A first approach to the characterization of water and sediments during the restoration of coal waste dumps in El Bierzo (NW Iberia)

Una primera aproximación a la caracterización del agua y sedimentos durante la restauración de escombreras de carbón: un caso en El Bierzo (NO de Iberia)

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ABSTRACT

Coal mining has been related to the problems of acid mine drainage (AMD) or acid rock drainage (ARD), causing high acidity and contamination by metals. Coal mining in El Bierzo coal basin, NW Iberian Peninsula, has resulted in several abandoned tailings from past mining that still affect water chemistry and sediment composition. Recent restoration actions, including the expansion of roads, have introduced fresh waste materials and accelerated the oxidative weathering and sediment transport into La Silva river. Water analyses continue to show low pH (~4.5) and high sulfate concentrations supporting sulfide oxidation. The VNIR-SWIR diffuse reflectance spectroscopy initially identified iron oxides such as goethite in the sediments, and later illite, a product of erosion and deposition of waste materials. This indicates that the runoff generated after the rainfall episodes has transported sediments of different mineral composition by mobilizing material from the waste dumps. The study highlights the importance of continuous monitoring to assess the evolving geochemical conditions and potential secondary alterations in the river system. Reflectance spectroscopy has proved to be a useful technique for rapid mineral identification, distinguishing oxidation effects from erosion impacts, making it a valuable tool for environmental assessments.

Key-words: *Diffuse reflectance spectroscopy, environmental impacts, mineralogy, restoration works, tailing.*

RESUMEN

La actividad minera está relacionada con problemas ambientales como drenaje ácido de mina (AMD) y drenaje ácido de roca (ARD), generando alta acidez y contaminación metálica. En la cuenca minera de El Bierzo (León), los residuos mineros abandonados siguen afectando a la química del agua y la composición de los sedimentos. Recientes trabajos de restauración, como la ampliación de caminos, han introducido nuevos materiales, intensificando la meteorización oxidativa y el transporte de sedimentos hacia el río La Silva. El análisis del agua muestra una acidez persistente (pH ~4.5) y altas concentraciones de sulfatos, resultado de la oxidación de sulfuros. La espectrorradiometría de reflectancia difusa identificó inicialmente óxidos de hierro como goethita en los sedimentos, y posteriormente illita producto de la erosión y deposición de materiales de los residuos. Esto indica que la escorrentía generada tras las lluvias ha transportado sedimentos de diferente composición mineral al movilizar material de las escombreras. El estudio resalta la importancia de la monitorización continua para evaluar las variaciones en las condiciones geoquímicas. La espectrorradiometría ha demostrado ser una herramienta útil para identificar minerales rápidamente, diferenciando los efectos de la oxidación de los impactos de la erosión.

Palabras clave: *Espectrorradiometría de reflectancia difusa, escombrera, impacto ambiental, mineralogía, restauración minera.*

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Introduction

Coal mining extracting activities led to environmental conditions which facilitate strong acidity and metal contamination. Normally, the easy alteration of sulfur present in the coal deposits, mainly as pyrite (FeS_2), is associated with the reducing conditions that prevailed during the forming deposit. The inevitable oxidation of pyrite and the acid generation in mine tailings and leachate steriles are related with the acidification process. The acid mine drainage (AMD) and, occasionally, the acid rock drainage (ARD) share several common characters (Shum y Lavkulich, 1999): high conductivity as a result of total dissolved solids, especially sulfates; an oxidative potential; an increase of suspended particulates; a relatively high turbidity; and metals that are soluble at low pH. These leachates exhibit acidic pH values due to a series of consecutive oxidative microbial reactions that unchain the extreme acidification of the water environment (Nordstrom, 1982; Bigham *et al*., 1990).

All these conditions facilitate the presence of numerous and complex secondary minerals (Nordstrom, 1982; Jönsson *et al*., 2006). Among them, Fe oxides and hydroxides species are the most frequent, with reddish ochreous coloured phases in these acid environments such as Schwertmannite [$Fe_{16}O_{16}(OH)_{12}(SO_4)_2$] and Ferrihydrite [$5Fe_2O_3 \cdot 9H_2O$], Goethite [α-FeO(OH)] or Hematite [α- Fe_2O_3]. More occasionally, K-Jarosite [$KFe_3(OH)_6(SO_4)_2$] may be found. The other frequent secondary minerals are Al species corresponding to Basaluminite [$Al_4(OH)_{10}SO_4$], Alunite [$KAl_3(SO_4)_2(OH)_6$] and even Jurbanite [$AlOHSO_4$].

