



Petrographic, mineralogical and geochemical characterization of the Serrinha coal waste pile (Douro Coalfield, Portugal) and the potential environmental impacts on soil, sediments and surface waters

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ABSTRACT

Serrinha is the largest coal waste pile resulting from mining activities in the Douro Coalfield, Portugal. The exploitation of anthracite in tens of small mines caused some environmental impacts, as is the case of the coal waste piles that exist in old mines and adjacent areas.

The Serrinha waste pile is essentially made up of 2 million tonnes of shales and carbonaceous shales, deposited in a topographical depression over about 30 years.

Despite the environmental restoration accomplished in the Serrinha waste pile, some environmental problems seem to persist. In this study a petrographic, mineralogical and geochemical characterization was done in order to recognize and understand these problems. The materials studied were coal waste, sediments and waters from the drainage system and decanting basins, soils from the surrounding areas, leachates from waste material and neofomed minerals formed at the bottom of the waste pile. The main lithologies (carbonaceous shale and lithic arenite) and coal from the Douro Coalfield were also analyzed.

Petrographic analysis shows some evidence of weathering (on organic and inorganic matter) related to the time of exposure to the weathering agents and the easy access of air within the waste pile (due to both the poor compaction and the heterogeneity of the material). Mineralogically, the composition of coal waste material has contributions from both the coal and the associated lithologies.

R-type cluster analysis of the waste pile material allows two distinct clusters to be identified. In the first cluster a sulfide fraction is represented by the association of As, Cd, Cu, Pb, Ni and Zn, while Fe clustered with Al, Co, and Ti indicates that some of the Fe and the other elements are likely associated with silicate minerals such as clays. The second cluster, represented by Cr, V, Zr, Rb, REE, Mn, Li and Ba, probably represent a silicate fraction, perhaps detrital accessory minerals.

The waste pile material, leachates, soils, sediments, neofomed minerals and water analyses indicate the existence of potential environmental impacts due to the acid mine drainage and associated leaching of heavy metals and other elements.

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1. Introduction

Despite the important contribution to the economic and social development of many countries, coal mining and coal consumption have a significant impact on the natural environment. The major environmental impacts associated with coal mining include changes in land use, subsidence phenomena, increased generation of noise and waste around mining installations, soil erosion, water pollution, acid mine drainage, potential impacts on local biodiversity, and release of methane (Suárez-

Ruiz and Crelling, 2008 and references therein). An overview of the environmental impacts of coal mining and associated wastes was carried out by Younger (2004). A typology of the environmental impacts related to coal mining that recognizes five major categories of hazards was presented in that work: air pollution, fire hazards, ground deformation, water pollution and water resource depletion.

Petrographic and geochemical characterization of coal may provide insights into the potential leaching of hazardous substances (Finkleman and Gross, 1999). The petrographic characterization and organic geochemistry of coal are generally not yet, considered when discussing environmental problems. However, the petrographic composition of coal may be useful in forecasting the leaching of potentially harmful compounds. The understanding of geochemical

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processes is a key to understand how the impacts occur and to develop sustainable mitigation strategies (Younger, 2004). The properties and characteristics of coal depend on its organic and inorganic constituents. Among the coal quality parameters, trace elements in coal can have great environmental, economic, technological, and human health impacts (Swaine and Goodarzi, 1995; Finkleman and Gross, 1999).

This integrative work discusses the potential environmental impacts caused by a coal waste pile that resulted from Douro Coalfield exploitation in the Serrinha area inferred from a petrographic, mineralogical and geochemical examination. The objectives of this work are: a) petrographic characterization of the waste material; b) mineralogical and geochemical characterization of waste material, sediments and waters from the associated drainage system and decanting basins, and soils from surrounding areas, in comparison with main lithologies and coal compositions from the Douro Coalfield; c) geochemical characterization of leachates from the waste material; d) mineralogical characterization of neofomed minerals at the bottom of the waste pile, and e) determination of the mobilization processes of elements in the waste pile.

2. Study area: geological and environmental setting

Geologically, the Douro Coalfield is the largest outcrop of terrestrial Carboniferous (Upper Pennsylvanian [Lower Stephanian C]) coal-bearing deposits in Portugal (Lemos de Sousa and Wagner, 1983; Wagner and Lemos de Sousa, 1983; Eagar, 1983; Fernandes et al., 1987). Fig. 1 illustrates the geological and geographic setting of Douro Coalfield. Mining of anthracite A (ISO 11760, 2005) started in the Douro Coalfield in 1795 and continued until 1994. There were two main centres of exploitation, Pejão mining area and S. Pedro da Cova mining area, and tens of small mines all over the basin, scattered an area of approximately 9 km² (Custódio, 2004).

The mining activities in the Douro Coalfield had economic and technological impacts as well as a cultural significance, and contributed significantly to the economic and energy sectors of Portugal (Custódio, 2004). Between 1930 and 1990 anthracite from the Douro Coalfield was the most important national fuel used for electricity generation and the principal fuel supplied to the Tapada do Outeiro Power Plant (1959–2004).

Mining activity has caused some impacts on the environment in the Douro Coalfield area, mainly because it started in the end of 18th Century, when there was no great concern for the environment. The most significant environmental concern in the Douro Coalfield area is the large number of coal waste piles emplaced all over the old mines

and adjacent areas. There are more than twenty waste piles, composed of the overburden material and discards from the washing plant. Some of these waste piles present very serious problems, as is the case of the largest one, Serrinha. A further three waste piles, namely, S. Pedro da Cova, Lomba and Midões, are also of a great environmental concern because they are self-burning (Ribeiro et al., 2010; Sant’Ovaia et al., 2010).

The development of the Serrinha waste pile resulted from the accumulation of overburden material from the Germunde underground mine (Pejão mining area), which is located 2 km NW from the waste pile (Gama and Arrais, 1996).

When Germunde mine closed in 1994, the waste material occupied 4 ha and had a volume of 1.2 million m³. The deposition of material, continued for about 30 years, was carried out by simple discharge in a topographical depression. The waste pile is essentially made up of 2 million tonnes of shales and carbonaceous shales, heterogeneous, dark in color and with a variable particle sizes (Gama and Arrais, 1996).

An environmental restoration was carried out to address the environmental problems associated with the Serrinha waste pile, mainly the low stability of the slopes (Gama and Arrais, 1996). This recovery included: platform regularization, establishment of intermediate landings on slopes, application of calcareous gravel on slope surfaces, land covering with vegetation, installation of a collection/drainage system and decanting basins, and implementation of a forestation and landscaping plan. The platform at the top of the waste pile is currently used as a landing strip for model aircrafts.

Despite the recovery accomplished some environmental problems seem to persist in the Serrinha waste pile, specifically leaching and drainage problems (Ribeiro and Flores, 2008).

3. Sampling and analytical methodology

3.1. Sampling

A total of 17 samples (each with a mass of approximately 1 kg) were collected for petrographic, geochemical and mineralogical analysis: 9 from the waste pile material (WP4, WP8, WP13, WP14, WP15, WP16, WP18, WP20 and WP21), 5 representing sediments from the drainage system and decanting basins (SS17, SS19, SS22, SS24 and SS26) and 3 from soils of the surrounding area (SO25, SO28 and SO29). Representative samples of coal (DC-coal) and the main lithologies of the Douro Coalfield (DC-lithologies), such as lithic arenite (LA) and carbonaceous shale (CS) were also analyzed. These samples were obtained from the collection of the Department of

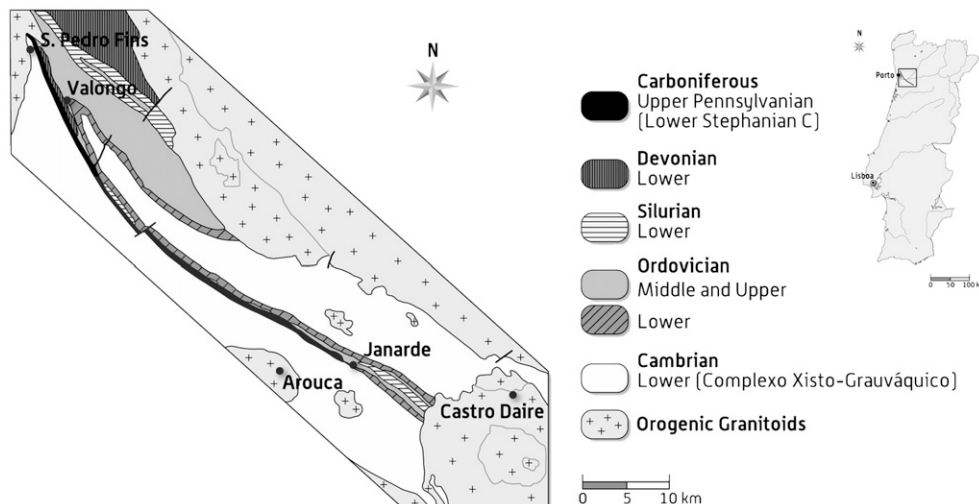


Fig. 1. Geological and geographic setting of the Douro Coalfield (modified from Pinto de Jesus, 2001).

