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# Geochemistry of self-burning coal mining residues from El Bierzo Coalfield (NW Spain): Environmental implications

Joana Ribeiro [a,b,*], Isabel Suárez-Ruiz [c], Deolinda Flores [a,b]

[a] Instituto de Ciências da Terra, Polo da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
[b] Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal
[c] Instituto Nacional del Carbón (INCAR-CSIC), Ap. Co. 73, 33080 Oviedo, Spain

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ABSTRACT

The geochemical composition of unburned and burned/burning coal waste piles from past mining activities in El Bierzo Coalfield (NW Spain) was determined for the comprehensive characterization of the coals waste materials, for the identification of the mode of occurrence of environmental sensitive trace elements, and for the identification of geochemical changes induced by the thermal effects resulting from the combustion process. The methodologies used for the geochemical characterization of the coal and coal waste material included proximate analysis, ultimate analysis, inductively coupled plasma mass spectrometry for the determination of the inorganic composition of major and trace elements, and scanning electron microscopy with energy dispersive X-ray spectrometry. Considering the potentially hazardous trace elements, the results demonstrated that the unburned material are enriched in Pb, Sb, and Th, comparatively with the background of black shales (BBS). Considering the enrichment/depletion behavior of the elements in burned vs. unburned material, it was observed that Fe, K, Na, S, and Ti are enriched in burned material, while Ca, Mg, and P are depleted. The trace elements Nb, Re, Ta, Te, and W are enriched in burned waste material while Cd, Cu, Mn, Zn, and REE are depleted. Higher contents of oxygen and total sulfur, and lower content of carbon were determined in the burned/burning materials. The enrichment/depletion behavior of the elements is attributed to the self-burning process and to the changes caused by thermal effects. The enrichment of some elements may result from the elements' concentration due to the volatilization of other elements and organic matter consumption during the combustion process. The depletion of some elements may be associated with their volatilization during combustion. However, other reasons for this behavior, such as the elements mode of occurrence, weathering and/or leaching, should be considered. The investigation about the mode of occurrence of the worldwide potentially hazardous trace elements in coal wastes reveals that As, Cd, Pb, Sb and U are preferentially organically associated. However, As and Cd also presents some affinity with mineral mater. The elements Be, Co, Cr, Mn, Ni, Se and Th exhibit a significant association with mineral matter.



## 1. Introduction and objectives

The environmental impacts and human health problems caused by coal have been considered for a long time, possibly from its first use as a fuel in China (Finkelman, 2004; Suárez-Ruiz and Crelling, 2008; Suárez-Ruiz et al., 2012). Both coal mining and coal consumption have significant impacts that are harmful to the environment and human health, despite the undeniable benefits to the economic and social sectors of many countries (Finkelman, 2004; Orem and Finkelman, 2004; Younger, 2004; Suárez-Ruiz and Crelling, 2008; Suárez-Ruiz et al., 2012). The potential environmental impact and health problems related to coal mining, processing and utilization depends on many factors, such as coal composition, geological setting, local hydrology, climate, topography, mining methods, combustion technologies, local regulations, amongst others (Suárez-Ruiz and Crelling, 2008; Suárez-Ruiz et al., 2012).

The environmental risks associated with coal mining may include changes in landscape and land use, soil erosion, increased noise generation, production of solid wastes, air pollution, surface and groundwater pollution, soils and sediments pollution, land instability, subsidence, coal mine fires and several impacts on local biodiversity (Bell et al., 2001; Younger, 2004; Suárez-Ruiz and Crelling, 2008). The generation and disposal of solid wastes, essentially made up of discarded and overburdened material resulting from mining activities, may cause various environmental problems from those mentioned above (Bell et al., 2001; Younger, 2004). The coal mine wastes disposal may lead to: atmospheric dispersion of particles; spontaneous combustion of waste piles; landslides and mass movements in the waste piles; and

* Corresponding author at: Instituto de Ciências da Terra, Polo da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal.
*E-mail address:* joanaribeiro@fc.up.pt (J. Ribeiro).

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mobilization of material, leaching of elements and formation of acid drainage caused by weathering and/or oxidation processes. The focus of the present study is the environmental impacts associated with the coal waste piles, with a special emphasis on self-burning coal waste piles.

The occurrence of coal related fires have been described worldwide by Stracher et al. (2011, 2013, 2015) and may occur during coal mining (opencast and underground), storage, transportation, and waste disposal. The spontaneous combustion of coal and coal wastes have been the subject of several studies (Ciesielczuk et al., 2014; Finkelman, 2004; Finkelman and Stracher, 2011; Gürdal et al., 2015 Misz et al., 2007; Misz-Kennan and Fabiańska, 2010, 2011; Pone et al., 2007; Querol et al., 2008; Ribeiro et al., 2010a,b, 2012, 2015, 2016; Stracher, 2007; Stracher and Taylor, 2004; Zhao et al., 2008), being some associated with impacts on environment and human health The self-burning of coal wastes piles resulted from coal mining activities represent a source of pollutants that can be emitted, released or leached to the surrounding environment. During the process, the emission of harmful gases and particulate matter into the atmosphere, the mobilization and leaching of hazardous elements may affect the atmosphere, soils, surface and groundwater, and consequently may cause environmental pollution and effects on human health and biodiversity. The comprehensive characterization of materials that constitutes the self-burning coal waste piles is needed for the identification of these impacts, to further contribute to their mitigation.

