Radiological Assessment of Copper Mining Wastes from the Iberian Pyrite Belt

Juan Antonio Ramírez Pérez[1], Alejandro Barba Lobo[2], Manuel Jesús Gázquez González[3], Juan Pedro Bolívar Raya[4]

[1]*Universidad de Huelva, Campus El Carmen, Facultad de Ciencias Experimentales, 21007 Huelva, Spain, juan.ramirez@dci.uhu.es, ORCID 0009-0003-6757-7066*

[2]*Universidad de Huelva, Campus El Carmen, Facultad de Ciencias Experimentales, 21007 Huelva, Spain, alejandro.barba@dci.uhu.es, ORCID 0000-0001-8335-1532*

[3]*Universidad de Cádiz, Campus de Puerto Real, Instituto de Investigación Marina (INMAR), 11510 Puerto Real, Cádiz, Spain, manueljesus.gazquez@uca.es, ORCID 0000-0002-0198-5732*

[4]*Universidad de Huelva, Campus El Carmen, Facultad de Ciencias Experimentales, 21007 Huelva, Spain, bolivar@uhu.es, ORCID 0000-0001-9258-6341*

Abstract

The Iberian Pyrite Belt (IPB) is in the southwest Iberian Peninsula. Due to heavy mining and processing of sulfide ores, large amounts of historic mining wastes are dispersed along this area, which are called as "legacy sites". Many of these wastes contain large quantities of metals and metalloids (e.g. As, Cd, Cu) including some potentially Naturally Occurring Radioactive Materials (NORM), which can constitute an important environmental threat and a substantial potential public health. Therefore, a novel radioactive and physicochemical characterization of the most relevant mining wastes was performed, including potential lines of valorization.

Keywords: Mining wastes, radioactive characterization, Iberian pyrite belt, radionuclides, radiological hazard index

Introduction

The Iberian Pyritic Belt (IPB), located in the southwest of the Iberian Peninsula, hosts the largest concentration of polymetallic massive sulfides deposits in the world. This area has been heavily mined for some 5000 years, but was particularly intense during the English period, especially between 1870 and 1930 (Yesares *et al*. 2015), generating a large amount of mining waste, belonging to the more than 100 mines located in this area, most of them abandoned. These wastes have a high content of metals/metalloids such as As, Cu, Zn, and Pb. Moreover, they are Naturally Occurring Radioactive Materials (NORM) wastes since metals extraction from mined minerals can generate materials with naturally occurring radioactive activity according to the EU regulation. Therefore, its radiological implications have to be evaluated. In addition, the toxic metals, metalloids, and associated contaminants as sulfursuppose a potential environmental risk and problems for public health, as they are close to towns and sensitive aquatic ecosystems(Álvarez-Valero *et al*. 2009).

Considering the potential environmental and human health problems related to these wastes, the main objective of this work has been to perform a comprehensive radioactive characterization of the different mining wastes located at these mines, as well as the evaluation of their radiological risks.

Methods

Three mining complexes representative of the mines developed in the IPB were selected for study: 1) Sotiel Coronada (SC), 2) Cueva de la Mora (CM), and 3) Tharsis (TH) (Almodóvar *et al*. 2019). The main processes developed by these mine complexes were extraction of polymetallic ores producing shales rejects (SH), pyrite flotation sludges (FP), roasted pyrite for sulfuric acid production (RP), pyrites leached with sulfuric acid (PY) and slags from minerals smelting (SL) (Tornos *et*