Geology, University of Porto. Water samples from the two decanting basins (WS9, WS27 and WS30) were also collected, as well as 2 samples of neformed minerals from the base of the Serrinha waste pile (NM1 and NM2). Fig. 2 shows a plain view of the Serrinha waste pile and sampling locations.

3.2. Petrographic analysis

Whole-rock polished blocks were prepared from the samples of waste pile material according to standard procedures (ISO 7404-2, 1985). Petrographic characterization of organic and inorganic matter and measurements of random vitrinite reflectance were performed following standard procedures and ICCP recommendations (ISO 7404-5, 1994; ICCP, 1998, 2001). The observations and measurements were carried out using a Leitz Orthoplan microscope equipped with a Discus-Fossil system under standard conditions.

3.3. Mineralogical and SEM analysis

The waste pile material, coal and the main lithologies from the Douro Coalfield were analyzed by X-ray powder diffraction (XRD) techniques. The selected samples for mineralogical analysis were: 2 samples of the waste pile material (WP18 and WP20), 2 samples of the main lithologies of the Douro Coalfield (LA and CS samples) and 1 coal sample. Each of the powdered samples was analyzed using a Philips PW1830 X-ray diffractometer with Cu K α radiation and a scan range of 2–60° 2 θ . Quantitative analysis of the mineral phases in each

sample were obtained from the X-ray diffractograms using Siroquant™, commercial interpretation software (Taylor, 1991), based on the Rietveld XRD analysis technique.

The powdered coal sample was subjected to low-temperature oxygen-plasma ashing using an IPC 4-chamber asher, as outlined in Australian Standard 1038, Part 22 (Standards Australia, 2000) prior to XRD analysis, and the mass percentage of low-temperature ash (LTA) was also determined.

The selected soil and stream sediment samples were mineralogically characterized by XRD using Philips PW1130/90 and PW3040/60 equipment and Cu K α radiation. Scans were run between 2 and 60° 2 θ .

Samples of neformed minerals collected in the bottom of the Serrinha waste pile were analyzed by scanning electron microscopy with X-ray microanalysis (SEM-EDX) and XRD. The SEM-EDX analyses were conducted at the Materials Centre of the University of Oporto (CEMUP) using an FEI Quanta 400FEG environmental scanning electron microscope (ESEM), equipped with a Genesis X4M energy dispersive X-ray (EDAX) analyzer. The XRD analyses were obtained with a Mini Flex Rigaku Benchtop X-ray diffractometer equipped with CuK α radiation and with a scan range of 2–70° 2 θ .

3.4. Geochemical analysis

Proximate analysis was carried out on samples of the waste material in accordance with ISO standards (ISO 1171, 1997; ISO 589, 2008). Carbon content was determined by LECO analysis. Chemical analysis of major and trace elements, using inductively coupled

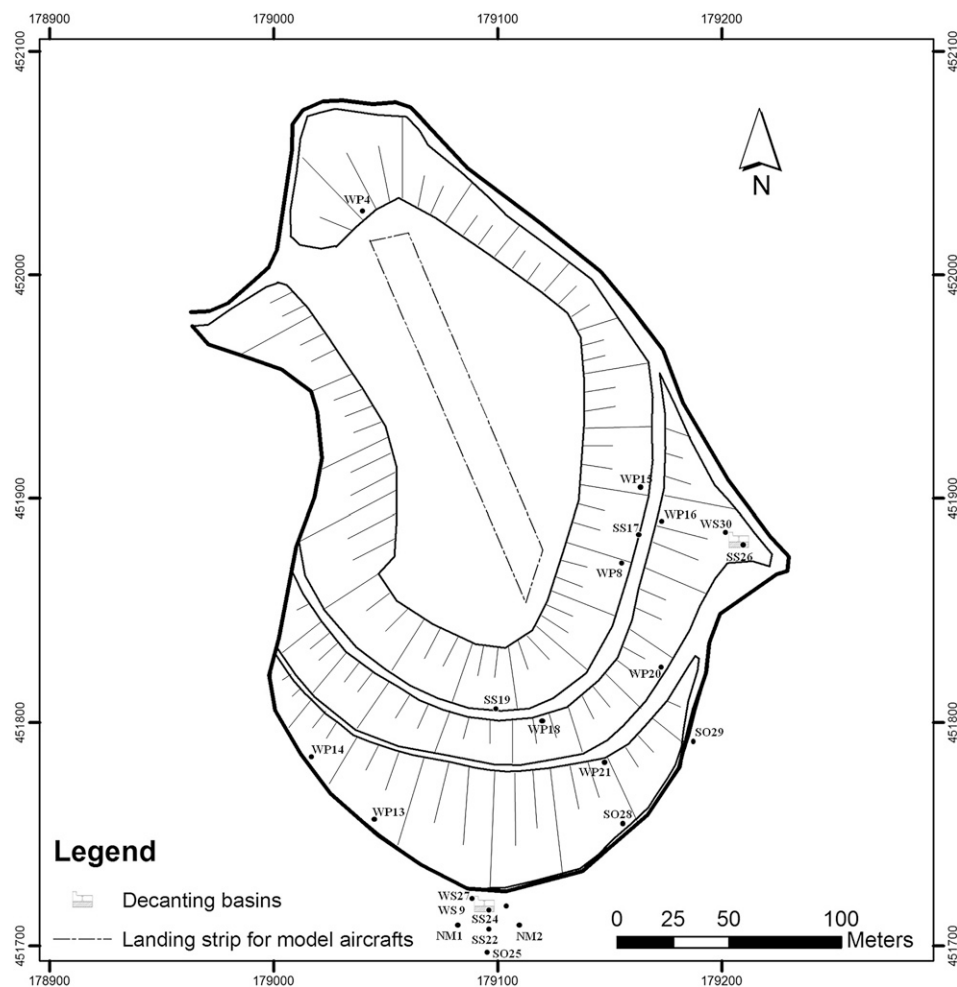


Fig. 2. Plain view of the Serrinha waste pile and sampling location. WP – Waste pile material; SS – Sediments from drainage system and decanting basins; SO – Soils of surrounding areas; WS – Water samples from decanting basins; NM – Neformed minerals.

plasma mass spectrometry (ICP-MS) techniques, was carried out on the waste pile materials, sediments from the drainage system and decanting basins, soils of the surrounding areas, and the coal and the main lithologies of the Douro Coalfield.

Leachates were obtained from 1.0 g samples of the waste pile materials rolled for two hours with 10 ml of distilled water (LWP4, LWP8, LWP13, LWP14, LWP15, LWP16, LWP18, LWP20 and LWP21); these were also analyzed by ICP-MS techniques. The chemical concentrations in the leachates were processed to obtain the percentages of each element leached from each sample tested. All ICP-MS analyses were performed by Acme Analytical Laboratories, Canada.

Some physicochemical parameters, specifically pH, Eh and electric conductivity, were also determined on samples of the waste material, as well as the sediment, soil and water samples, using HANNA HI255 multiparameter equipment in accordance with ISO 10390 (2005). pH and electric conductivity were also measured in waste material leachates.

4. Results and discussion

4.1. Petrographic, mineralogical and geochemical characterization of Serrinha coal waste pile, coal and lithologies from Douro Coalfield

4.1.1. Petrographic characterization

Petrographic and geochemical data from the Douro Coalfield have already been published by Lemos de Sousa (1973, 1978), Marques et al. (2009) and Ribeiro et al. (2010), and some of this information was used for comparison with data from the Serrinha waste pile (Table 1).

