Sulfide-Rich Waste Classification Using a Fast and Cost-Effective Reactivity Index

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Abstract

Mining operations pose a major challenge in terms of environmental pollution, mainly due to weathering processes that lead to the formation of acid mine drainage, resulting in extensive degradation of aquatic ecosystems. This study presents a practical approach to evaluate the reactivity of mining waste accumulations at the São Domingos mine within the Iberian Pyrite Belt. The approach aims to establish an easily obtained in-field index for classifying mine wastes based on their acid-generating potential, as indicated by the paste pH. The classification ranges from non-reactive (paste pH > 5) to highly reactive (paste pH < 3). The results show a clear correlation between waste properties, expressed by their reactivity, and water hydrochemistry. Thus, this research aims to provide valuable insight into a globally recognized problem and to assist regulators in the timely and cost-effective identification of contamination in the field.

Keywords: Mining wastes, paste pH, cost-effective reactivity index, São Domingos, Iberian Pyrite belt

Introduction

Mining exploitations represent a serious problem of environmental contamination. One example is sulfide extraction, associated with deposits of metals and coal that generate large amounts of waste, typically stored in piles around the mine (Lottermoser 2010; Gomes et al. 2024). In this situation, acid mine drainage (AMD) is formed, producing acidity and sulfate and releasing potentially toxic elements (PTE) into the environment, promoting the complete degradation of the water ecosystem (Nordstrom et al. 2015). The waste found in piles is often moved, given its usefulness for some applications. In other words, the current location results to *a certain extend of the existence of transport and not to its original site*. The primary aim of this study is to present a methodology for classifying mine waste deposits at the São Domingos Mine according to their reactivity. This approach facilitates a straightforward classification of the waste accumulations, relying on assessing paste pH. Although there are numerous static and kinetic tests to perform the acid-base account characteristics of rock and waste samples (e.g. Price and Kwong 1997; Morin and Hutt 2001), the paste pH is widely recognized as a reliable indicator of the acid-generating potential inherent in sulfide-rich waste materials (Weber et al. 2006).

The São Domingo Mine was closed in 1966 without remediation measures. It is in the Iberian Pyrite Belt (IPB)), known as one of the largest metallogenic provinces in the world, and represents a typical mining contamination scenario without complete remediation to date. Mobilizing more than 20 Mt of materials, fresh and acidic water reservoirs, and land sterilized by metallurgical processing dictated the radical alteration of 296 ha of the 6000 ha comprising the mining complex (Gomes et al. 2022). Nowadays, numerous waste dumps from different mining periods (from the Roman times until the XX century) are dispersed along the entire mining complex. The wastes present high variability in gran size and lithological composition, which controls their reactivity and, consequently, their contaminant potential. Thus, the present work intends to contribute in-depth knowledge of an issue known to affect worldwide and assist the competent authorities in quickly and inexpensively identifying major problems to implement best practices for water resources and environmental protection in old mining areas.

Methods

The methodological protocol was based on the waste characterization performed at the end of 2017. The procedures contemplate field surveys, sampling (fig. 1), and determination of the paste pH and EC in a suspension of 1:2.5, following the procedure described by Sobek et al. (1978) for several samples and replicates. Multi-parameter equipment (Thermo Scientific Model Orion Star A Series) was used for *in situ* measurements. The following Orion probes were used: combined pH/ATC electrode Triode ref. 91-07WM and a conductivity cell DuraProbe ref. 013010. This procedure was accompanied by petrographic and mineralogical analyses (x-ray diffraction) of the samples collected in the waste accumulations. Also, secondary minerals and acidophilic algae were used as indicators of acidity. In addition, pH, EC, and redox potential (Eh) were measured in the receiving watercourse. Samples were georeferenced using Garmin GPSMAP 76CSx. Topographic map 559-Santana de Cambas (1:25000), aerial photographs, and the QGIS 2.12 software will assist in further spatial modeling.