Previous studies demonstrated that the petrographic, mineralogical and chemical compositions of self-burning coal waste materials are affected by the combustion process (Ciesielczuk et al., 2014; Misz-Kennan and Fabiańska, 2011; Ribeiro et al., 2010a,b, 2012, 2015, 2016). Therefore, the characterization of self-burning coal wastes allows: the evaluation of factors responsible for the spontaneous combustion and self-burning processes, the identification of the changes that are taking place in the affected materials, and provide insights about the associated potential environmental impacts.

The main goal of this study is to establish the geochemical composition of the coal mining residues from Arroyo Galladas, Arroyo Mourin and Fabero coal waste piles, resulted from past mining activities in El Bierzo Coalfield (NW Spain). It is also expected to contribute for the comprehensive characterization of these coal waste piles since the petrographic and mineralogical compositions were already investigated (Ribeiro et al., 2014, 2016). The specific objectives are: (i) to determine the organic and inorganic geochemical composition of coal from El Bierzo Coalfield and coal mining wastes from Arroyo Galladas, Arroyo Mourin and Fabero coal waste piles; (ii) to identify the mode of occurrence of environmental sensitive trace elements; (iii) to identify the geochemical changes induced by the thermal effects resulting from the combustion and self-burning processes; and, (iv) to identify potential environmental impacts associated with the coal mining residues disposal and those related with the spontaneous combustion and self-burning processes.

## 2. Case study

The detailed description of the case study, i.e., the El Bierzo Coalfield and the Arroyo Galladas, Arroyo Mourin and Fabero coal waste pile is fully described in Ribeiro et al. (2016), that focuses on the petrographic and mineralogical characterization of the waste materials. However, some key issues are summarized below.

The El Bierzo Coalfield (Region of Fabero, Province of Leon, Spain) is the westernmost and largest Stephanian coalfield in the Cantabrian Mountains. Stephanian B–C coal-bearing series are widespread in the Cantabrian Mountains, unconformably overlying basement units ranging from Precambrian to Carboniferous age (Suárez-Ruiz and Jiménez, 2004; Colmenero et al., 2008). The coal from El Bierzo Coalfield has a rank ranging from bituminous A to anthracite C, B, A (vitrinite reflectance between 1.87% and 5.25%), low to high ash yield, and vitrinite as a major organic constituent (> 96%, mmf basis) (Colmenero et al., 2008).

The rejects from coal mining in El Bierzo Coalfield were dumped for many years and have been exposed at natural alterations that include physical, chemical and biological processes. These alterations generate many impacts on air, water and soils, as the spontaneous combustion of coal or like acid mine drainage, which releases heavy metals in the environment and cause a negative visual impact on the landscape (Hernández-Mendoza et al., 2013). The Arroyo Galladas, Arroyo Mourin and Fabero coal waste piles resulted from mining activities in El Bierzo Coalfield. The Arroyo Galladas waste pile is the focus of this study because is currently under self-combustion process. In this waste pile the mining residues were disposed in a valley associated with the Galladas stream. The Arroyo Mourin and Fabero coal waste piles are located relatively close to Arroyo Galladas coal waste pile and were also investigated. Fig. 1 shows the location (Fig. 1A) and a general view of the studied area (Fig. 1B). Fig. 1C, D and E show a zoom out of Arroyo Galladas waste pile, Arroyo Mourin waste pile and Fabero waste pile, respectively.

## 3. Sampling and methodology

The information about sampling is fully detailed in Ribeiro et al. (2016) however, some important aspects are described in this section. The coal waste material from Arroyo Galladas waste pile was sampled in six different points (Fig. 1C), all with evidences of self-burning occurrence; these samples were collected close to surface (until 20 cm depth). In three of these sampling points (GWP 2, GWP 5, and GWP 6) additional samples were collected in small wells (20–30 cm, 30–40 cm, and 40–50 cm, respectively). The field observations during sampling campaigns and the macroscopic observation of the collected samples reveal that the waste material is very heterogeneous within the Arroyo Galladas coal waste pile, containing lithic fragments, mainly shales, arenites and coal, with particles size ranging from few μm to some cm. This heterogeneity was also noticed in the petrographic and mineralogical characterization of the Arroyo Galladas waste material (Ribeiro et al., 2016).

The field observations also indicate that part of Fabero coal waste pile was under intense self-burning or spontaneous combustion process in the past, since the material is completed calcined. Samples of this calcined material (samples FWP 1 and FWP 2) and unburned coal waste material and/or coal cleaning rejects (sample FWP 3) were collected in this coal waste pile (Fig. 1E) to be compared with the coal waste material from Arroyo Galladas waste pile. In addition, three coal samples from El Bierzo Coalfield were also collected (Fig. 1C–E), so that some characteristics of the original unburned material, including both the organic and the inorganic material, could be characterized. In Arroyo Mourin coal waste pile, which is a non-burning coal waste pile, was also collected a sample of coal waste material (MWP), aiming the comparison with the burning waste material from Arroyo Galladas waste pile.

In the laboratory the coal waste material samples (2 to 3 kg each), as well as the coal samples were homogenized, dried and quartered to obtain representative samples and then were crushed to obtain <212 μm fraction.

The methodologies used for the geochemical characterization of the coal and coal waste material included: proximate analysis for the determination of moisture, ash and volatile matter yields in accordance with ISO standards (ISO 1171, 2010; ISO 589, 2008; ISO 562, 2010); ultimate analysis for determination of carbon, hydrogen, nitrogen, and total sulfur in a LECO S-2000 and LECO S-632 apparatus; and inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS analyses were performed by Acme Analytical Laboratories (Canada), for the determination of the inorganic composition of major and trace elements in studied materials. After acid digestion with an acid solution of