Petrographic analysis of coal waste pile material shows that the organic fraction of the samples is represented mainly by macerals of the vitrinite group, although the presence of inertinite is also significant. Fig. 3 shows some petrographic aspects of the samples studied. The vitrinite group macerals are represented by detrovitrinite (Fig. 3F) and, in smaller quantities, gelinite and collotelinite. Macerals of the inertinite group appear mostly in the form of inertodetrinite, but semifusinite and fusinite (Fig. 3B and C) are also present. The organic matter shows optical anisotropy (Fig. 3C) and some particles appear with cracks (Fig. 3D) even completely cracked (Fig. 3A). Mineral matter comprises lithic fragments showing organic layering (Fig. 3E), clay minerals, quartz, iron oxides, oxidized framboidal pyrite and, rarely, non-oxidized pyrite.

Mean random vitrinite reflectance ranges between 4.8% and 5.6%. The results obtained from the present study are consistent with data from Lemos de Sousa (1973, 1978), Marques et al. (2009) and Ribeiro et al. (2010), and the slight variations may due to the weathering processes.

Other evidences of weathering were identified, specifically organic particles with cracks and the presence of iron oxides and oxidized framboidal pyrite. These characteristics are related to the time of exposure to the weathering agents and the easy access of air within the waste pile, due to both the poor compaction and the material heterogeneity.

4.1.2. Mineralogical characterization

The mineralogical composition of the Serrinha waste pile material as well as the coal (DC-coal) and the main lithologies from the Douro Coalfield (DC-lithologies) are presented in Table 2. The major mineral

phases found in samples of Serrinha waste material are quartz and clay minerals. Illite is clearly the most abundant mineral in these samples, followed by quartz, muscovite, chlorite and pyrophyllite. Traces of other minerals such as rutile, anatase and jarosite, were also identified. In the LTA of the coal sample the main mineral phases identified were illite as the most abundant, muscovite, quartz, kaolinite, siderite and, in lesser quantities, anatase, pyrite and jarosite. The mineralogical composition of the lithic arenite from the Douro Coalfield includes muscovite, quartz, chlorite and rutile, while the carbonaceous shale mainly comprises quartz, muscovite, illite, kaolinite, pyrophyllite and traces of rutile and anatase. It thus appears that the composition of coal waste material has contributions from both the coal and the surrounding lithologies. Quartz and muscovite are present in all samples, whereas siderite and pyrite are present only in the coal. Kaolinite is present only in the coal and carbonaceous shale. The illite found in the waste material appears to be derived mainly from the coal, chlorite from the lithic arenite, and pyrophyllite from the carbonaceous shale.

4.1.3. Geochemical characterization

The results of proximate analysis are presented in Table 3. The waste pile material has a high ash yield, ranging from 75.0 to 86.6 wt.% (air dry basis) as they represent overburden material. The carbon content ranges from 8.3 to 19.5 wt.%.

Table 4 summarizes the concentration of major elements and trace elements obtained for the Serrinha waste pile material. For comparison, the geochemical compositions of the coal (DC-coal) and the main lithologies from the Douro Coalfield (DC-lithologies), average world coal compositions (Swaine, 1990) and background values for black shales (Palmer et al., 2004; Ketris and Yudovich, 2009) are also reported in Table 4.

The major elements in the waste pile samples are dominated by Al, Fe, and K, while the other remaining elements (Ca, Mg, Na, S and Ti) have concentrations of <1.0%. The values are similar to those obtained from the Douro Coalfield coal and main lithologies samples, with slight variations of some elements (Fe, S). Based on the mineralogical analysis, it is inferred that the Al, K, and Mg are predominantly associated with the clay minerals, while the iron content of the samples is primarily controlled by the abundance of S (i.e., pyrite) and the clay minerals.

The coal waste material is in fact a mixture of carbonaceous shales and lithic arenites with a variable amount of disseminated coal, promoting a dilution effect in elements concentration. Generally, the chemical composition of coal waste material seems to be between the chemical compositions of Douro Coalfield lithologies and coal, being much more close to the carbonaceous shales and lithic arenites.

When compared with the mean values of Douro Coalfield lithologies, the waste materials show significant enrichments in As, Cr, Cu, Mo, Rb and Sb. Slightly higher contents of Cs, Ga, Pb, Th, U and Y were also documented. On the other hand, the wastes show depletion in Ba, Co, Li, Mn, Ni, Sr, and Zn, and a slight depletion in Hf, Sc, Sn, W and Zr. It is important to note that the mean concentration values for all the elements in waste samples (except for Hf, Sb and Zr) are lower than the mean values for coals from the Douro Coalfield.

The chemical composition of the waste pile samples is different in some ways to the geochemical background data for black shales. The waste material shows an enrichment in Cs, Li, Rb, Sb and Th that is, probably, due to the contribution of granitic rocks to the sediments

Table 1
Mean random vitrinite reflectance data.

Sample	WP4	WP8	WP13	WP14	WP15	WP16	WP18	WP20	WP21	Ribeiro et al. (2010)	Marques et al. (2009)	Lemos de Sousa (1973, 1978)
Rr (%)	5.49	4.81	5.02	5.06	4.93	4.96	5.41	5.58	4.95	3.76–5.00	4.68–6.25	4.10–5.30
SD	0.98	1.07	1.00	1.12	1.06	1.06	1.02	1.07	1.26	–	–	–

WP – waste pile sample; Rr – mean random vitrinite reflectance; SD – standard deviation.

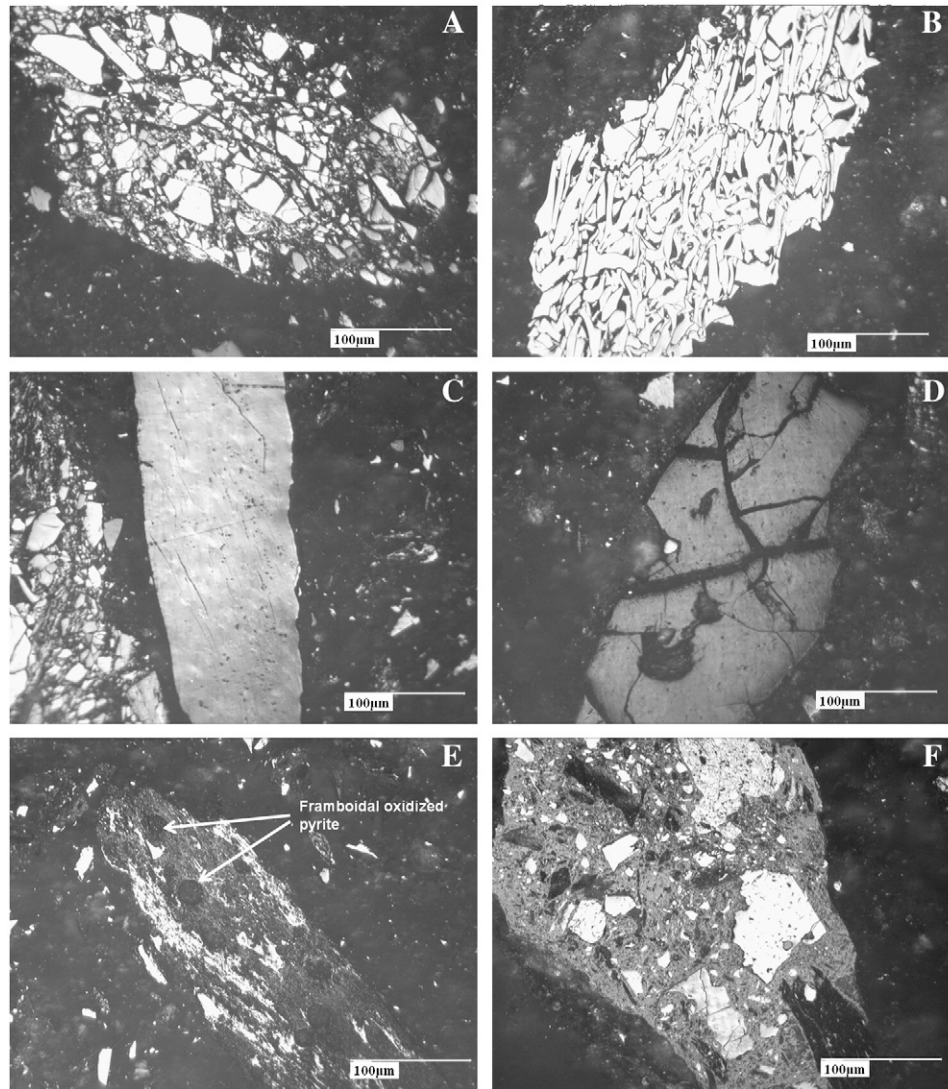


Fig. 3. Photomicrographs showing organic and mineral matter in Serrinha coal waste pile samples, taken in reflected white light. A – Weathered organic particle completely cracked. B – Fusinite. C – Semifusinite with anisotropy. D – Organic particle with cracks. E – Lithic fragment showing organic layering and framboidal oxidized pyrite. F – Mineral matter associated with detrital organic particles.

that produced the main lithologies of the Douro Coalfield (carbonaceous shale and lithic arenite).