In this context we find the study area, located in El Bierzo coal mining basin (NW of Iberian Peninsula), around La Silva river. There, coal mines were closed decades ago and are being restored nowadays. During this process, some roads are being widened to allow the transit of heavy machinery. Thus, the road waste material is deposited over a small old tailing and located in a hillslope near the river. These new waste steriles are a mixture of natural soils, parent rock and old tailing material where mainly shales and sandstones composition of heterometric sizes predominates. The new exposure to oxidative weathering conditions of this mixture and their consequent weathering involves new impacts in the study area by acidic leachates. In addition, the fine-grained size sediments are mobilized and transported by surface runoff, what facilitates reaching the river due to its proximity. The direct consequence of this transfer is also an increase in the load of suspended solids and sedimentation on the riverbed.

Therefore, the main goal of this study is to analyse the effects in the water chemistry and the sediment mineralogy, after starting mine restoration works, due to the new materials deposited over the old tailing, as well as evaluating the applicability of spectrorradiometry analysis. For this purpose, several samples were taken in two time periods and the mineralogical characterization with VNIR-SWIR spectroscopy and geochemistry analysis were carried on.

Study area

The study area is located in La Silva river basin (León, NW of Iberian Peninsula), upstream Torre del Bierzo town (Fig.1). The climate of this area is a transition between two types, the Mediterranean and Atlantic. From a geological point of view, the study area is framed in the Asturoccidental Leonesa Zone, in El Bierzo basin, the stratigraphic succession presents a detritic series of Middle Cambrian-Lower Ordovician age, over which there are Ordovician transition layers, known as Luarca Slates, with frequent pyrite mineralization (Heredia *et al*., 1994). Discordant over these materials are Carboniferous rocks composed mainly of sandstones and shales with variable amounts of conglomerates and frequent intercalations of coal layers. The slates and phyllites are composed mainly of quartz, sericite and have as accessories muscovite, chlorite, tourmaline, biotite, Fe metal ore, sphene, illite, zircon, rutile and graphite (Heredia *et al*., 1994).

Samples	July	September/ October
Water	EK-W1	EK-W1
Sediments on the riverbed	EK-W1-R1 EK-W1-R2	EK-W1-RT4
Tailings	-	EK-T004A EK-T004B EK-T004C

Table I.- Number of water, sediments and tailing samples taken in the study area.
Tabla I.- Número de muestra de agua, sedimentos y escombrera, tomadas en el área de estudio.

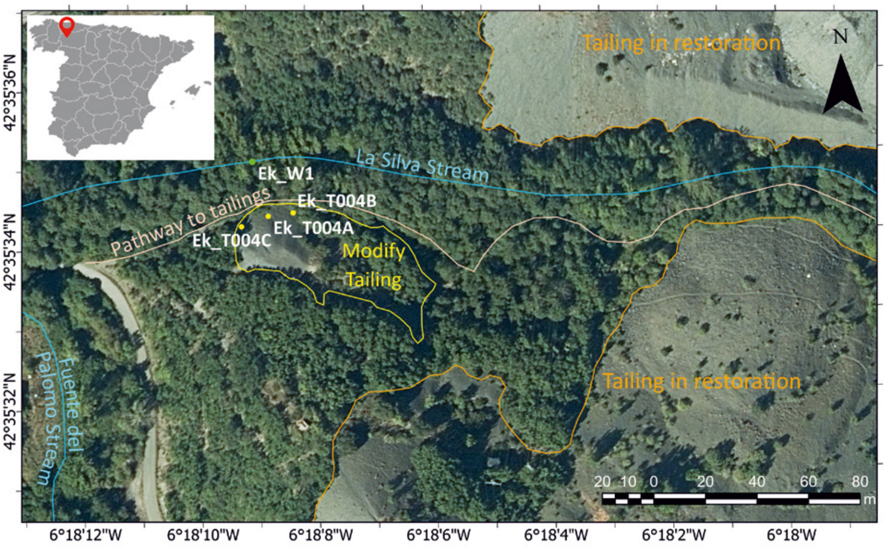

Fig. 1.- Location of the study area. Ver figura a color en la web.
Fig. 1.- Localización del área de estudio. See color figure in the web.

