

Contribution of data analysis for the environmental study of post-closure coal ash landfill

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Abstract

To support future remedial decisions on a coal ash landfill a hydro-geochemical characterisation program assessing the metal leaching and acid rock drainage potential has been performed.

Several studies on the field and laboratory were carried out to characterise bedrock, soil, coal ashes and water in the landfill area.

The application of advanced data analysis tools allowed highlighting relationships between variables that contribute to the understanding of groundwater contamination, which is not possible to detect through the basic periodic monitoring procedures.

Keywords: Acid drainage, coal ash landfill, groundwater contamination, remediation solutions.

Introduction

During most of the 20th century, the burning of coal was the most important source of energy in Western Europe. The lack of environmental regulations allowed the disposal of the wastes from thermal power plants without any special precautions. The characteristics of ash landfills are very heterogeneous, since they depend on: a) the physical, chemical and mineralogical properties of the coal; b) burning conditions; c) disposal technologies; d) climate, geological and hydrogeological conditions of the region in which they are inserted (Dellantonio et al. 2008; Haynes 2009; Pen-Mouratov et al. 2014; Krgović et al. 2015; Voltaggio et al. 2015). Thus it is not possible a generalisation of the type of mitigation measures to be implemented. Nowadays, coal ash landfills constitute an environmental concern under current European legislation.

The present work deals with the evidence of groundwater contamination (acid drainage and high levels of sulfate, aluminium, manganese, zinc, iron and nickel) revealed by the periodic monitoring that has been carried out since the closure of a coal ash landfill in Portugal. Thus, an assessment plan was established to understand what measures should be taken to support future remedial decisions

for coal ash landfill. A geochemical characterisation program assessing the metal leaching and acid rock drainage potential was also performed.

Materials and Methods

Study area

The Coal ash landfill area is located in the north of Portugal. Since the middle of 20th century, the area was extensively used to deposited coal combustion products without effective environmental care system to protect soils and groundwater. The landfill (confidential location) occupies about seven ha area and was built on hillside slope upon a water line that drains away to the main river. After the closure of the thermoelectric power plant, the landfill was sealed. It has been the target of environmental monitoring since then with the installation of a piezometric control network, comprising 5 piezometers (Pz1, Pz2, Pz3, Pz4, and Pz5), 1 discharge point at the base of the landfill (FC) and 1 monitoring point in the receiving river from the landfill (RD) (fig. 1).

The geological characteristics of the area consist of a unit of schist and greywackes. In hydrogeological terms this unit is essentially a homogeneous and impervious unit, consti-





Figure 1 Location of the piezometers and core drills plotted in an aerial view of the study area.

tuting an anisotropic fractured medium that does not define a regional aquifer. The coal burned in the thermal power plant was anthracite of variable composition, nevertheless with a high content on ash and sulphur.

Fieldwork

To better characterise bedrock, soil, coal ash, and surface and groundwater in the landfill area, new field works were needed. Thus, the fieldwork involved a drilling campaign of four boreholes (S1, S2, S3 and S4) to core sampling and the construction of two new piezometers (Pz6 and Pz7) (fig. 1). Water sampling campaigns in all the piezometers available (seven), periodic measurements of piezometric heads and permeability in situ tests were also done. The water samples were then sent to an independent laboratory for analysis.

Laboratory work

A total of 15 solid samples were taken from the cores at different depths (PZ6S, PZ6B, PZ7S, PZ7I, PZ7B, S1S, S1I, S1B, S2S, S2I, S2B, S3S, S3B, S4S and S4B); plus four composite samples representing the drilled cores (S1c, S2c, S3c and S4c) were submitted to several characterization laboratory tests, namely: elemental chemical analysis, total organic carbon content (TOC), particle size distribution, scanning electron microscopy (SEM-EDS), respirometry, natural dynamic and percolation leaching as well as static and

kinetic acid generation potential tests. All the samples were oven dried at 105 ° C for 24 hours and after that partitioned with the aid of a Jones separator and stored in sealed containers for use in subsequent laboratory tests. Firstly, they were submitted to chemical analysis by X-ray fluorescence by dispersive energy, using INNOV-X-SYSTEM portable equipment, model α -4000S. Only the samples (S1S, S1I, S1B, S2S, S2I, S2B, S3S, S3B, S4S and S4B) from the drill cores reproduce the natural material as found in the landfill area were submitted to granulometric analysis by dry sieving. From the fractions passed on the 200 mesh screen, small samples were taken for analysis of fines on a Malvern Mastersizer 200 laser granulometer with Hydro 2000 G module.