The chemical compositions of samples of coal waste as well as coal from Douro Coalfield have higher contents of almost all trace elements than the world coal composition (Swaine, 1990). Elements in coal may be associated with either the organic components or with mineral matter (silicates, sulfides, oxides, carbonates, phosphates, sulfates, etc.), (Swaine, 1990; Finkleman and Gross, 1999; Suárez-Ruiz and Crelling, 2008 and references therein).

A total of 16 trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Rb, Sr, U, V, Zn and Zr), as well as Fe, Ti and Al and rare earth elements (REE), were selected and evaluated. Cluster analysis was used for classification of the 9 samples and the selected major and trace elements, in order to highlight groups of variables with similar characteristics and provide information for their organic or inorganic affinities. In cluster analysis, basic measurement of similarities and the criteria for combining variables into clusters should be considered. In this work, the best dendrograms were obtained using the Euclidean distance and the Ward method (Lu et al., 1995). The results are illustrated in the dendrograms from Hierarchical Cluster Analysis (Fig. 4).

According to the results of the R-type cluster analysis (Fig. 4), two distinct clusters can be identified. The variables Al, Fe, Be, Co, U, Ti, Cd,

As, Zn, Sr, Cu, Pb and Ni were clustered into one group (Cluster 1). In this cluster a sulfide fraction is represented by the association of As, Cd, Cu, Pb, Ni and Zn (Lu et al., 1995), while Fe clustered with Al, Co, and Ti indicates that some of the Fe and these other elements are likely associated with silicate minerals such as clays. Iron is positively correlated with Co ($r=0.62$, $p<0.05$), Zn ($r=0.59$, $p<0.05$) and S ($r=0.45$, $p<0.05$) indicating that it is also associated with sulphides (pyrite). Despite Be having a strong tendency to form organometallic complexes (associated with organic substances in coal – see Lu et al., 1995; Finkleman and Gross, 1999; Kortenski and Satirov, 2002), in some coal samples an intermediate affinity with aluminium silicates (clays) could be established (Zhuang et al., 2000; Eskenazy and Valceva, 2003), which explains the association of Be with Al, Co, Fe and Ti.

The second cluster, represented by Cr, V, Zr, Rb, REE, Mn, Li and Ba, probably represents a silicate fraction, perhaps detrital accessory minerals. These results are similar to those obtained to the Lomba, Midões and S. Pedro da Cova waste piles (Ribeiro et al., 2010).

Finkleman (1995) discusses 25 environmentally sensitive elements in coal, including Ag, As, B, Ba, Be, Cd, Cl, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Tl, Th, U, V and Zn. From these elements As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb, Se and radionuclides (e.g., U) are

Table 2
Mineralogical composition of Serrinha waste pile material, coal and main lithologies of Douro Coalfield, soil and stream sediment samples (values in wt.%).

Sample	Waste pile material		DC-coal	DC-lithologies		SO29	SS26
	WP18	WP20	Coal	LA	CS		
Anatase	1.0	0.3	0.4	–	0.6	1.5	–
Anhydrite	–	–	–	–	–	2.0	5.0
Arsenopyrite	–	–	–	–	–	1.5	3.5
Brokite	–	–	–	–	–	–	3.0
Calcite	–	–	–	–	–	–	2.0
Chlorite (Fe-rich)	8.4	7.6	–	17.3	–	–	–
Goethite	–	–	–	–	–	–	1.5
Graphite	–	–	–	–	–	3.0	2.0
Gypsum	–	–	–	–	–	–	1.0
Illite	47.2	44.3	67.8	–	39.0	–	–
Ilmenite	–	–	–	–	–	1.0	3.0
Jarosite	1.8	–	1.9	–	–	–	–
Kaolinite	–	–	5.7	–	6.1	1.5	6.0
K Feldspar	–	–	–	–	–	11.5	7.0
Lepidocrocite	–	–	–	–	–	–	Tr
Muscovite	12.0	10.0	11.1	56.7	13.0	5.0	14.0
Opal-CT	–	–	–	–	–	2.0	–
Pyrolusite	–	–	–	–	–	Tr	1.5
Plagioclase	–	–	–	–	–	4.0	3.0
Pyrite	–	–	0.8	–	–	1.0	1.5
Pyrophyllite	8.1	9.3	–	–	11.5	–	–
Quartz	20.8	27.7	6.8	24.5	29.0	55.0	43.0
Rutile	0.7	0.8	–	1.4	0.8	1.0	1.0
Siderite	–	–	5.6	–	–	1.5	2.0
Thenardite	–	–	–	–	–	5.0	–

WP – waste pile sample; DC-coal – coal from Douro Coalfield; DC-lithologies – lithologies from Douro Coalfield; LA – lithic arenite; CS – carbonaceous shale; SO – soil sample; SS – stream sediment sample; Tr – trace amount.

identified as potentially Hazardous Air Pollutants (HAPs) by the U.S. Clean Air Act Amendments U.S. Environmental Protection Agency (US-EPA), 1990. Considering the obtained results, the environmentally sensitive elements in coal (Finkelman, 1995) and the list of potentially hazardous air pollutants identified by the U.S. Clean Air Act, some elements were analyzed in detail to point out their mode of occurrence.

Arsenic and Cd are defined as prime environmentally sensitive elements (Swaine and Goodarzi, 1995; Gurdal, 2008). I wide range of association modes of occurrence for As was suggested by Swaine and Goodarzi (1995). From these elements As in coal is generally thought to be associated with pyrite but it may also be organically associated. There is a positive correlation between As and Cd ($r=0.83$) and As and Zn ($r=0.71$).

The concentration of Cd is low in the studied waste pile samples however are higher than DC lithologies which may be related to the DC coal composition. Cadmium occurs mostly in sphalerite and pyrite (Swaine, 1990; Finkelman, 1994, 1995). There is a positive correlation between Cd and As ($r=0.83$) and Cd and Zn ($r=0.91$), suggesting that Cd could be associated with the mineral matter in coal. However Cd could also be associated with clays and carbonates (Goodarzi, 2002), which explains the partition between the two groups of cluster 1.

The concentration of Cr in samples is high when compared to DC lithologies but lower than concentration in DC coal. Chromium appears

Table 3
Ash and carbon content of Serrinha coal waste pile samples (values in wt.%).

Sample	WP4	WP8	WP13	WP14	WP15	WP16	WP18	WP20	WP21
W	1.5	1.8	1.8	1.5	1.2	1.3	1.3	1.0	1.4
Ash ^a	75.0	76.2	81.5	81.5	83.3	80.9	79.7	84.8	86.6
C	19.5	18.2	14.4	14.3	11.2	13.8	15.0	10.3	8.3

WP – waste pile sample; W – moisture C – carbon.

^a Air dry basis.

to be mostly associated with the clay minerals in the organic fraction (Finkelman, 1995) which is corroborated by the cluster analysis.