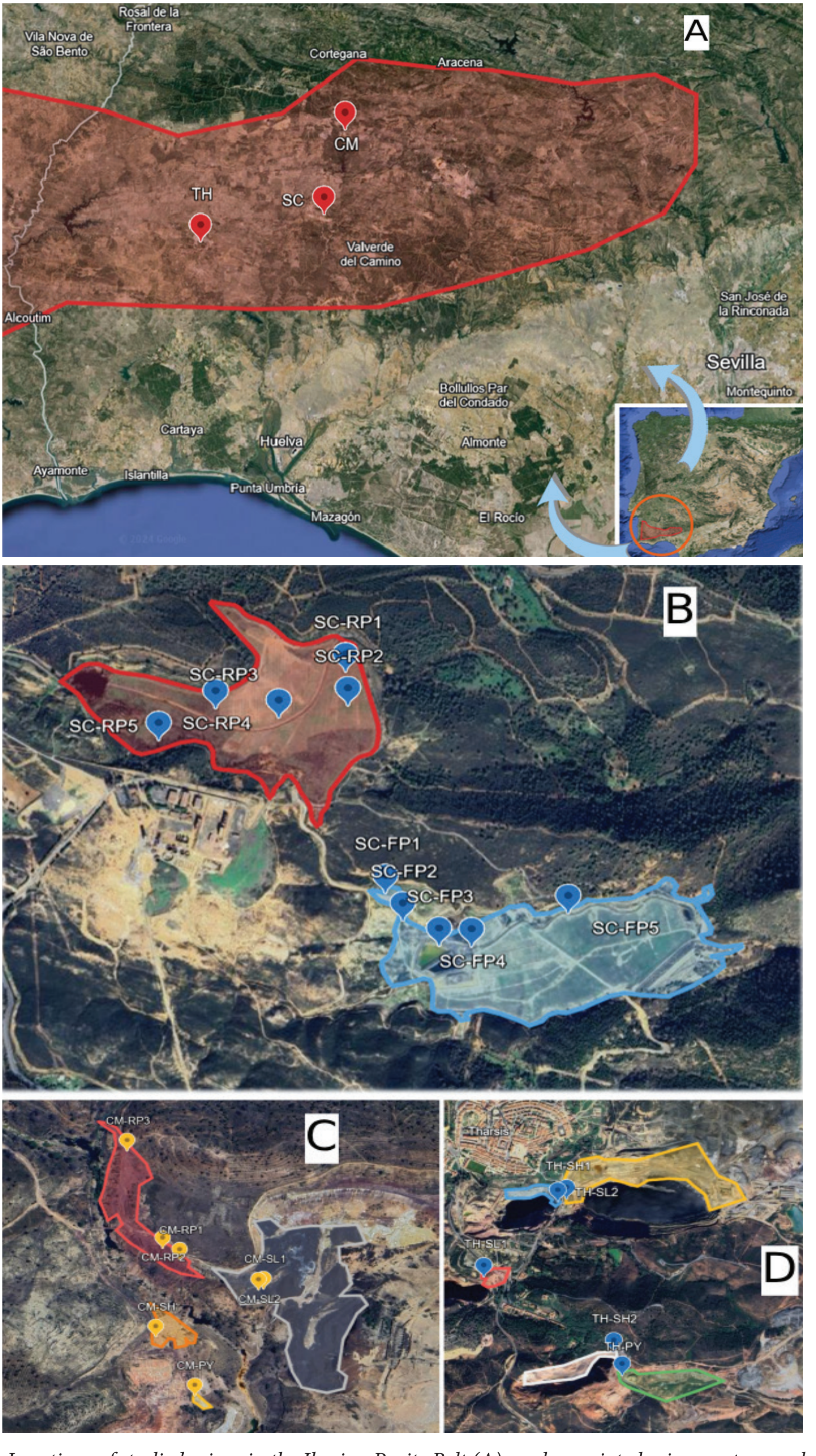


Figure 1 *Locations of studied mines in the Iberian Pyrite Belt (A), and associated mine waste sample sites at Sotiel Coronada (B), Cueva de la Mora (C) and Tharsis (D). Each colour represents an area with the same type of waste.*

al. 2000). In Fig. 1 can be seen the locations of mines in relation to the IPB and associated samples.

Regarding the methodology, first the most characteristic waste piles in the area were sampled. One sample (1 kg) was taken per mound, but in case the extent was too large, several samples were taken from that area for better comparison. The mining wastes were collected subsurface with a shovel, eliminating the upper 5 cm most affected by weathering. The samples were stored in hermetically sealed bags. Subsequently, pre-treatment (drying, milling…) and the measurement of physicochemical parameters were carried out. Afterwards, multi-elemental analysis was carried out by ICP-MS/ICP-OES & XRF and radionuclide concentrations measurement by alpha and gamma spectrometry. Radiological risk indices (Ra_{eq}, Hex, Hin and Ic; Eke *et al.* 2024 ; Paschoa & Steinhäusler 2010) were also calculated. Quality control was applied through blanks, replicates, certified reference samples (IAEA-375 & IAEA-327) and inter-comparisons.

Results

The average concentrations of the major elements in percentage are shown in Fig 2. Each residue has characteristic concentrations for each element. The main elements are Fe, Si and Al. The leached pyrites and flotation residues have a high sulfur content, 3-4 orders of magnitude higher than undisturbed soil. The pyritic waste could generate a possible environmental impact from acid mine drainage (AMD) (Moreno-González *et al.* 2022). Also, all wastes have concentrations 3-4 orders of magnitude above typical soil in metals/metalloids such as As, Cu, Zn and Pb, which could lead to high toxicity (Álvarez-Valero *et al.* 2009).