Results and discussion

The results reveal that the total area occupied by waste of different types, ages, and compositions is 145 ha: 30% of the area (70 ha) is in waste dumps; in landfills, the largest portion of the area (33%, in a total of 71 ha) is occupied by waste, slag, old precipitates, and Fe oxides-rich materials. Table 1 summarizes the results obtained regarding the general properties of the accumulation areas and the respective reactivity index obtained through the paste pH. These results show that the amount and type of sulfides control this pH, which is expressed through the respective reactivity index. The proposed classification based on the pH of the paste of the materials analyzed defined four ranges areas: very reactive (paste pH < 3.0); reactive (paste pH 3.0–3.5); low reactive (paste pH 3.5–5.0); non-reactive (paste pH > 5.0). The different types of materials were related to their respective reactivity indices.

Contaminated areas far prevailed over non-contaminated areas. Based on the reactivity index and other indicators (e.g. the presence of saline efflorescence) (fig. 2), it was possible to identify the landfills with the greatest contaminating potential. They are essentially in the North sector of the mining complex (in the vicinity of the pit lake) and in the industrial area of Achada do Gamo (PAT7), in line with the results obtained for hydrochemistry (lower pH was

Figure 1 *Picture depicting the sampled material macro characteristics as detected in the field*

***Table 1** The general properties of landfills were analyzed, emphasizing the different degrees of contamination. LF: Landfill; C: contaminant; NC: not contaminant; nd: not determined; AWS: acid water stream; Py: pyrite; Jrs: jarosite. +++ very reactive (paste pH < 3.0); ++ reactive (paste pH 3.0–3.5); +little reactive (paste pH 3.5–5.0); - non-reactive (paste pH > 5.0). Adapted from Cordeiro et al. (2017).*

LF	Area (ha)	C or NC	pH paste	Reactivity Index	EC paste	General properties
A1	14.6	C	2.59–3.07	+++ ++	6.92 - 7.21 mS/cm	Heterogeneous granulometry of various origins: tailings, wastes from smelted ore, remains of old precipitates, and iron oxides. There is strong evidence of acidity, like salinization (Al-Fe and Mg-Cu sulfates, mainly at the landfill base) and filamentous algae. There is abundant jarosite as a cover over the rock fragments. Fragments of jasper were also identified.
A2	2.15	NC	> 5	–	n.d.	Fine to very fine materials from metallurgical treatment.
A3	1.37	C	3.27	++	10.97 mS/cm	Very heterogeneous granulometry, predominance of highly oxidized material, strong red color. Features like the oxidized material of E9.
A4	3.42	NC	> 5	–	n.d.	Very heterogeneous material (volcanics and shales) and granulometry, not calcined, very high degree of revegetation.
A5	3.31	C	2.71–2.86	+++	2.05 - 2.32 mS/cm	At the western boundary of this landfill, there is the formation of a depression where the accumulation of very fine sediments is observed, with a fine, beige color deriving from transport.
A6	1.92	C	2.51	+++	7.70 mS/cm	Fine sediment deriving from the leaching of the surrounding landfills, providing the accumulation of fine material. The contaminant character is evidenced by corrosion phenomena and the presence of supergenic neoformations, namely jarosite / Fe sulfates, besides the pH of the paste and the finer residues.
A7	7.71	NC	> 5	–	n.d.	Shale and gossan fragments with variable granulometry.
A8	2.71	NC	> 5	–	n.d.	Fragments of volcanics and shales with variable granulometry.
A9	3.49	C	3.35	++	297 µs/cm	Predominantly, fragments of shale nature sporadically occur in large mineralized blocks that show signs of incipient oxidation and sanitization.
A10	10.09	C	3.05–3.31	++	595 - 1525 µs/cm	Similar characteristics to A1: heterogeneous granulometry and diverse origins. There are also recent precipitates, but there are scattered accumulations of old slag and a greater proportion of rocks with iron oxides, variable granulometry, and a greater proportion of shales.
A11	0.28	C	2.14	+++	12.050 µS/cm	Washed pyrite, fine granulometry, occurs covering the debris deposited below (A10).
A12	1.76	NC	> 5	–	n.d.	Shales, medium particle size, non reactive, without vegetation.
A13	6.58	NC	> 5	–	n.d.	Similar characteristics to A12, shale material, medium particle size, non-reactive, without vegetation.