Concentrations of Cu are high in the waste pile samples when compared to DC lithologies. Copper in coal is generally thought to be associated with chalcopyrite and pyrite (Swaine, 1990; Finkelman, 1995). Copper contents exhibit a strong correlation with Ni ($r=0.69$) and with Pb ($r=0.91$) indicating sulfide fraction (probably pyrite) affinity, similar to results obtained from the Lomba, Midoes and S. Pedro da Cova waste piles (Ribeiro et al., 2010).

Finkelman (1994) noted that Pb occurs predominantly as sulfides or associated with sulfide minerals, whereas Swaine (1990) suggests that an organic association may be possible, but mostly in lower rank coals (which is not the case here). Lead shows a positive correlation with Cu ($r=0.91$), Li ($r=0.87$), Sr ($r=0.84$) and Ni ($r=0.61$) for 95% of significance level. The strong correlation between Li and Sr probably indicates that this element might be associated with the presence of carbonaceous shales that could be enriched in this element.

Nickel is reported to be associated with both the organic and inorganic matter of coal (Finkelman, 1995) and also with sulfides (Querol et al., 1998; Spears and Zheng, 1999; Goodarzi, 2002). A positive correlation does exist in the waste pile samples between Ni and Zn ($r=0.82$), Ni and Cu ($r=0.69$) and Ni and Co ($r=0.50$), possibly indicating an inorganic origin.

Vanadium concentrations are similar to concentration in DC lithologies. This element may occur both in clays and the organic matter in coal (Finkelman, 1995; Querol et al., 1996; Goodarzi, 2002). A positive correlation between V and U ($r=0.83$), V and Ba ($r=0.82$), V and K ($r=0.76$) and V and Al content ($r=0.69$) was been observed, suggesting a silicate association also deduced in cluster analysis.

Uranium present higher concentrations when compared to DC lithologies. The association with organic fraction and silicates was discussed in (Finkelman, 1995). The cluster analysis and positive correlation with U and V already presented suggests a silicate association in these samples.

The zinc content of the waste pile material is lower when compared to the DC lithologies. Zinc is mostly associated with sphalerite and pyrite sulfides (Finkelman, 1995). A positive correlation between Zn and As ($r=0.71$), Zn and Cd (0.91), Zn and Ni (0.82) indicates that Zn is thought to be associated with sulfides.

The Σ REE, LREE and HREE concentrations are shown in Table 4. The Σ REE range from 117.5 to 147.1 mg kg⁻¹ and no significant variations of the LREE/HREE ratio (10.6 to 12.5) characterize the coal waste pile samples. The RRE are much higher in coals from Douro Coalfield than in waste material and in main lithologies (lithic arenites and carbonaceous shales).

The normalization of REE concentrations to NASC can act as an indicator of REE enrichment. Fig. 5a illustrates that the NASC-normalized REE patterns for the coal waste pile samples indicate a strong depletion of HREE. This depletion could be related with the higher mobility of HREE under weathering conditions (Eskenezay, 1987), which is occurring in Serrinha waste pile. The negative Ce anomaly is relatively common in oxidized samples, suggesting oxidation of Ce(III) to the Ce(IV) state under the prevailing oxidizing conditions.

Low values of pH were observed in the waste pile materials (pH ranging from 3.4 to 4.5), while Eh values were more homogeneous (152.3 mV and 211.7 mV). The electric conductivity values range between 86.9 μ S/cm and 327.0 μ S/cm.

4.2. Potential environmental impacts of wastes on soil, sediments and surface waters

4.2.1. Leachates from the coal waste material

In order to evaluate the impacts of the coal waste pile, samples were tested by leaching with water in order to estimate the amount of elements that could be mobilized. Table 5 presents the major and trace elements concentration of the leachates of the tested samples.

Table 4
Inorganic geochemistry of major (%) and trace elements (mg kg^{-1}), pH, Eh (mV) and electric conductivity ($\mu\text{S/cm}$) from Serrinha waste pile material, Douro Coalfield lithologies and coal and data from background of black shales and world coal compositions.

Sample	Waste pile material ($n=9$)										DCL ($n=3$)	DCC ($n=3$)	BSB	WCC
	WP4	WP8	WP13	WP14	WP15	WP16	WP18	WP20	WP21	Mean				
Al	9.4	8.4	8.8	8.4	10.8	9.8	9.8	8.7	9.3	9.3	9.2	11.7	n.a.	n.a.
Ca	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.3	n.a.	n.a.
Fe	3.1	4.9	3.0	3.5	3.0	3.2	3.1	3.1	3.4	3.4	2.7	4.5	n.a.	n.a.
K	2.6	2.2	2.4	2.2	2.8	2.5	2.5	2.2	2.7	2.4	2.5	2.6	n.a.	n.a.
Mg	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.5	0.5	n.a.	n.a.
Na	0.3	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.4	0.3	0.4	1.0	n.a.	n.a.
S	0.4	0.5	0.2	0.2	0.2	0.2	0.6	0.2	0.3	0.3	0.1	0.1	n.a.	n.a.
Ti	0.4	0.3	0.4	0.5	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.6	n.a.	n.a.
As	60	55	55	114	44	42	47	34	45	55.0	11	142	10–80	0.5–80
Ba	574	529	557	527	605	560	549	501	567	552	667	1187	270–800	20–1000
Be	4.0	4.0	4.0	3.0	4.0	3.0	3.0	3.0	4.0	3.6	3.3	12	1–3	0.1–15
Bi	0.8	0.6	0.6	0.8	0.6	0.6	0.6	0.4	0.6	0.6	0.2	1.8	0–4	0.1–1
Cd	0.2	0.4	0.3	0.5	0.3	0.2	0.2	0.2	0.3	0.3	0.1	1.1	2–12	0.1–3
Co	3.0	8.0	3.0	4.0	3.0	4.0	5.0	4.0	7.0	4.5	8.6	73.3	10–30	0.5–30
Cr	116	94	153	158	124	126	131	119	133	128	86	184	50–160	0.5–60
Cs	23	24	21	23	22	19	19	14	16	20.0	19	78.3	2–7	0.3–5
Cu	28	33	72	53	35	35	36	38	43	41.6	8.8	131	35–150	0.5–50
Ga	27	23	25	23	28	25	25	23	25	24.8	23	36.4	9–25	1–20
Hf	3.3	3.8	3.8	3.7	3.6	3.3	3.4	3.0	3.5	3.5	3.9	3.0	2.5–6.0	1–5
Li	68	135	242	275	85	82	72	99	103	129	155	497	15–50	1–80
Mn	59	156	68	97	75	91	83	89	145	95.9	233	313	200–800	5–300
Mo	2.3	2.0	2.6	3.2	2.1	2.3	2.4	2.0	2.5	2.4	0.7	25.8	6–60	0.1–10
Ni	17	28	31	34	19	23	24	22	32	25.5	39	483	40–140	0.5–50
Pb	38	38	62	49	34	32	32	34	38	39.5	37	88.6	10–40	2–80
Rb	164	127	126	117	165	148	147	123	140	140	121	164	40–120	2–50
Sb	9.1	5.3	10	13	7.1	9.1	9.8	21	27	12.4	5.3	8.8	2–11	0.5–2.5
Sc	13	14	14	14	14	13	12	13	13	13.3	14	20.8	7–20	1–10
Sn	5.2	3.9	4.6	3.9	5.4	4.8	4.6	4.3	5.0	4.6	5.0	10.2	2–10	1–10
Sr	62	69	87	84	63	64	55	72	76	70.2	103	568	100–300	15–500
Th	12	11	12	11	13	12	10	12	12	11.5	10	15.0	4–11	1–10
U	5.4	4.8	5.7	5.5	6.4	5.3	5.3	4.8	5.8	5.4	4.1	10.4	4–25	0.5–10
V	114	114	125	111	130	117	121	108	123	118	118	321	100–400	2–100
W	1.8	1.5	2.1	3.2	1.8	1.7	1.7	1.5	1.8	1.9	2.1	6.6	0–15	1–5
Y	9.5	9.9	11	8.8	9.9	9.0	7.8	9.1	9.8	9.4	7.0	23.5	15–40	2–50
Zn	26	85	48	116	33	40	38	55	71	56.9	65	215	60–300	5–300
Zr	114	126	128	124	130	111	112	103	123	119	133	103	60–190	5–200
Σ LREE	120.7	128.6	126.2	126.5	133.7	121.8	107.5	136.2	120.1	124.6	128.3	255.8	n.a.	n.a.
Σ HREE	11.2	11.5	11.9	10.9	12.3	10.7	10.0	10.9	11.7	11.2	9.3	28.8	n.a.	n.a.
REE	131.9	140.1	138.1	137.4	146.0	132.5	117.5	147.1	131.8	135.8	137.6	284.5	n.a.	n.a.
pH	n.a.	n.a.	3.7	3.9	3.5	3.4	3.4	4.5	3.7	3.7	n.a.	n.a.	n.a.	n.a.
Eh	n.a.	n.a.	192.2	184.8	205.1	211.7	209.2	152.3	195.0	192.9	n.a.	n.a.	n.a.	n.a.
Elec. Cond.	n.a.	n.a.	136.2	110.8	278.2	327.0	255.5	86.9	1410	372.1	n.a.	n.a.	n.a.	n.a.