Samples S1c, S2c, S3c and S4c were subjected to natural leaching tests according to NEN-EN 12457. The results of the short-time leach tests (24 and/or 48 h) in addition to allowing the identification of the fastest soluble components, complement the tests for the determination of acidic drainage (static and dynamic). In the dynamic leaching experiments performed, 100 g subsamples of the samples S1c, S2c, S3c and S4c were taken and were stirred for 24 h in distilled water, in a solid/liquid ratio of 1/10 (w/v). After 1, 3, 12 and 24 hours of agitation, the physicochemical parameters of the liquid phase (pH, conductivity, TDS and salinity) were measured. This procedure was also applied to subsamples from the samples PZ6B and PZ7B, and only continuous leaching was carried out without measurement of the initial parameters to produce leachate and to analyse its properties.

Static acid generation capacity (NAG) tests were performed for all solid samples, after milling until to have $\leq 75 \mu\text{m}$ in mean size. The Acid Generation (NAG) tests consist of oxidising 2.5 grams of sample. Due to the oxidation of the sulphides, sulfuric acid is formed assuming that all the acidity produced is due to this phenomenon and the neutralising particles reduce the acidity produced. After oxidation, a titration with NaOH is carried out to quantify the acidity produced in the form of kg of sulfuric acid per ton of sample (Stewart et al. 2006). In addition to NAG at pH 4.5 and 7.0, NAPP (Net Acid Producing Potential) was also determined for all samples. NAPP



allows quantification of the neutralization capacity of the samples, although the NAG tests considering the neutralization effects of the sample, do not allow its quantification. The graphical representation of both allows to classify the products tested in one of three categories: NAF - Non Acid Forming for the case of a negative NAPP and a pH above 4.5 in the final NAG; PAF - Potential Acid Forming reveal acid generation in both tests - NAG pH below 4.5 and a NAPP positive; or UC - Uncertain to classify samples that the acid production is not clear). Typically, samples classified as UC require further analysis, and samples classified as PAF are likely to have a high sulfur concentration. Dynamic tests of acid generation potential in columns were also performed for the composite samples of the drilled cores (S1c, S2c, S3c and S4c). Dynamic tests are distinguished from static tests in that they attempt to simulate the natural oxidation reactions occurring in the field by using a larger amount of sample (ranging from 100 g to 2 kg) and the creation of several cycles of wetting and drying during the period of several days of the test to pattern the field meteorological conditions. The duration of these tests cannot be standardized due to the heterogeneity of the natural materials (mineralogical composition, porosity, permeability, etc.). The dynamic tests consisted of maintaining 100 grams of sample in an acrylic column, alternately submitting to 6 cycles of humidification and drying, for 12 days. In the humidification cycles, distilled water was percolated into the column, measuring the properties of the leachate at the end of the percolation. The drying cycles consisted of drying the solid material contained in the column immediately after a humidification cycle by injecting compressed air.

Data treatment and multivariate statistical methods

Exploratory data analysis and Principal Component Analysis (PCA) techniques were used to reveal the correlation structure of the variables allowing characterisation and interpretation of main processes affecting the study area.

Results

The field surveys made possible to identify three distinct layers in the landfill area: ash

landfill, yellow schist and grey schist (fig. 2). The layer corresponding to the ash landfill is naturally thicker at the sites of Pz3, Pz4 and Pz7 because they are within the landfill area. The presence of ash in the Pz2 and Pz5 surveys, which are outside the landfill area, may be due to the various terrain modelling that have been performed over time in that area. Pz1 and Pz6 piezometers are located outside the landfill's influence zone, and their monitoring was carried out to know the regional background values of waters, soils and rocks. The values obtained were compared with other published studies of the hydrogeochemical background of the region. The water table is varied (fig 2). The recharge waters percolate the entire thickness of the landfill until they reach equilibrium in the yellow altered schist layer which is more permeable than the grey schist stratum that is underneath.

