



Characterization and Modeling of Acid Mine Drainage in a Highly Acidic Stream (Trimpancho Mining Complex, SW of Spain)

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Abstract

The Trimpancho mining complex is a group of abandoned mines affected by acid mine drainage. The present work was focused on studying the hydrochemical behavior of the receiving stream and the secondary phases associated with potential natural attenuation processes. The results indicate extreme acidity conditions, with pH in the range of 1,97 to 2,87. At the time of the sampling campaign, no clear spatial distinction was observed in relation to the different sources of acid mine drainage. Several secondary minerals were identified, mainly close to the waste dumps or suspended in the watercourse. Besides the ability to immobilize pollutants through precipitates, this abandoned area requires rehabilitation as it still has a high environmental risk of water contamination.

Keywords: Physicochemical characterization, secondary minerals, modeling, saturation index, Iberian Pyrite Belt

Introduction

Acid mine drainage (AMD) is one of the most severe environmental problems worldwide without an efficient solution. This ecological problem leads to water acidification and potentially toxic elements mobilization, contaminating surface waters (Nordstrom 1982) and promoting precipitation of newly formed minerals. The secondary phases, regulated by thermodynamic equilibrium conditions, influence the fate and transport of pollutants (Basallote et al. 2019; Yolcubal et al. 2023). Therefore, these phases can be part of the solution due to their natural attenuation implications. However, the metallic and acidity attenuation can be temporary, especially for the sulfate salts, since the climate conditions control their formation (Hammarstrom et al. 2005). Thus, knowledge about the role of secondary products as drivers of natural attenuation is needed to assess the ecosystems' resilience to AMD. Metallogenic provinces that are highly

contaminated, such as the Iberian Pyrite Belt (IPB) in southwest Europe, are key sites to study the processes and effects of AMD, its evolution, and the fate and transport of pollutants in the ecosystem.

The present study was focused on (i) determining the hydrochemical spatial evolution in a highly acidic system in the IPB and (ii) understanding the relationship with the secondary mineral phases controlling the formation of AMD and metal cycling. This mineralogical characterization was accompanied by geochemical modeling that simulated precipitation and dissolution processes for the Trimpancho mining complex data.

Methods

The Trimpancho mining complex (fig. 1) is in the extreme west of the Spanish sector of the IPB, one of the largest metallogenic provinces in the world (Inverno et al. 2015). It is characterized by massive sulfide deposits

(VMS), with pyrite, sphalerite, chalcopyrite, galena, arsenopyrite, and sulfosalts. In the IPB, crossing the border between Portugal and Spain, AMD is a long-lasting problem due to the large number of abandoned mines with wastes exposed to weathering (Gomes et al. 2018). The Trimpancho complex is characterized by four abandoned medium-sized mines: Volta Falsa (VF), Trimpancho Group (TG), La Condesa (LC), and Nuestra Señora del Carmen (NSC) (Grande et al. 2017). The leachates associated with the sulfide-rich wastes drain into the Trimpancho River, a tributary of the Chança River (fig. 1), where a water dam is used for human supply (Chança dam).

A sampling campaign was performed at the end of the winter season (February 2022) with a collection of surface water and secondary mineral phases (efflorescent salts and ochre materials). Seventeen sampling sites were established in the Trimpancho River (fig. 1), from a point located a few meters before the waste dump of Nuestra Señora del Carmen mine (TS), representing the hydrochemical background, until the confluence with the Chança River (CR_Plume). Therefore, CR_Plume is a sampling site where Trimpancho and Chança River waters mix. The other locations represent open pits and the watercourse affected by AMD. In the Trimpancho stream, the water samples were collected immediately upstream and downstream from each mine waste dump to evaluate leachate's effects on the systems' physical-chemical parameters.

Water parameters like pH and electrical conductivity (EC) were measured *in situ* with a multiparameter (Thermo Scientific Model Orion Star A Series) combined with a pH electrode triode (Orion 9107BNM) and conductivity cell (Orion 01310MD). Redox potential (Eh) was analyzed using an ORPTestr 10. Acidity and sulfate were obtained using volumetric titration and turbidimetry methods (Standard method 2310 B and 4500- SO₄ -2 E). Metals and arsenic were analyzed by inductively coupled plasma mass spectrometry in filtered and acidified aliquots until pH < 2. Iron speciation was obtained using the Standard 3500 D-phenanthroline method. The accuracy of the methods was verified using certified reference materials, and the precision was within the relative standard deviation (RSD) of 5% for all methods.