WP – waste pile sample; DCL – Douro Coalfield lithologies; DCC – Douro Coalfield coal; BSB – background of black shales (Ketris and Yudovich, 2009); WCC – world coal compositions (Swaine, 1990); n.a. – data not available; Elec. Cond. – electric conductivity.

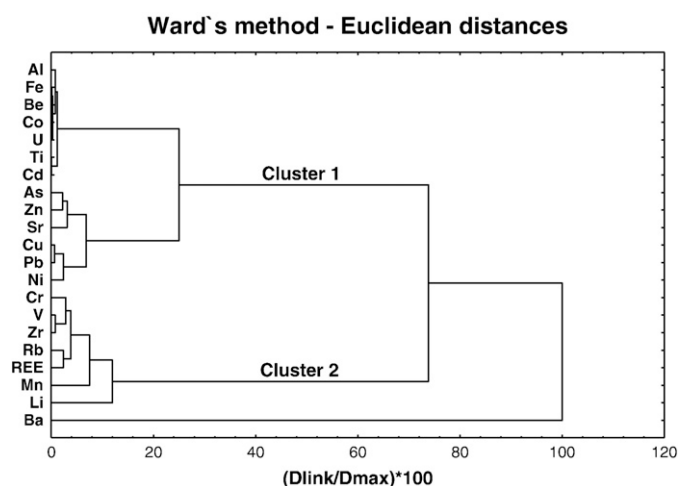


Fig. 4. Dendrogram showing hierarchical cluster analysis (A) R-type cluster analysis.

The detectable trace elements with the highest levels in the leachates included Cd, Co, Cu, Fe, Mn, Ni, and Zn in all the studied samples and Y in samples LWP8 and LWP21. Comparing the concentrations in the leachates with the total element concentrations it appears that the percentages extracted range between 1.1% and 16.6% for Cd, 3.4% and 35.9% for Co, 0.1% and 0.6% for Cu, 1.8% and 23% for Mn, 0.7% and 9.8% for Ni and 1.3% and 11.5% for Zn, indicating that these elements are partly associated with H_2O -soluble compounds. Metals associated with such phases are readily available and relatively mobile for biological uptake. Thus, a high environmental risk factor is associated with higher availability of these metals.

The Σ REE, LREE and HREE concentrations in the leachate samples are shown in Table 6. The Σ REE values range from 117.5 to 147.1 mg kg^{-1} and no significant variations occur in the LREE/HREE ratio (3.8 and 6.8, except for sample LWP4 which shows a highest ratio value 12.7). The NASC-normalized REE patterns for the leachates show typical characteristics of HREE-enriched NASC-normalized REE patterns (Fig. 5b), and could be related to the higher mobility of HREE under weathering conditions (Eskenezay, 1987).

The pH values of leachates vary from 3.7 to 4.6 and electric conductivity ranges between 48.0 $\mu\text{S/cm}$ and 465.0 $\mu\text{S/cm}$.

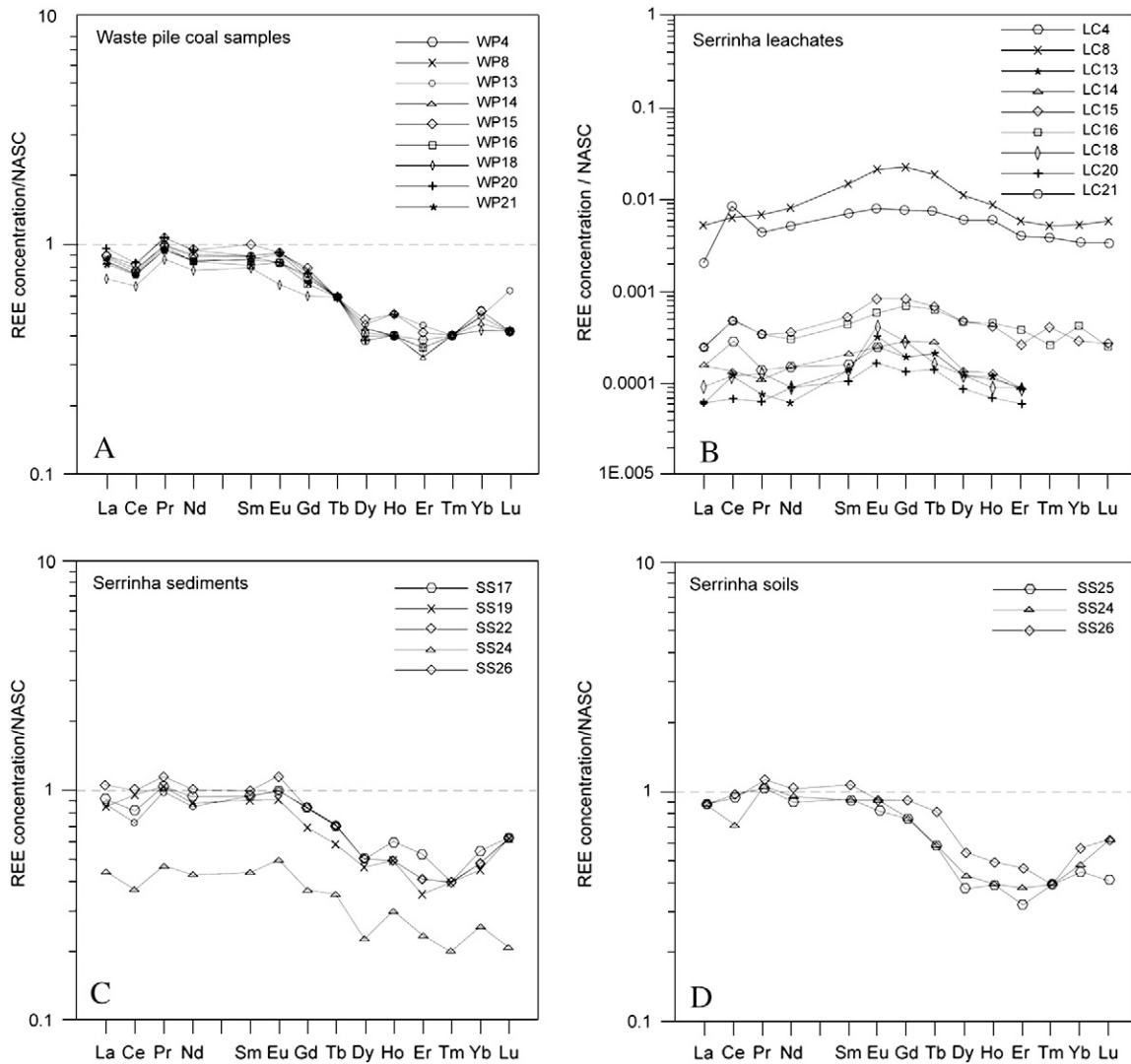


Fig. 5. The NASC normalized distributions of REE of the Serrinha coal waste pile samples (a), leachates (b), soil samples (c) and sediment samples (d).

4.2.2. Neoformed minerals

SEM-EDX and XRD techniques were used to identify the neoformed minerals collected in the bottom of the Serrinha waste pile, dispersed around a decanting basin that exists there. Two samples were collected, analysis of which revealed that the only neoformed mineral in the material is pickeringite. SEM images and EDX spectra of pickeringite are presented in Fig. 6 and X-ray diffractogram in Fig. 7.