Particle size analysis allowed classifying the coal ashes as silt-sandy material (fig. 3a). Although the obtained grain-size curves show a well-balanced distribution of the particle diameter, in the surface samples is possible to verify the predominance of coarser grain size whereas the deeper samples possess much finer particle diameters.

The elemental composition obtained by XRF of the samples representative of the core drills (S1c, S2c, S3c and S4c) and the rock substrate (PZ6B and PZ7B) revealed the predominance of sulfur and iron (indicators of sulfides in the mineral matrix), besides the common elements of rock matrices such as K, Ca and Ti, must be noted. The samples have an identical average chemical composition regardless its depth and location. However, the values of arsenic and lead, which are an exception to this standard, are higher in ashes than those on the rock substrate.

Coal ash composition depends on parent coal rock and coal combustions' method (Valentim et al. 2018). SEM analysis performed on two samples - one representing the rocky substrate and the other the coal ash - recognise diverse morphotypes constituents. Coal ash sample has an elevated concentration of neoformation minerals like aluminosilicate glass (spheres or irregular shapes), glassy silica spheres and Fe-Ti oxides. Coal, which has not undergone combustion, has an irregular and angular shape, just like the primary min-



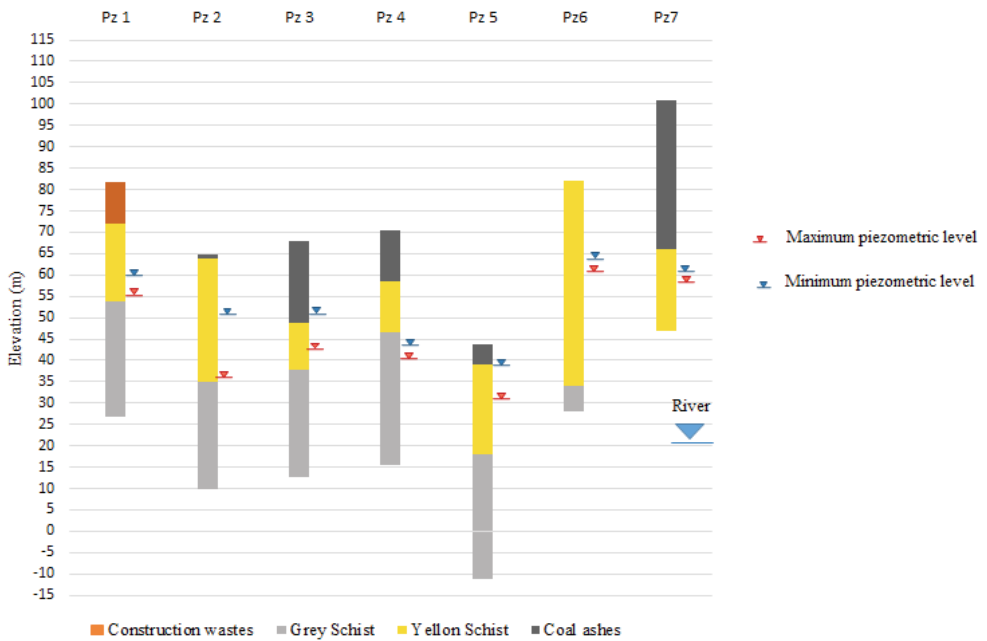


Figure 2 Distinct layers identified in log core and maximum and minimum piezometric levels recorded during monitoring (years 2012-2016) for the piezometers.

