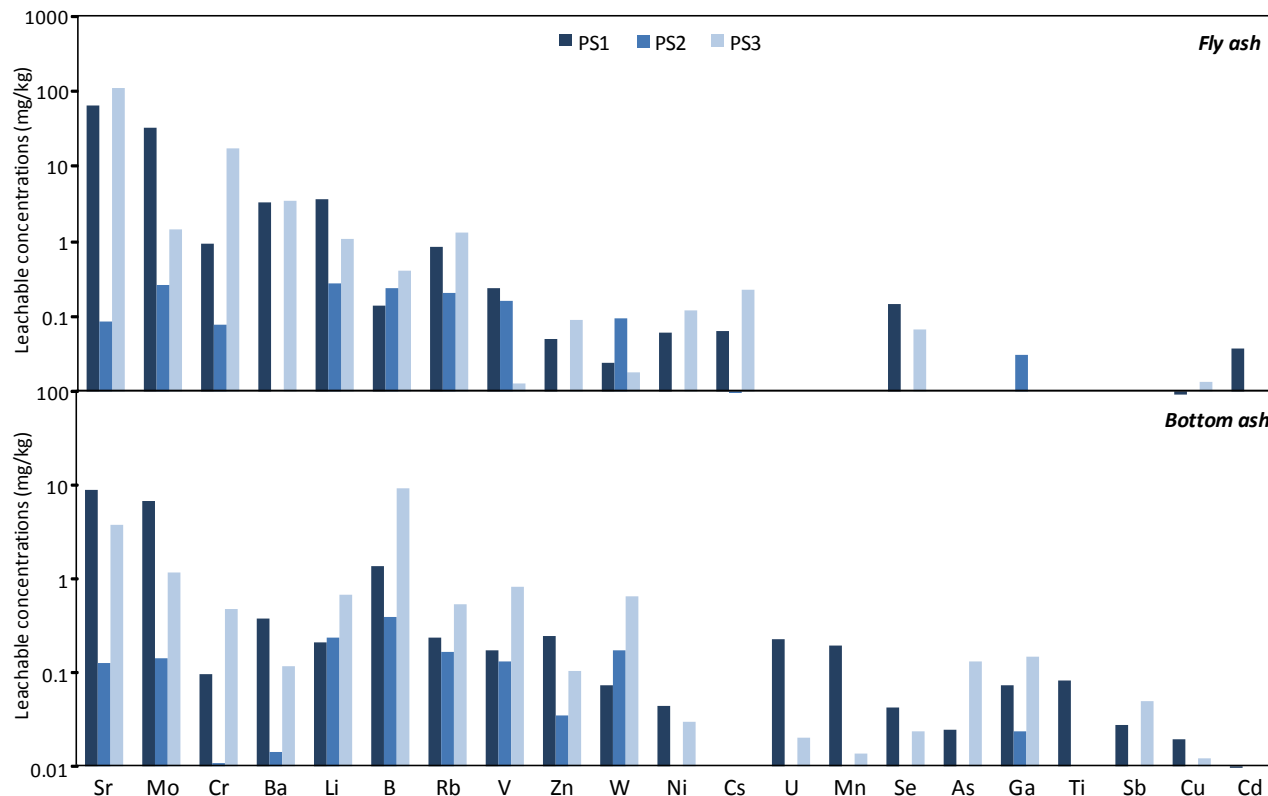


Figure 3. Leachable concentrations of trace elements according to EN 12457-4 leaching test. Values in leached mg per kg of dry bulk sample. Elements not depicted were leached below the detection limit.

A number of environmentally relevant elements, namely Be, Bi, Co, Cu, Ge, Hf, Mn, Nb, Pb, Rare Earth elements, Ta, Th, Ti, Tl, Sc, Sn, Y and Zr were leached in levels close or below the detection limit whatever the sample (Figure 3). Ni, Zn, Cs and U were leached in levels not exceeding 0.2 mg/kg. Most of the above listed elements display a strong aluminosilicate or iron oxide affinities in ash<sup>23</sup> that would account for their low solubility (<0.1% water extractable) in the mild leaching conditions applied. This is of particular relevance given the anomalous enrichment in Ni, Pb, Zn and other pollutants in Hellenic lignites at local or regional level. Their leachable concentrations in the ash remain at very low levels regardless of the metal loads in the lignite.

Oxyanionic-forming elements such as As, B, Cr, Mo, Se, Sb, V and W are known to be mobile under neutral-alkaline conditions. B, Cr, Mo, V and W can be organically bound in lignites, while As, Se and Sb are associated with the sulphide fraction in coal<sup>23</sup>. These affinities make them more prone to volatilise during combustion and condense on fly ash in sparingly soluble oxyanionic forms. Other factors need to be also taken into account to fully explain their leaching behaviour. Given the ubiquitous Ca in the studied

ashes, it is reasonable to assume that their solubility is primarily controlled by the precipitation/dissolution of Ca-metallates. Thus, the large availability of Ca in the leachates promoted the precipitation of hydrated Ca-arsenates and dropped the leachable As to <0.1 mg/kg (Figure 3). The formation of these poorly water soluble compounds is common in Ca-rich ash<sup>24</sup>. Arsenic is therefore unlikely to be an element of environmental concern in calcareous-natured fly ash, not only from Greece but worldwide. In the strongly alkaline systems of PS1 and more importantly PS3 ash, the high Ca contents in the leachate would also favour insoluble Ca-vanadates to precipitate thus removing V from leachates. This would explain why V is more soluble in the higher-aluminosilicate and lower-Ca PS2 ash (around 1%) than in the remaining samples (0.1%).