According to Gaines et al. (1997), the chemical composition of pickeringite is $MgAl_2(SO_4)_4 \cdot 22H_2O$ (halotrichite group); the mineral occurs as a common secondary mineral formed by the alteration of pyrite in aluminous rocks or in coal seams, in the oxidized zone of pyritic hydrothermal mineral deposits, typically in arid and post-mining regions. The oxidation of pyrite, present in some of the rocks and coals from the Douro Coalfield, could supply the necessary sulfate, and sulfuric acid, which reacts with silicate minerals and releases aluminum. The formation of pickeringite is often related to acid mine drainage. Cody and Biggs (1973) suggest that surface evaporation of groundwater concentrates causes the precipitation of the sulfates.

In the case of the Serrinha waste pile, the surface evaporation of leachates from the waste pile and the drainage system cause the precipitation of pickeringite. The presence of considerable aluminum in these evaporites may be an indicator of the low pH in the pore waters. Because Al^{3+} must have been in solution to form pickeringite,

the pH of the solution has to be below 4.5 (Dacal, 1975). Oxidation of sulfides in the coal waste pile materials is generating sulfuric acid, which aggressively attacks the aluminosilicates in the rock. The weathering process introduces considerable aluminum, iron, magnesium, and potassium into solution. As the pore water in the weathering residue evaporates, these ions precipitate out as jarosite and pickeringite (Parnell, 1983).

4.2.3. Sediments from drainage system and decanting basins and soils from surrounding areas

The XRD results from the soil and sediment samples show that the major mineralogical phases identified were quartz, feldspar, mica, plagioclase and kaolinite. In addition samples also contained potentially heavy metal-bearing minerals such as lepidocrocite, arsenopyrite, pyrite jarosite, goethite and siderite, as indicated in Table 2.

The major and trace elements analyzed in soil from surrounding areas and sediment samples from the drainage system and decanting basins are shown in Table 6. The results indicate that the sediment and soil samples have a strong influence from the composition of the waste materials and consequently the local geological environment.

The sediment and soil samples are characterized by dominance of Al followed by Fe and K. Among the trace elements As, Cu, Pb, Sb, and Zn showed much higher concentrations in the sediment samples than

Table 5
Inorganic geochemistry of major and trace elements, pH and electric conductivity from leachates of the waste pile material.

Sample		LWP4	LWP8	LWP13	LWP14	LWP15	LWP16	LWP18	LWP20	LWP21
Al	mg kg ⁻¹	15	226	9	8	22	211	9	8	58
Ca	mg kg ⁻¹	68	176	30	23	59	129	229	38	794
K	mg kg ⁻¹	108	36	29	34	60	69	51	75	56
Mg	mg kg ⁻¹	22	588	26	16	37	37	27	24	353
Na	mg kg ⁻¹	42	32	19	17	25	23	18	30	24
S	mg kg ⁻¹	282	1496	141	105	260	317	289	177	1328
Cl	mg kg ⁻¹	25	26	27	26	31	33	26	39	27
As	µg kg ⁻¹	16	22	10	58	12	11	7	12	14
Ba	µg kg ⁻¹	170	100	100	40	120	130	60	80	110
Be	µg kg ⁻¹	18	127	29	34	31	29	9	8	60
Cd	µg kg ⁻¹	2	60	4	9	5	6	4	3	39
Co	µg kg ⁻¹	86	2942	83	118	129	203	99	111	1164
Cs	µg kg ⁻¹	41	29	18	19	37	28	19	18	24
Cu	µg kg ⁻¹	151	323	111	206	189	144	70	52	260
Fe	µg kg ⁻¹	6000	16000	7100	14400	9500	10200	4700	5500	10200
Mn	µg kg ⁻¹	1110	95350	1590	3880	4560	5530	3040	3070	33310
Mo	µg kg ⁻¹	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ni	µg kg ⁻¹	255	7006	294	253	393	498	304	304	3114
Pb	µg kg ⁻¹	4	<3	9	<3	4	7	5	<3	<3
Sb	µg kg ⁻¹	2	2	2	2	1	2	1	6	9
Sn	µg kg ⁻¹	<1	<1	<1	<1	<1	<1	<1	<1	<1
Th	µg kg ⁻¹	<2	<2	<2	<2	<2	<2	<2	<2	<2
U	µg kg ⁻¹	1	39	1	2	4	3	1	1	11
V	mg kg ⁻¹	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Y	µg kg ⁻¹	3	214	3	4	12	14	3	3	154
Zn	µg kg ⁻¹	520	9780	1220	1590	1620	2040	1340	950	5730
Σ LREE	µg kg ⁻¹	33.0	1039.1	14.4	22.1	62.7	58.2	16.8	11.1	861.6
Σ HREE	µg kg ⁻¹	2.6	273.3	2.7	3.4	11.3	10.8	3.2	1.79	135.4
REE	µg kg ⁻¹	35.6	1312.4	17.1	25.5	74.0	69.0	20.0	12.9	997.0
pH		3.9	3.7	4.1	4.1	3.8	4.1	4.5	4.6	4.2
Elec. Cond.	µS/cm	126.0	465.0	53.0	48.0	108.0	65.0	130.0	62.0	393.0

LWP – leachates of waste pile samples; Elec. Cond. – electric conductivity.

the soil samples. On contrary Ba, Mn, Zr and REE present higher concentrations on soil samples. The REE concentrations and the NASC-normalized REE patterns are similar to those obtained from the coal waste samples, indicating a strong depletion of HREE, due with the higher mobility of HREE under weathering conditions (Eskenezay, 1987).

The pH was in the acidic range in all the sediment (3.3–5.4) and soil (4.6–5.1) samples. These results show that the acidic pH of the sediments and soils in the vicinity of the coal waste piles is caused by oxidation of metal sulphides.

The values of Eh present some homogeneity and range as follows: in sediments between 98.4 mV and 214.3 mV and in soils between 118.0 mV and 146.3 mV. At these low pH values, the solubility of Al, and Fe is high. Many heavy metals become more water soluble under acid conditions and can move downward with water through the soil, and in some cases move to surface streams.

Following the Ontario aquatic sediment quality guidelines (Persaud et al., 1993), some samples exceed the 'severe effect' level for Cu and Cr, and thus are deemed 'grossly polluted'. Most sediment and soil samples also exceed the lowest effect level for As (6 mg kg⁻¹), Cu (16 mg kg⁻¹), Cr (26 mg kg⁻¹), Ni (16 mg kg⁻¹) and Pb (3 mg kg⁻¹) and so are 'marginally-significantly polluted' by these metals.

4.2.4. Water from decanting basins

Analysis of the water samples indicates that the pH and Eh vary significantly, probably due to the locations of the decanting basins where the samples were collected. Samples WS9 and WS27 were collected in a decanting basin that exists in the bottom of the waste pile and sample WS30 was collected in a decanting basin that exists in an intermediate platform of the waste pile. The water accumulated in the bottom of the waste pile (sample WS9 and WS27) has the lowest values of pH (2.6–3.0) and the highest values of electric conductivity (9.3 mS/cm and 12.5 mS/cm) and Eh (235.9 mV and 241.8 mV). On the other hand, sample WS30 has a pH value of 5.9, Eh of 70.2 mV and

electric conductivity of 0.2 mS/cm. These waters result from the accumulation of leaching solutions, and the pH, Eh and electric conductivity values could explain some of the geochemical processes that are occurring in the waste pile. The low pH value, specifically in the bottom of the waste pile, indicates that acid mine drainage is taking place.

5. Conclusions

A petrographic, mineralogical and geochemical study was carried out on the Serrinha coal waste pile in order to identify and understand some of these environmental problems. The materials studied were: coal waste, sediments and waters from decanting basins of the drainage system, soils from the surrounding areas, leachates from the waste material and neofomed minerals formed in the bottom of the waste pile. Samples of the two main lithologies (carbonaceous shale and lithic arenite) and coal from the Douro Coalfield were also investigated.

The results indicate the occurrence of acid mine drainage. The oxidation of sulfides present in the coal wastes exposed to atmospheric O₂ generates acidic waters during leaching of meteoric waters. The low pH may promote further dissolution and leaching of elements.