Mineral samples were stored in closed vessels and transported to the laboratory for mineralogical and chemical characterization. Air temperature and humidity were measured at each sampling site with HANNA digital Thermo-hygrometer HI9564 and probe HI 70602. X-ray diffraction (XRD), Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and Fourier-transform infrared spectroscopy (FTIR) were used to characterize minerals phases. Mineralogical identification was obtained with a Philips PW1710 (APD-version 3.6 j) diffractometer, with CuK α radiation at 40 kV and 30 mA. XRD spectra were processed with the X'pert Pro-MPD software.

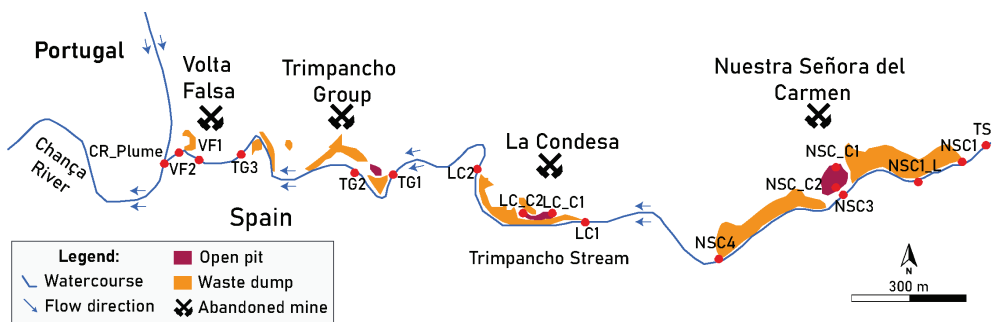


Figure 1 Location of the sampling network defined in the Trimpancho mining complex (adapted from Grande et al. 2017)

Morphological and compositional features were analyzed by SEM-EDS using the VP SEM Hitachi S - 3400N. FTIR measurements of the samples were carried out using a PerkinElmer Spectrum Two spectrometer equipped with an ATR accessory. All spectra were recorded with a resolution of 4 cm⁻¹ in the wavelength region 4000-400 cm⁻¹ by averaging 16 scans. Geochemical modeling of precipitation reactions of the water samples was conducted using PHREEQC code (version 3.7.3.15968) (Parkhurst and Appelo, 1999) with the WATEQ4F database (Ball and Nordstrom, 1991).

Results and discussion

Table 1 shows the physical-chemical parameters analyzed along the river system (fig. 1). Overall, the water samples in contact with the leachates from the waste dumps exhibit extreme acidity conditions, with pH in the range of 1,97 to 2.87, except for the NCS1_L. This is a point of water mixing from a pristine tributary of the Trimpancho, leading to the pH increase to 4.85. TS and CR_plume water

points have neutral pH values of 7.48 and 7.28, respectively. Sulfate concentration reached high values in the contaminated samples (between 666 mg/L and 171 639 mg/L) and much lower concentrations in the clean and mixing waters (20.4 mg/L and 51.17 mg/L, respectively). EC and acidity behave similarly to the sulfate concentration, while Eh shows the same range of values for all the sampling sites.

The spatial evolution suggests the closest relation of hydrochemistry with the type of water environment rather than the mining groups, contrary to the tendency described by Grande et al. (2017). Figure 2A shows this trend since the samples with the most substantial mining influence are grouped and separated from the mixing water and background samples (NSC1_L, CR_Pume, and TS). Moreover, in Figure 2B, besides NSC1_L (mixing water site), the NCS1 is also separated from the group because it is an extremely acidic and sulfated water. This sample was collected in a puddle of stagnant leachates at the base of the waste dump, while

Table 1 Physicochemical proprieties of the AMD water collected in the Trimpancho mining complex