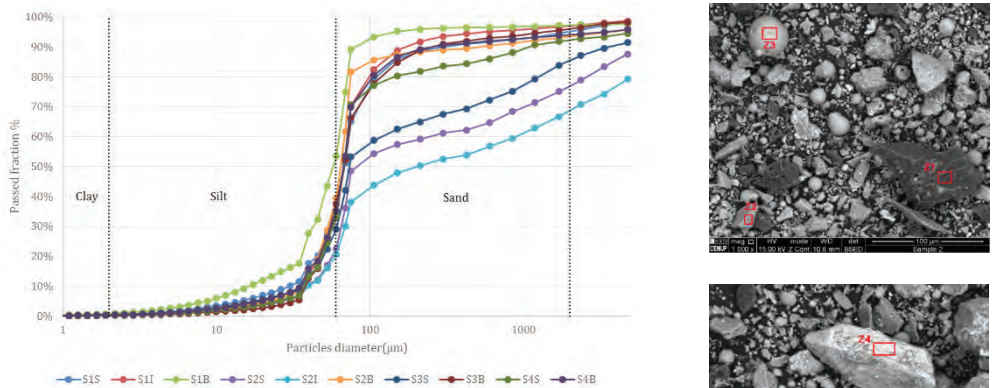


Figure 3a) Particle size distribution. b) Microphotographs of the coal ash samples. 1: Z1 - Unburned carbon; Z2 - particle consisting essentially of aluminium, silicon, oxygen and iron; Z3 - Vitreous sphere consisting essentially of silica; 2: Z4 - titanium oxide.

erals that have resisted combustion (fig. 3b).
 The results of the TOC analysis of solid samples revealed a high percentage of organic carbon in the ashes as opposed to their absence on schists (samples PZ6S, PZ6B and PZ7B). The static NAG tests to which the 19 solid samples were submitted showed results that point to moderately acidic materials. From the results of ANC and MPA (Maximum Potential Acidity, based on the sulfur

content of the samples), it was possible to calculate the NAPP (Neutralizing Acid Production Potential), whose comparison with the NAG allowed to classify the samples in the quadrant chart. All samples tested fell in the first quadrant of the graph that classified them as potentially acid forming (fig. 4).
 The multivariate statistical analysis applied monitoring water parameters are summarized in figure 5. The left plot (fig. 5a) shows



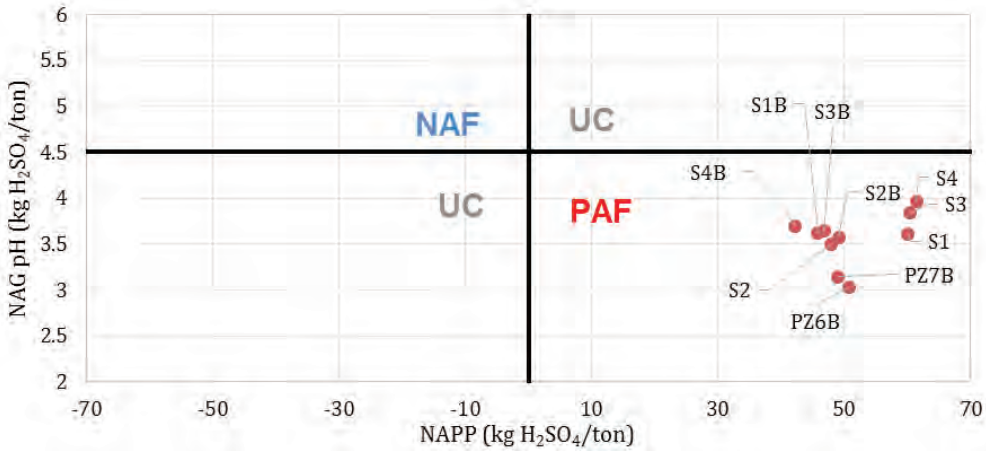


Figure 4 Results of NAG and NAPP tests allowed to classify both ashes and schists as potentially acid-forming materials.

the projection of variables on the first factorial plan. F1 represents 75% of the variation of the matrix data. This axis shows an opposition between electric conductivity (EC), SO_4^{2-} , Al, Fe, Mn, Zn, Cu and Ni (negative side) and pH (positive side). This negative correlation is typically observed between pH and concentrations of many metals and metalloids, base cations and sulfate in mine water (Banks 2004).