The main soils are Umbric-Humic Leptosols and Dystric and Lithic Leptosols with Dystric Cambisols and Regosols. Their textures correspond to loam towards sandy loam or sandy with a moderate-high content of organic matter. In general, they are acid soils, sometimes very acid ones, with high gravel fraction and good drainage capacity (Alcalde-Aparicio *et al*., 2022).

Materials and Methods

Sampling

All sampling sites were located downstream the modified tailing (Fig.1). Water samples were collected in duplicate at the sampling point EK-W1 (42°35'35"N, 6°18'12"W) on July 17 and October 10, 2024. There, *in situ* measurements of pH, electrical or redox potential (Eh, mV), electrical conductivity (EC, µS/cm), and temperature (°C) were recorded using a Hach Instruments Intellical portable multiparameter probe (Table II). The total dissolved solids concentration (TDS) was obtained by conductivity and temperature conversion in mg/L.

Sediment samples decanted on river cobbles and boulders (EK-W1-R1 and EK-W1-R2; EK-W1RT4) were collected in the riverbed under the water, in the same coordinate than EK-W1 in July and October.

Additionally, three new samples were collected from the waste dump tailing during the September 28 sampling campaign. The samples were collected individually in zipped plastic bags and stored at air temperature. Sample EK-T004B represents the most upstream area of the tailing, where old and thick layer waste steriles predominate. The other two samples, EK-T004A and EK-T004C, were collected slightly down the slope of EK-T004B, closer to the main road and where the tailing material covering the surface was less extensive (Table I). The three samples were cleaned of plant debris and sieved through a 2 mm sieve in laboratory. The decanted sediments on the surface of the cobbles were scraped off resulting in the samples EK-W1-R1, EK-W1-R2 and EK-W1-RT4. Both types of samples (from tailing and settled sediments) were air-dried at room temperature and prepared for spectral measurements.

Methods

In the Instrumental Techniques Laboratory at the University of León, cations and metallic elements of interest (Al^{3+} and Fe^{3+}) were analyzed in triplicate using an Agilent 5110 SVDV Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-OES). Calibration was performed using standards and Y solution as internal standard. For anion determination (e.g., sulfates), ion chromatography was performed using a Metrohm 881 Compact IC Pro (IC) equipped with a Metrohm Metrosep A Supp 7 column. The mobile phase consisted of 3.6 mM sodium carbonate.

Deposited sediments from the river and tailing samples were analysed spectroscopically using an ASD FieldSpec-4 Standard-Res spectroradiometer (Analytical Spectral Devices, Inc., Boulder, CO, USA) at laboratory in the University of León. Spectral measurements were taken, capturing diffuse reflectance in the VNIR-SWIR range (350–2500 nm) with spectral resolutions of 3 nm (350–1000 nm) and 5 nm (1000–2500 nm). Each measurement yielded a spectrum composed of 2,551 bands. Each sample was subdivided into three subsets, with three measurements taken clockwise per subset. After confirming low standard deviation among curves, an averaged spectral curve was calculated for each subset. This last curve was compared with referenced spectral curves to identify their mineral content (Hunt, 1977; Crowley *et al.*, 2003).

Sampling date	pH	CE (µS/cm)	Eh (mV)	T (°C)	Al^{3+}	Fe^{3+}	SO_4^{2-}	TDS
July 17	4.47	611.00	370.80	17.34	11.10	0.98	216.00	391.00
October 10	4.66	481.50	334.05	12.27	3.78	0.13	142.00	308.00

Tabla II.- Measured parameters and element concentrations from stream water sampling EK-W1 on two dates. TDS (Total dissolved solids) in mg/L. Elements concentration in parts per million (ppm).

Tabla II.- Parámetros medidos y concentración de elementos del muestreo de las aguas EK-W1 del arroyo en dos fechas. TDS (Sólidos disueltos totales) en mg/L. La concentración de los elementos en partes por millón (ppm).

Results

Water geochemistry

The water chemistry at EK-W1 site presents low pH around 4.5 in July and 4.7 in October, with a high oxidative redox potential for the two sampling periods (Table II). Moreover, high electrical conductivity (EC) values of 611 and 482 µS/cm were obtained respectively for each sampling date. It means a high reduction from July to early October. This seems to be the result of dilution. It could be explained by some events of precipitation some days before. It is remarkable the 45 mm daily rainfall occurred in September 27. Before the last sampling date, two episodes of around 15 and 16 mm of daily rainfall took place. As a result, the total dissolved solids (TDS) were lower on the second date (Table II), reaching 308 (mg/L). The sulfates concentration was also reduced, 216 in the first period to 142 ppm in the second sampling date (Table II). Besides, the load of particles in suspension was also higher during the first sampling period, as well as the EC and, consequently, a relatively higher turbidity was observed too. Fe total dissolved concentration was 0.98 ppm and less in October sampling with 0.13 ppm. The concentration is reduced by more than half in the case of Al: 11.10 ppm in July and 3.78 in October.