	pH	EC μS/cm	Eh mV	T °C	Sulfate mg/L	Acidity mg/L CaCO ₃	Alkalinity mg/L CaCO ₃
TS	7.28	481	488	12,8	20.4	---	130.5
NSC1	2.87	51 260	535	10,2	171 639	125 250	---
NSC1_L	2.62	2 916	452	15,5	846	22	---
NSC_C1	2.54	7 682	686	13,7	5 870	2 890	---
NSC3	2.52	6 718	616	8,3	4 278	2 080	---
NSC_C2	2.55	7 659	695	14,3	5 781	2 880	---
NSC4	2.46	9 144	644	15,3	6 211	2 970	---
LC1	2.37	9 959	671	14,1	7 510	3 565	---
LC_C1	2.30	9 790	692	14,8	9 405	6 645	---
LC_C2	2.45	9 850	699	13,6	9 263	6 825	---
LC2	2.30	9 471	652	15,6	7 387	3 515	---
TG1	2.49	5 492	636	11,5	3 484	1 517	---
TG2	2.70	8 656	664	10,8	6 354	3 046	---
TG3	2.50	4 599	622	15,3	3 455	1 645	---
VF1	4.85	4 592	624	13,4	3 426	1 655	---
VF2	1.97	3 261	447	14,6	666	238	---
CR_PLUME	7.48	416	623	15,6	51.2	---	100.5

the rest of the sampling points had water flow. The As concentration is higher than the detection limit for the samples collected at the open pits and NSC1 (fig. 2C). Regarding the Fe speciation, Fe³⁺ is the dominant ion, except for the NSC1 sample. At this sampling site, Fe²⁺ and Fe³⁺ have identical values (16818 mg/L and 15582 mg/L, respectively).

In the field, secondary minerals were found, mainly at the base and cavities of the waste dumps or in suspension in the riverbed (fig. 3 A-C). Powdery or globular aggregates and small particles with different colors (white, greenish, brownish, and yellow) were some of the macroscopic aspects observed during sample collection. The results of mineralogical analyses are presented in Figure 3 D-F. The secondary phases identified along the system are listed in Table 2. Figure 3 C illustrates the NSC1_L sampling site, where a white precipitate is observed in the watercourse, possibly indicating the presence of aluminum sulfate (Basaluminite). However, the FTIR spectrum only shows the typical vibration bands of SO₄²⁻ (611, 984, and 1072 cm⁻¹), OH⁻ (3301 cm⁻¹) groups, and H₂O (1673 cm⁻¹) (fig. 3F) (Lu et al. 2021).

Saturation indices of precipitating minerals were predicted using PHREEQC (fig. 4).

The model indicates oversaturation of jarosite for the NSC and LC mining groups. Still, jarosite was also founded in the TG group. Basaluminite has oversaturation indices at the mixing water (NSC1_L and CR_Plume) and background (TS) sites. However, the mineralogical identification could not be obtained. The model also predicts undersaturation relative to melanterite and epsomite for all the sampling points. However, these mineral phases were identified predominantly in the NSC waste dump. Discrepancies between observed and modeled results can be explained by the microenvironments of the temperature/evaporation conditions experienced in the mining areas.

Conclusions

The Trimpancho mining complex shows the typical characteristics of an abandoned mining area with intense AMD problems. The results suggest the dynamic behavior of this highly acidic environment. For example, despite being composed of several waste dumps with different paragenesis, no relevant differences were detected in hydrochemical patterns as described by a previous study (2017). This distinction can be explained by

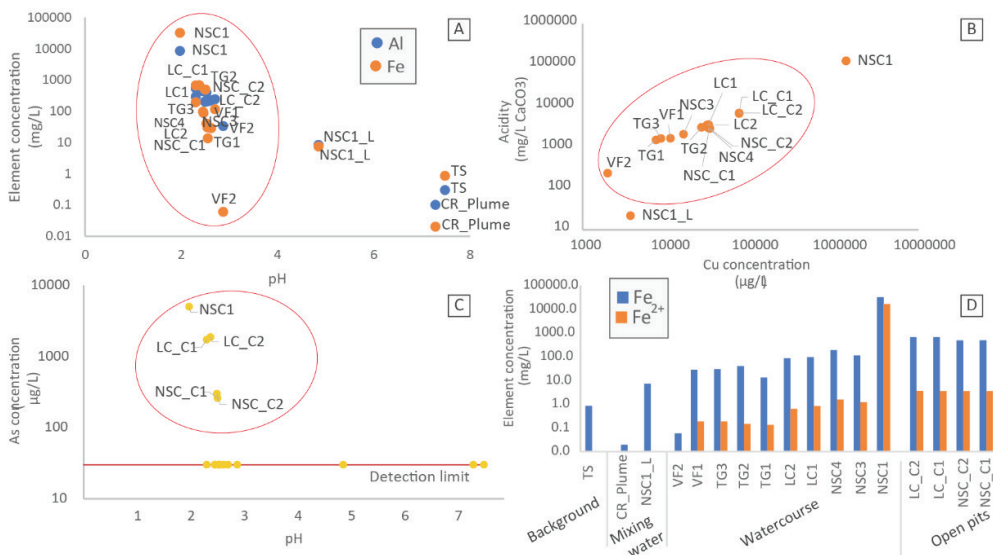


Figure 2 Hydrochemical relationships for the 17 sampling points. (A) – relationship between pH and the Fe and Al; (B) – relationship between Cu and acidity; (C) – relationship between pH and As; (D) – Fe speciation