The mean values of natural radionuclide activity concentrations for different wastes are shown in Fig 3 and Fig 4. For the ^{238}U series, it can be seen that there is secular equilibrium between the radionuclides, and that each waste has distinctive activity concentrations, with slag and leached pyrites having the highest activity concentrations. The observed values for the waste are consistent with those of typical soil (^{238}U: 26-82 Bq/kg ; Monty 2001). For the ^{232}Th decay series and for ^{40}K the same conclusions can be applied, distinctive values for each residue are those expected for undisturbed soil (^{232}Th: 11-84 Bq/kg; ^{40}K: 25-1650 Bq/kg; Charles 2001).

The radiological risk indices calculated were radium equivalent activity (Ra_{eq}), the external (H_{ex}) and internal (H_{in}) radiation indices and the activity concentration index for building materials (Ic) (Fig 4). These are defined by the expressions (Eke *et al.* 2024; Paschoa & Steinhäusler 2010):

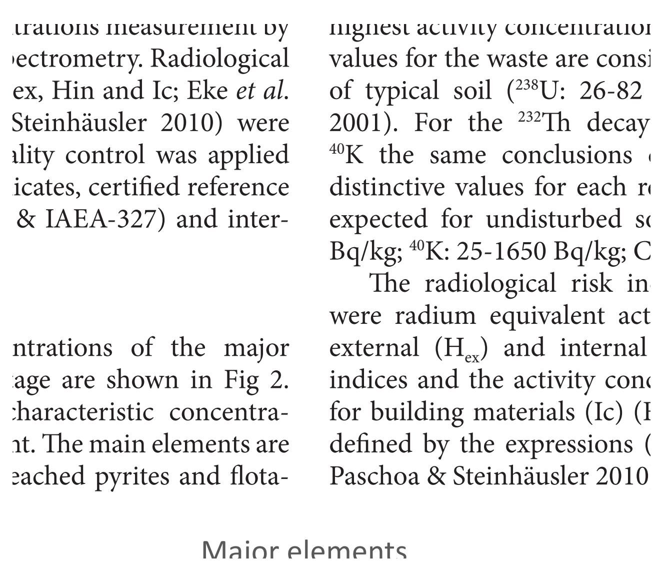


Figure 2 Average concentrations in percentage of the major elements of pyrite flotation (FP), pyrite roasting (RP), smelting slags (SL), leached pyrite (PY) and shale rejects (SH).

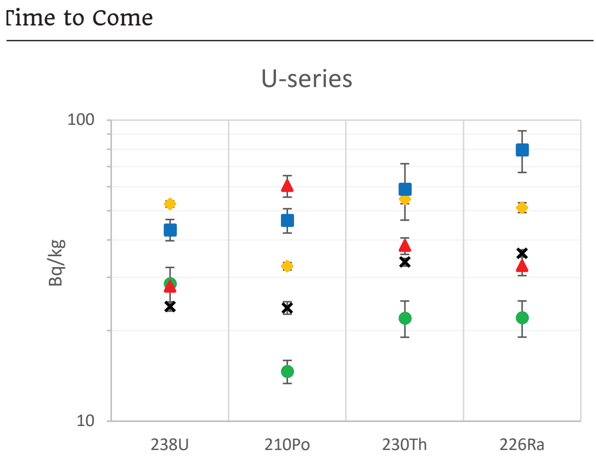


Figure 3 ^{238}*U series activity concentrations of pyrite flotation (FP), pyrite roasting (RP), smelting slags (SL), leached pyrite (PY) and shale rejects (SH).*

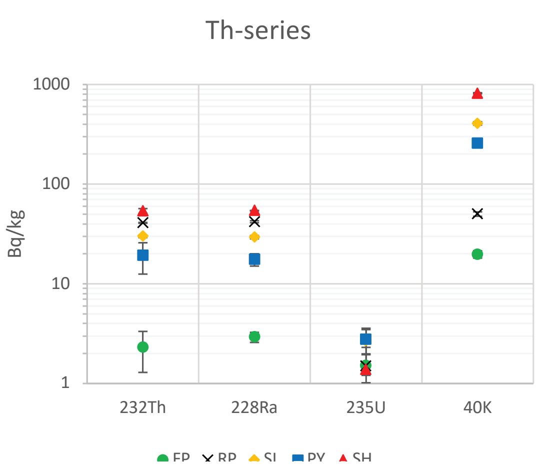


Figure 4 ^{232}*Th series and* ^{40}*K activity concentrations of pyrite flotation (FP), pyrite roasting (RP), smelting slags (SL), leached pyrite (PY) and shale rejects (SH).*

$$Ra_{eq}\,(Bqkg^{-1}) = C_U + 1.43C_{Th} + 0.077C_K \quad (1)$$

$$H_{ex} = \frac{C_U}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (2)$$

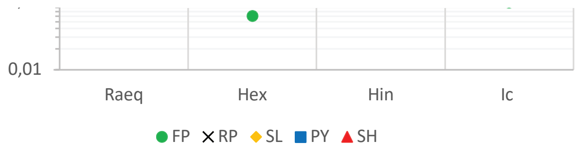
$$H_{in} = \frac{C_U}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (3)$$