0.80, in dry period) (Gomes et al. 2022). The EC, when measured, was inversely proportional to the pH of the paste, as expected. So, this approach confirms the great influence of the materials' geogenic characteristics in the surrounding area and the influence of their composition on the mineral-water interaction (Wolkersdorfer et al. 2020). A table (Table 1) was drawn up describing the main characteristics of the accumulations of waste scattered throughout the mining complex. Drainage from the most reactive areas is responsible for the worst contamination scenario observed in the watercourse, as referred by Cordeiro et al. (2017).

Conclusion

The approach presented in this work was applied to the waste accumulation of one of the largest mining complexes in the IPB (São Domingos Mine). The different waste accumulations, which were very different in composition, were classified in terms of their acid-generating potential, here used as an estimation of reactivity. The easily obtained index allowed a practical and inexpensive classification of waste accumulation areas based on paste pH, confirming the influence of the nature of the waste in the surrounding area. Composition, amount and type of sulfides, and particle size are relevant properties for the reactivity index. Consequently, the reactivity index of the waste controls the contamination potential reflected in the receiving water.

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References

Cordeiro M, Valente T, Grande JA, Gomes P (2017) Mapping mining wastes and analyzing affected areas through expeditious physico-

Figure 1 a) North view of landfill A1 highlighting the presence of saline efflorescences of sulfates (Al/Fe and Mg/Cu) at the landfill's base; b) General view of the A11 landfill composed predominantly of washed ore. Note the typical grey color with salt coverage; c) structures resulting from erosion in fairy chimneys; d) Abundance of sulfate blooms and filamentous acidophilic algae.

chemical parameters. XII Congreso Nacional de Geoquímica / XI Congreso Ibérico de Geoquímica, Linares, 26 a 28 de Setembro, p 178-183.

Gomes P, Valente T, Marques R, Prudêncio M, Pamplona J (2022) Rare earth elements - Source and evolution in an aquatic system dominated by mine-Influenced waters. J.Environ. Manage. Volume 322,116125, ISSN 0301-4797. https://doi.org/10.1016/j.jenvman.2022.116125.

Gomes P, Valente T (2024) Seasonal impact of acid mine drainage on water quality and potential ecological risk in an old sulfide exploitation. Environ. Sci. Pollut. Res., https://doi.org/10.1007/s11356-024-32367-1

Lottermoser B (2010) Mine wastes – characterization, treatment and environmental impacts. Springer, 3rd edition, Berlin, 400p.

Morin KA, Hutt NM (2001) Environmental geochemistry of minesite drainage: Practical theory and case studies, Digital Edition. MDAG publishing, Vancouver.

Nordstrom K, Blowes DW, Ptacek CJ (2015) Hydrogeochemistry and microbiology of mine drainage: an update. J. Appl. Geochem., 57:3–16.

Price WA, Kwong YTJ (1997) Waste rock weathering, sampling and analysis: Observations from the British Columbia Ministry of Employment and Investment database. p. 31 – 45. In: Proceedings of the Fourth International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Inc. (SME), Vancouver.

Weber P, Hughes JB, Conner LB, Lindsay P, Smart RStC (2006) Short-term acid rock drainage characteristics determined by paste pH and kinetic NAG testing: Cypress Prospect, New Zealand In: 7th International Conference on Acid Rock Drainage (ICARD), March 26–30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502. https://doi.org/10.21000/JASMR06022289

Wolkersdorfer C, Nordstrom DK, Beckie RD, Cicerone DS, Elliot T, Edraki M, Valente T, França SC, Kumar P, Oyarzún Lucero RA, Soler I, Gil A (2020) Guidance for the Integrated Use of Hydrological, Geochemical, and Isotopic Tools in Mining Operations. Mine Water Environ 39: 204–228. https://doi.org/10.1007/s10230-020-00666-x