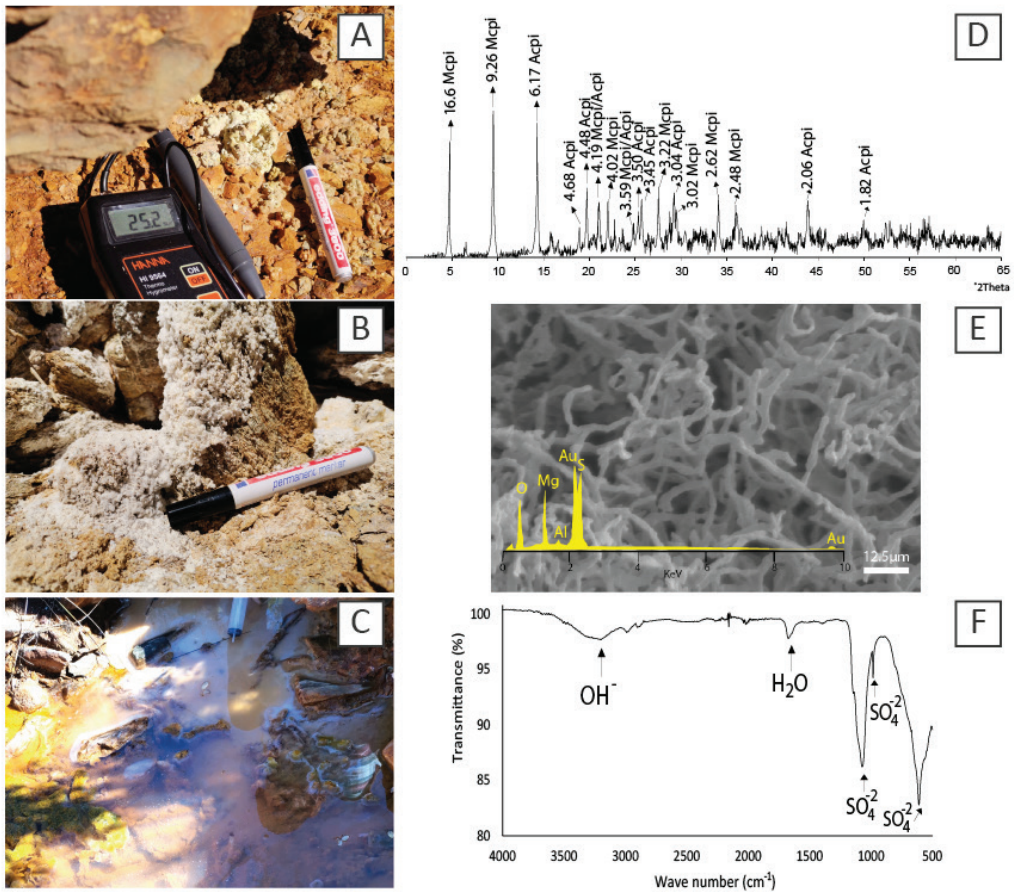


Figure 3 (A-C) - Example of mineral phases observed in the Trimpancho mining complex; (D) - XRD pattern of a yellow aggregate composed of magnesiocopiapite and aluminocopiapite; (E) - SEM-EDS analysis of a white powdery aggregate composed by epsomite, hexahydrate, and rozenite; (F) - FTIR analysis of amorphous aluminum sulfate

Table 2 Secondary minerals identified in the Trimpancho mining complex

Mineral	Formula
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Rozenite	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
Copiapite	$\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Magnesiocopiapite	$\text{MgFe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Aluminocopiapite	$\text{Al}_{2/3}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
Halotrichite	$\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Coquimbite	$\text{AlFe}_3(\text{SO}_4)_6(\text{H}_2\text{O})_{12} \cdot 6\text{H}_2\text{O}$
Jarosite	$\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$