The leaching of Mo appears to be dependent on the total content in the ash and in the parent lignite. This accounts for very important releases from the Mo-rich ash in PS1. Being organically bound in the parent Hellenic lignites<sup>7</sup>, Mo is not assimilated in the aluminosilicate matrix or refractory minerals during combustion. The extraction yields (15-30%) were in good agreement with other studies conducted on coal and co-fired fly ash<sup>25</sup>, which strengthens Mo as one of the pollutants of real concern in alkaline combustion wastes. The above observations suggest a predictable behaviour that may be useful in determining potential Mo releases from ash on the basis of the contents in coal.

The leached levels of Se are of little environmental relevance in the studied samples (<0.1 mg/kg) but these represent extractable ratios of 1-2%. Selenate compounds have a high solubility compared to other metallates, particularly Ca-selenate dehydrate. Up to 7% extractable W was measured, being more mobile in bottom ash. Greater amounts were leached from the PS2 ash in line with higher W inputs in the xylite fired. Sb was leached to lesser degrees whatever the sample considered. The total and leachable amounts of Sb are too small to draw reliable trends.

Cr was poorly extracted and displayed diverse water extractable yields. Despite the fact that PS1 and PS3 were fed with high Cr lignite blends (Figure2) and their combustion by-products showed similar concentrations (Figure 1), the mobility drastically increased in PS3 fly ash (Figure 3). The different leaching behaviour could be attributed to differences in the depositional setting of peat and their position in relation to the source of metals. The mineralogy and metal assemblage in the lignite fired in PS1 suggests that Cr would reach the peat-forming environment in particulate form, occurring in refractory phases such as spinel-like minerals or Cr-rich illites (19). Cr<sup>3+</sup> would therefore remain in insoluble oxide form or assimilated by the glassy matrix of ash during combustion. By contrast, the geochemistry of PS3 lignite points to lacustrine depositional environments consistent with Cr inputs in aqueous form during flooding episodes. Cr<sup>3+</sup> could have been leached by surface/groundwaters draining Cr-Ni-rich weathered ultramafic bodies and subsequently deposited in the peat-forming area, forming authigenic minerals or associated with macerals, as reported for Ni<sup>2+</sup><sup>7,19</sup>. Such organic bounds would allow Cr volatilization during combustion, oxidation and

precipitation of slightly soluble chromates on fly ash particles, while refractory Cr<sup>3+</sup>-bearing species would concentrate in bottom ash.

## CONCLUSIONS

The high ash and high Ca contents in lignite offer optimal conditions for SO<sub>2</sub> and other gaseous pollutants to interact with ash particles. High free CaO/SO<sub>2</sub> ratios enhance the scavenging potential for sulphur. As, Se and Sb were also captured in calcareous ash during the naturally occurring desulphurisation.

Anomalous enrichments in trace elements fingerprint regional and local geological settings of the lignite basins. The regional enrichment in Cr, Ni, U, W and Zn in conjunction with local enrichments in Cd, Co, Cu, Mo, V, Pb are consistent with alkaline depositional paleoenvironments and the proximity of ultramafic bodies. This results in concentrations surpassing the average for lignite coal worldwide. For most trace elements, enhanced contents in lignite lead to higher contents in fly ash, but highly volatile elements prone to react with free lime did not follow this trend. Bottom ash revealed similar response.

A broad array of trace elements including Be, Bi, Co, Cs, Cu, Ge, Hf, Mn, Nb, Ni, Pb, Rare Earth elements, Ta, Th, Ti, Tl, Sc, Sn, Y, Zn and Zr were immobile under alkaline conditions. The main concern of alkaline natured ash in terms of leaching should be directed towards a number of oxyanionic-forming species, organically bound in the lignite. The organic affinity makes them more prone to volatilise during combustion and condense on fly ash in sparingly soluble oxyanionic forms.

The large amounts of Ca in leachates promoted the precipitation of solubility-limiting Ca-metallates with the consequent removal of As and V from leachates. Mo and W formed sparingly soluble compounds with leachable concentrations governed by the inputs via lignite. Cr revealed a dual leaching behaviour that could be related to the mode of occurrence in the parent lignite. The results bring into prominence the role of lignite features in the leaching of combustion by-products and, consequently, in the possible applications. The outcomes of this study could assist in addressing the impact of high ash or high calcium co-fuels on the leaching properties of by-products.

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