Figure 5b shows the projection of the water samples on the first factorial plane. It allows distinguishing different levels of contamination: groups A and B include the piezometers with higher contamination (Pz3 and Pz4); group C represent the variation of discharge point at the base of the landfill and group D contain the monitoring points where contamination is lower or does not exist. According to the interpretation of the 1st facto-

rial plan, the contaminated sites are on the negative side of F1.

PCA results for the variables determined on solid samples are present in figure 6. In respect to variables (fig. 6a) is noticeable the group form by acid forming elements (S, Fe and Cr). Figure 6b it is possible to distinguish bedrock (Pz6B and Pz7B) from ashes (S1, S3 and S4).

Conclusions

The chemical characteristics of groundwater are strongly influenced by the presence of the landfill and the pathway through it. The highest anomalous concentrations are found in discharge point at the base of the landfill (FC) and in the piezometers located inside the landfill (Pz3, Pz4 and Pz7). The analysis by SEM-EDS allowed distinguishing the min-

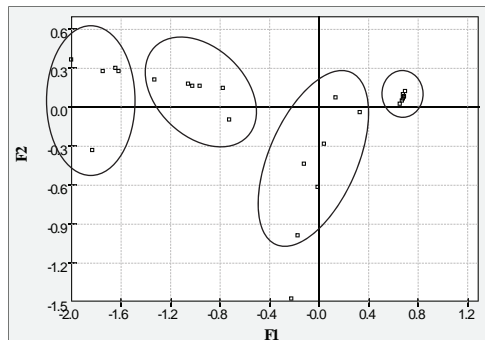
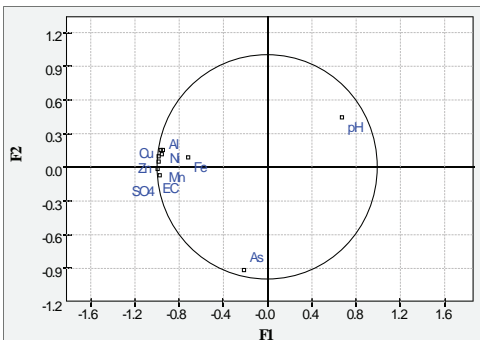


Figure 5a) Projection of variables on the 1st factorial plan; b) Distribution of different water samples on the 1st factorial plan



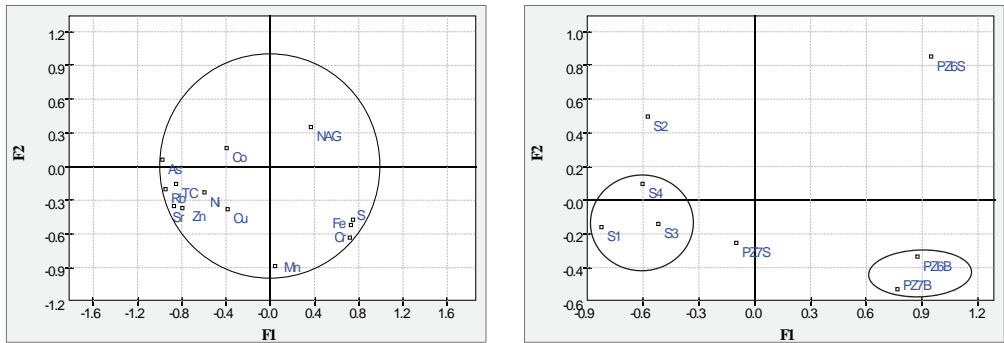


Figure 6a) Projection of variables on the 1st factorial plan; **b)** Distribution of different solid samples on the 1st factorial plan

erals of neof ormation from the primary minerals and the unburned coal. The analysis of the total carbon and the inorganic carbon in the solid samples showed a high concentration in the ashes that contrasts with the low concentrations of the rocky substrate. The tests of acid generation potential performed on 19 samples show moderately acidic materials. Multivariate statistical techniques are a good approach to the identification of hydro-geochemical variations in a dataset.

This technique allowed to delimit the contamination of the waters by acid drainage spatially and to associate the elements that are related to the same one.

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