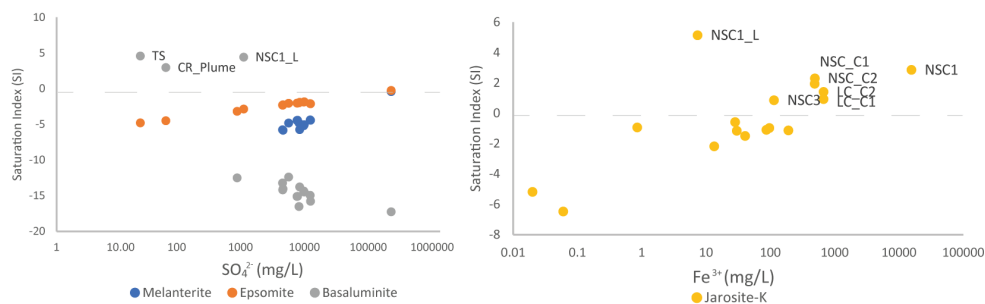


Figure 4 Saturation indices of AMD solutions obtained by PHREEQC and WATEQ4F database

the meteorological conditions experienced during the sampling periods of each work, since in 2022, the Trimpancho River had low flow, and sometimes the watercourse was dried or with stagnant water.

Several secondary minerals that precipitate from the mine leachates were identified. They can act as a sink of potentially toxic elements and other metals in the mining environment. The efflorescence salts observed in the field have a temporary role since they are very soluble minerals that can be dissolved rapidly with humidity variations. In contrast, jarosite is a more stable mineral and more efficient in pollutant immobilization. However, it is to highlight that this area, abandoned for decades, still has a high environmental risk of water contamination.

Acknowledgements

This research was funded by FCT (Fundação para a Ciência e a Tecnologia, Portugal) by the research fellowship under the ICT-UMinho (Institute of Earth Sciences, Pole of University of Minho) supported by FCT, I.P. with reference UI/BD/151330/2021. This work was also co-funded by FCT through projects UIDB/04683/2020, UIDP/04683/2020, UID/QUI/0686/2020, and Nano-MINENV 029259 (PTDC/CTA-AMB/29259/2017).

References

APHA Standard Methods for the Examination of Water and Wastewater, 20th ed.; (2012) American Public Health Association, American Water Works Association, Water Environment Federation: Washington, DC, USA.

Ball, J. W., & Nordstrom, D. K. (1991). User's manual for wateo4f, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. US Geological Survey.

Basallote, M. D., Cánovas, C. R., Olias, M., Pérez-López, R., Macías, F., Carrero, S., ... & Nieto, J. M. (2019). Mineralogically-induced metal partitioning during the evaporative precipitation of efflorescent sulfate salts from acid mine drainage. *Chemical Geology*, 530, 119339.

Gomes, P., Valente, T., & Pereira, P. (2018). Addressing quality and usability of surface water bodies in semi-arid regions with mining influences. *Environmental Processes*, 5, 707-725.

Grande, J. A., Santisteban, M., Valente, T., de la Torre, M. L., & Gomes, P. (2017). Hydrochemical characterization of a river affected by acid mine drainage in the Iberian Pyrite Belt. *Water Science and Technology*, 75(11), 2499-2507.

Hammarstrom, J. M., Seal Ii, R. R., Meier, A. L., & Kornfeld, J. M. (2005). Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. *Chemical Geology*, 215(1-4), 407-431.

Inverno, C., Díez-Montes, A., Rosa, C., García-Crespo, J., Matos, J., García-Lobón, J. L., ... & Sousa, P. (2015). Introduction and geological setting of the Iberian Pyrite Belt. 3D, 4D and Predictive Modelling of Major Mineral Belts in Europe, 191-208.

- Kirk Nordstrom, D. (1982). Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. *Acid sulfate weathering*, 10, 37-56.
- Lu, C., Yang, B., Cui, X., Wang, S., Qu, C., Zhang, W., & Zhou, B. (2021). Characteristics and Environmental Response of White Secondary Mineral Precipitate in the Acid Mine Drainage From Jinduicheng Mine, Shaanxi, China. *Bulletin of Environmental Contamination and Toxicology*, 107(6), 1012-1021.
- Parkhurst, D. L., & Appelo, C. A. J. (1999). User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water-resources investigations report*, 99(4259), 312.
- Yolcubal, I., Doğrul Demiray, A., Çiftçi, E., & Sangu, E. (2023). Role of Secondary Sulfate Minerals on Metal Recycling in an Abandoned Copper Deposit: Kuvarshan (Artvin), Northeastern Turkey. *Mine Water and the Environment*, 1-18.