Mineral identification

A reflectance spectrum study was conducted to identify mineralogy in the collected samples based on diagnostic features. The reflectance spectra of the EK-W1-R1 (Fig.2) sediment sample collected in July shows clear absorption features. A strong absorption at 944 nm and a broad feature at 482 nm suggest the presence of goethite. However, the 944 nm feature is slightly shifted to shorter wavelengths, which may indicate the presence of jarosite or other heavy metals also spectrally active in this wavelength region (Hunt, 1977). The spectrum also shows a sharp absorption at 2207 nm, linked to Al-OH bonds indicating the presence of clay minerals. The broad and asymmetric 1400 nm water absorption feature suggests that these clays predominantly belong to the smectite group.

Similarly, the EK-W1-R2 (Fig.2) spectra shows a broad absorption at 958 nm and another at 479 nm, both consistent with goethite. An absorption feature at 2205 nm, along with the broad and asymmetric 1400 nm water absorption suggest a dominant presence of smectite-group clays. Additionally, the presence of alunite is suggested by an absorption feature at 1780 nm in the sample EK-W1-R2 (Fig.2).

In contrast, the reflectance spectrum of the EK-W1-RT4 (Fig.2) sediment sample, collected in October, shows notable differences from the July samples. The Fe-related absorption features at 486 nm and 915 nm are shallow and do not correspond to any specific secondary Fe oxide, suggesting a mixture of Fe-bearing minerals with much lower Fe content compared to the July samples. Additionally, an absorption at 2201 nm, associated with clays, is present. The sharp and symmetric 1400 nm water absorption feature suggests a dominant presence of illite-group clays.

The tailing samples EK-T004A and EK-T004B (Fig.2) display broad and shallow absorption features at 486 nm and 915 nm in EK-T004A, and at 495 nm and 897 nm in EK-T004B. These features do not match any known secondary Fe oxides, again suggesting a mixture of Fe-bearing minerals. In contrast, the EK-T004C (Fig.2) sample shows no Fe-related absorption features, indicating an absence of Fe oxides in this sample. All the tailing spectra show Al-OH absorption features around 2200 nm, which are associated with illite as explained before.

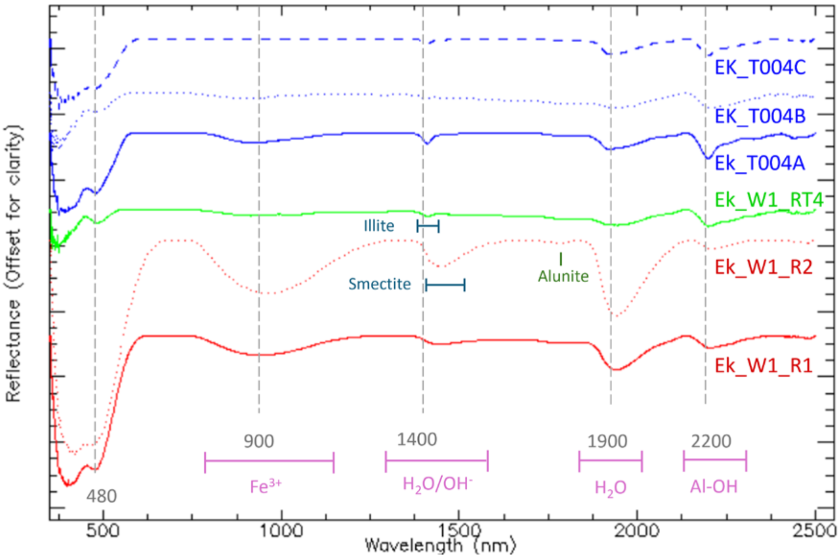

Fig. 2.- Reflectance spectra from the study samples. Ver figura a color en la web.

Fig. 2.- Espectros de reflectancia de las muestras de estudio. See color figure in the web.

Discussion

Water chemistry was analysed to compare two sampling periods after starting the restoration works in an abandoned coal waste tailing in July and October 2024. Besides, the mineral identification of the sediments collected in both periods was performed looking for compositional differences.