$$I_C = \frac{C_{Ra}}{300} + \frac{C_{Th}}{200} + \frac{C_K}{3000} \quad (4)$$

where C_U, C_{Th}, C_K and C_{Ra} are the activity concentrations of ^{238}U, ^{232}Th, ^{40}K and ^{226}Ra respectively in Bq/kg. The Ra_{eq} values obtained are less than 370 Bq/kg, so they can be marketed in the USA. The H_{ex} and H_{in} values are below the limit value 1, so they do not pose a radiological risk (Eke *et al.* 2024). Likewise, the Ic being less than 1 in all samples, they can be used as building materials without radiological restrictions (Santos *et al.* 2022).

Conclusions

A multi-elemental analysis of different mining wastes from 3 mines located in the FPI: Sotiel Coronada, Cueva de la Mora and Tharsis has been carried out, with the following conclusions:



ues of radiological risk indices Ra_{eq} (Bq/kg), H_{ex}, H_{in} and I_c for pyr
melting slag (SL), leached pyrite (PY) and slate rejects (SH).

concentrations 3-4 orders
above typical soils for
ds with high toxicological

tes have been radioactively
with results for activity

Eke, B. C., Akomolafe, I. R., Uk
Onyenegecha, C. P. (2024). Asses
Hazard Indices Due to Natural
Soil Samples from Imo State U
Nigeria. Environmental Healt
11786302231224581.

Figure 5 *Average values of radiological risk indices Ra_{eq} (Bq/kg), H_{ex}, H_{in} and I_c for pyrite flotation (PF), pyrite roasting (RP), smelting slag (SL), leached pyrite (PY) and slate rejects (SH).*

1. All wastes have concentrations 3-4 orders of magnitude above typical soils for metals/metalloids with high toxicological implications.
2. The mining wastes have been radioactively characterised, with results for activity concentrations of natural radionuclides in the range for typical Spanish soils.
3. The calculated radiological risk indices demonstrate that the wastes do not pose a radiological risk.
4. Finally, these wastes comply with the Spanish regulations required for gamma radiation emitted as construction materials.

Acknowledgements

This work has been supported by the project "Diagnosis and proposals for the environmental recovery of areas affected by industrial and mining activities; Implications for the Huelva estuary" (RESTOREHU), Ref.: TED2021-130361B-I00.

References

Almodóvar, G. R., Yesares, L., Sáez, R., Toscano, M., González, F., & Pons, J. M. (2019). Massive sulfide ores in the Iberian Pyrite Belt: Mineralogical and textural evolution. Minerals, 9(11), 653.

Álvarez-Valero, A. M., Sáez, R., Pérez-López, R., Delgado, J., & Nieto, J. M. (2009). Evaluation of heavy metal bioavailability from Almagrera pyrite-rich tailings dam (Iberian Pyrite Belt, SW Spain) based on a sequential extraction procedure. Journal of Geochemical Exploration, 102(2), 87-94.

Eke, B. C., Akomolafe, I. R., Ukewuihe, U. M., & Onyenegecha, C. P. (2024). Assessment of Radiation Hazard Indices Due to Natural Radionuclides in Soil Samples from Imo State University, Owerri, Nigeria. Environmental Health Insights, 18, 11786302231224581.

Charles, M. (2001). UNSCEAR Report 2000: sources and effects of ionizing radiation.

Moreno-González, R., Macías, F., Olías, M., & Cánovas, C. R. (2022). Temporal evolution of acid mine drainage (AMD) leachates from the abandoned tharsis mine (Iberian Pyrite Belt, Spain). Environmental Pollution, 295, 118697.

Paschoa, A. S., & Steinhäusler, F. (2010). legal Aspects of natural Radiation. In Radioactivity in the Environment (Vol. 17, pp. 141-151). Elsevier

Santos, Á. M., Teresa, L. C. A., Llácer, J. M. M., Romero, M. I., Manjón, M. D. M. P. P., & del Llano, S. L. L. Real Decree 1029/2022 of 20 December, approving the Regulation on health protection against the risks arising from exposure to ionising radiation: Questions and answers?

Tornos, F., Barriga, F. J. A. S., Marcoux, E., Pascual, E., Pons, J. M., Relvas, J. M. R. S., ... & Blundell, D. (2000). The Iberian pyrite belt. Database on Global VMS Districts, Codes-Geode, 19-52.

Yesares, L., Sáez, R., Nieto, J. M., De Almodovar, G. R., Gómez, C., & Escobar, J. M. (2015). The Las Cruces deposit, Iberian Pyrite Belt, Spain. Ore Geology Reviews, 66, 25-46.