Petrographic analysis shows some evidence of exposure to weathering agents and the easy access of air within the waste pile, due to either the poor compaction or the heterogeneity of the material. Mineralogically, the composition of the coal waste material has contributions from both the coal and the associated lithologies.

R-type cluster analysis of the waste pile material shows that two distinct clusters can be identified. In the first cluster a sulfide fraction is represented by the association of As, Cd, Cu, Pb, Ni and Zn, while Fe clustered with Al, Co, and Ti indicates that some of the Fe and these other elements are likely to be associated with silicate minerals such as clays. The second cluster, represented by Cr, V, Zr, Rb, REE, Mn, Li

Table 6

Inorganic geochemistry of major (%) and trace elements (mg kg⁻¹), pH, Eh (mV) and electric conductivity (μS/cm) of sediments from drainage system and the decanting basins and soils of surrounding areas.

Sample	Sediments						Soils			
	SS17	SS19	SS22	SS24	SS26	Mean	SO25	SO28	SO29	Mean
Al	12	9.1	8.9	5.2	9.8	8.9	8.7	8.1	8.0	8.3
Ca	0.0	0.0	0.1	0.1	0.2	0.1	0.0	0.0	0.1	0.0
Fe	3.8	4.2	2.8	5.4	3.0	3.8	3.6	3.4	3.7	3.6
K	2.9	2.7	2.6	2.3	2.3	2.6	2.8	2.6	2.6	2.7
Mg	0.3	0.3	0.4	0.3	0.3	0.3	0.4	0.3	0.3	0.4
Na	0.4	0.2	0.4	0.4	0.3	0.4	0.3	0.3	0.3	0.3
S	0.3	0.2	0.4	0.7	0.2	0.3	0.0	0.0	0.1	0.0
Ti	0.4	0.3	0.4	0.2	0.3	0.3	0.3	0.4	0.5	0.4
As	55	122	34	21	56	57.7	24	55	36	38.3
Ba	712	668	574	410	581	589	631	581	1628	947
Be	4.0	3.0	4.0	2.0	3.0	3.2	3.0	3.0	2.0	2.7
Bi	0.7	0.5	0.5	0.3	0.7	0.5	0.4	0.4	0.4	0.4
Cd	0.3	0.3	0.9	0.3	0.5	0.5	0.2	0.2	0.2	0.2
Co	3.6	4.2	7.2	5.3	5.5	5.2	6.8	3.5	16	8.7
Cr	115	122	99	45	92	94.6	92	89	96	92.3
Cs	24	13	12	7.3	16	14.2	8.8	11	9.2	9.7
Cu	62	56	114	47	61	67.7	32	41	37	36.5
Ga	28	24	23	13	26	22.0	23	22	22	22.5
Hf	4.0	4.4	3.6	1.7	3.1	3.4	4.4	3.5	3.9	3.9
Li	137	54	89	39	94	82.7	58	80	66	67.9
Mn	84	74	176	154	95	117	177	82	158	139
Mo	2.2	2.1	1.8	0.7	2.3	1.8	1.5	1.0	0.8	1.1
Ni	20	16	28	18	22	20.7	21	16	28	21.4
Pb	107	314	44	23	69	111	31	31	31	30.8
Rb	157	125	126	114	127	130	141	122	122	128
Sb	24	513	14	12	24	118	12	34	35	27.0
Sc	17	18	18	7.0	17	14.0	14	13	12	12.9
Sn	6.3	6.4	4.7	3.5	5.2	5.2	4.5	4.1	4.6	4.4
Sr	109	55	84	54	95	79.5	51	75	66	64.0
Th	13	10	15	7.3	12	11.6	12	10	12	11.4
U	5.9	5.5	9.2	2.6	5.5	5.7	4.1	4.1	4.6	4.3
V	136	140	122	61	117	115	123	132	129	128
W	2.0	1.1	1.7	1.0	2.0	1.6	1.7	1.8	2.5	2.0
Y	12	8.6	11	6.3	11	9.9	8.1	11	12	10.1
Zn	47	50	78	61	118	70.7	71	42	58	57.0
Zr	133	150	124	61	112	116	147	118	136	134
Σ LREE	133.6	139.8	121.5	61.1	153.9	122.0	142.5	126.0	146.2	138.2
Σ HREE	13.7	11.5	13.0	6.2	13.2	11.5	11.0	11.9	14.2	12.4
REE	147.3	151.3	134.5	67.3	167.1	133.5	153.5	137.9	160.4	150.6
pH	3.7	4.0	3.8	3.3	5.4	4.0	5.1	4.6	4.7	4.8
Eh	196.1	176.1	189.5	214.3	98.4	174.9	118.0	146.3	134.4	132.9
Elec. Cond.	291.1	129.1	1423	1640	119.9	720.5	35.5	54.4	49.1	46.3

SS – sediment samples; SO – soil samples; Elec. Cond. – electric conductivity.

and Ba, probably represents a silicate fraction, perhaps detrital accessory minerals.

The trace elements with the highest concentrations in the leachates included Cd, Co, Cu, Fe, Mn, Ni, and Zn, indicating that these elements are associated with H₂O-soluble compounds under the acid pH conditions. Metals associated with such phases are relatively mobile and readily available for biological uptake. Thus, a high

environmental risk factor is associated with higher availability of these metals.

The neoformed pickeringite (MgAl₂(SO₄)₄•22H₂O) found in the bottom of the waste pile is the result of the surface evaporation of leachates from the waste pile and the drainage system. The weathering process introduces considerable aluminum, iron, magnesium, and potassium into solution.

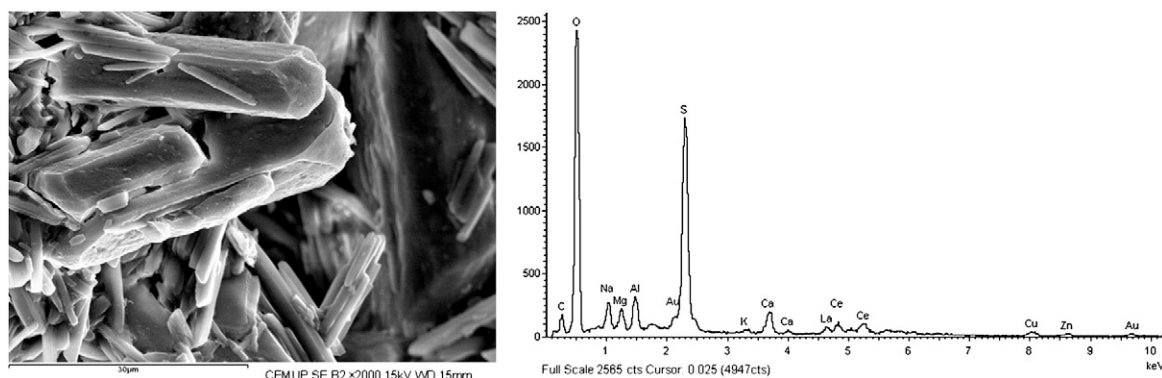


Fig. 6. SEM image and EDX spectra of pickeringite formed in the bottom of Serrinha coal waste pile.

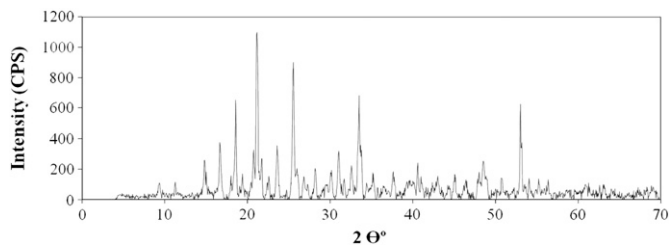


Fig. 7. X-ray diffractogram of pickeringite formed in the bottom of Serrinha coal waste pile (P – pickeringite).

The results indicate that the sediment and soil samples have a strong influence from the composition of the waste materials and consequently the local geological environment. Due to the low pH values the solubility of Al and Fe is high. Many heavy metals become more water soluble under acid conditions and can move downward with water through the soil, and in some cases to streams. The pH, Eh and electric conductivity values found in the water samples, particularly from the bottom of the waste pile, also indicate that acid mine drainage is occurring.

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