La Silva stream has been severe affected by AMD and ARD for several some decades (Rodríguez-Gómez *et al.*, 2010). The stream currently presents a poor quality and high degradation, despite several remediation treatments carried out upstream (Santofimia and López Pamo, 2016). The data show actual high acidity in July and continues also in October with a low neutralizing capacity in both periods. This together with the high oxidative potential help to understand the actual active sulfides oxidation and mineral alteration process (Nordstrom and Alpers, 1999); Fe and Al are found as major metallic components. Both are soluble at low pH and precipitate with a pH>2.5 and 4.5 for Fe and Al phases respectively (Nordstrom and Alpers, 1999; Shum and lavkulich, 1999). The high sulfates concentration as well as the total dissolved solids are also consequent with the AMD/ARD reactions, generated from sulfides oxidation (Nordstrom, 1982).

The water chemistry composition, with low pH around 4.5, gives the ideal conditions to find precipitates of secondary Fe minerals and possible secondary Al minerals such as alunite on the riverbed (Villa *et al*., 2008). The possible mineral species which may precipitate frequently are Fe oxydydrosysulfates such as Schwertmannite (Bigham *et al*., 1990). These minerals could be more or less oxidized to Fe oxides and oxihydroxides, such as goethite and hematite or even mixtures of ferric phases.

The spectral data (Fig.2) suggest that in July, the sediment samples (EK-W1-R1 and EK-W1-R2) contained oxidized secondary Fe minerals, primarily goethite, along with smectite. However, significant rainfall in September likely led to the mobilization of newly deposited, unstable material from the tailings, resulting in a different mineralogical composition observed in the October sample. The EK-W1-RT4 sample closely resembles the tailing samples (EK-T004A, EK-T004B, and EK-T004C), showing a decrease of Fe oxides and an increased presence of illite, which is also quite abundant in these parent rocks (Alcalde-Aparicio *et al*., 2022). Ribeiro *et al*. (2016) also identified mica/illite as the major mineral in coal residues from Fabero sector in El Bierzo coal basin. This similarity indicates that the EK-W1-RT4 sample may be mobilized and transported tailing material, without an intense alteration process, reflecting mainly the impact of recent erosion and sediment transport.

The results of this study suggest that spectroradiometry analysis could be a valuable tool to differentiate the two kinds of processes that impact in those rivers near a tailing, before and after the material accumulation is being altered by the enlargement of a path: the Fe oxidation in July and the new sediment incomes from altered tailing. Although it does not allow a detailed quantification of the minerals, this is a technique that shows an easy and quick result about the mineral presence, working with non-processed and untreated samples. This quick response gives an advantage compared to other laborious analysis, such as X-ray diffraction which are also complementary. However, not all minerals exhibit a spectral response in this wavelength range and some, like calcite and dolomite, may be undetectable in phyllosilicate-rich mixtures (Santamaría & Suárez, 2024). Though effective in identifying major minerals, others are likely present beyond those detected.

Conclusions

At present, the water geochemistry indicates ideal conditions for the occurrence of secondary Fe minerals (oxides and oxihydrosulfates) and, less commonly, Al phases as precipitated solids and later decanted sediments. In addition, surface runoff during the rainy season results in the presence of other clay minerals derived from newly eroded, transported and deposited material from the tailing.

The mineral identification suggests Fe oxides as goethite and smectite in the sediments, substituted by illite due to the erosive and depositional conditions associated with the tailings. The results also indicate that recent rainfall events have transported new sediments of different mineral composition by mobilising the tailing material. Reflectance spectroscopy was found to be a useful analytical technique for rapid mineral identification of majority minerals. It allows oxidation effects to be distinguished from erosion effects, making it a valuable tool for environmental assessments.

The current environmental impacts should be monitored and evaluated periodically. It is possible that the newly found sediments may undergo a second alteration process, resulting in new geochemical conditions in the stream.

Contribution of the authors

S.A.A.: structure and conceptualization, data procurement, formal analysis, project administration, validation, writing-original draft, review and editing. I.P.: data procurement, formal analysis, figures, writing-original draft, review and editing. J.A.C.: research/analysis, writing-original draft, review and editing. I.R.: research/analysis, writing-original draft, review and editing. M.B.: data procurement. F.F.: validation, writing-original draft, review and editing. M.F.J.: structure and conceptualization, validation, writing-original draft, review and editing.

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