

Monitoring, Control, and Prevention of Excess Hg in Acid Mine Drainage (AMD) in an Abandoned Metal Sulfide Mine (SW Portugal), using Nature-Based Solutions

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Abstract

This study aims to monitor the behavior of Hg in watercourses drained by a huge pile of tailings in an abandoned mine located in the Iberian Pyritic Belt (IPB), and to test the most effective low-cost technology in retaining Hg. The water collected in two consecutive years from the watercourses showed meaningful values in areas near the tailings (16-28 μ gL⁻¹), above the reference value, 0.3 μ gL⁻¹ (EU Regulation, 2009). Bench scale tests were conducted to evaluate the effectiveness of nature-based materials in retaining Hg by analyzing ion exchange capacity, kinetic tests, and simulating "ponds" containing different proportions of materials vs mine water.

Introduction

Metal Pollution affects all mining sectors, has a combined worldwide economic impact and its impacts can continue for more than 2,000 years (Taylor, 2012). This kind of pollution, in metallic ores, is in general associated with acid mine drainage (AMD), a multi-factor pollution formed from complex chemical, physical, and biological interactions that takes place under ambient conditions in abandoned and active mines (Ighalo *et al.*, 2022). The producing of acid metal-rich waters, their spread in the environment, and the interconnectivity of water systems, has environmentally significant consequences on the delicate and highly vulnerable aquatic systems (Ferreira da Silva *et al.*, 2015), contaminating local surface waters, groundwaters and stream sediments.

In areas impacted by mining of metal sulfides, mercury (Hg) is one of the most critical contaminants in the environment, due to its potential toxicity and the easiness with which it leads to a widespread contamination over a wide area (Sørmo *et al.*, 2022). In water systems, the conversion to more toxic

Hg-forms, as methylmercury (MeHg), is dominated by biotic methylation under anoxic conditions. In this process, sulfur reducing bacteria have been identified as the main methylators (Sørmo *et al.*, 2022), which increases the overall risk of Hg in aquatic environments affected by metallic sulfides mining sites. To avoid this major threat to water systems, the Hg present in acid drainage resulting from the leaching of mining waste must be retained before it reaches groundwater and surface water bodies. This study aims to (1) monitor the spatial and temporal behavior of Hg in the watercourses affected by a huge pile of mining wastes at Caveira Mine (SW Portugal), located in the Iberian Pyritic Belt, and (2) test the most effective technology in retaining Hg, using nature-based materials.

Case Study

The Caveira mine is in South Portugal, in the SW extreme limit of the Iberian Pyritic Belt (IPB), one of the most important metal bearing areas in the world, due to the unusual polymetallic (Cu, Pb, Zn, Fe, As, Sb, Co, Mn)

sulfides concentration (Fig.1) in large and medium sized mineral deposits (Ferreira da Silva *et al.*, 2015). The mine is embedded in Paleozoic formations and the geological sequence is represented from bottom to top by phyllites and quartzites, followed by a volcanic sedimentary complex sequence, hosted of the polymetallic massive sulfide mineralization. It has a long exploitation history that started in the Roman period and past mining activities included pyrite (FeS_2) and Cu extraction. The mine ceased operations in the 1960s and the lack of maintenance of the large volumes of tailings and waste dumps produced by the mining activities (estimated to be higher than 2 Mt), has contributed to its identification as one of the most problematic abandoned mining areas in the IPB, with evidence of intense long-term acid mine drainage (AMD) and other impacts on the surface environment. Rainwater circulates and percolates easily over and through these tailing materials causing significant erosion and transport of debris, harmful compounds and potentially toxic elements (PTE), posing severe environmental problems to nearby soils and waterways of the Sado watershed. Previous studies conducted by Ferreira da Silva *et al.* (2005), reported the occurrence of stable forms of mercury (such as cinnabar and other mercury sulfides) at the

surface around the mine. Different materials deposited along the main streams and in the dump areas trace the historical evolution of ore processing in those sites.

Methods

A total of 49 water samples (18 in 2022 and 31 in 2023) were collected from a grid of 1 km \times 1 km, in small and narrow creeks, that receive the drainage waters from the mine tailing piles, also including points outside the mining activity that represent the background of the area tributaries (Fig. 1). These streams flow to the Grândola Stream, in Sado basin, the second-largest hydrographical basin in Southern Portugal. The samples were taken in two consecutive years (2022–2023) representing different climate scenarios: 2022 reflects a very dry winter with anomalous values in terms of precipitation and temperature, and 2023 a regular rainy winter. Sampling was followed by immediate readings of pH, redox potential, dissolved oxygen (mg/L), conductivity ($\mu S/cm$), resistivity ($K\Omega cm$), total dissolved solids (mg/L), temperature ($^{\circ}C$) and turbidity (NTU), using a portable multi-parameter (Hanna Instruments, HI98494/10) and a turbidimeter (Hanna Instruments HI98713-02). Mercury (Hg) was analyzed in refrigerated samples stored in dark glass

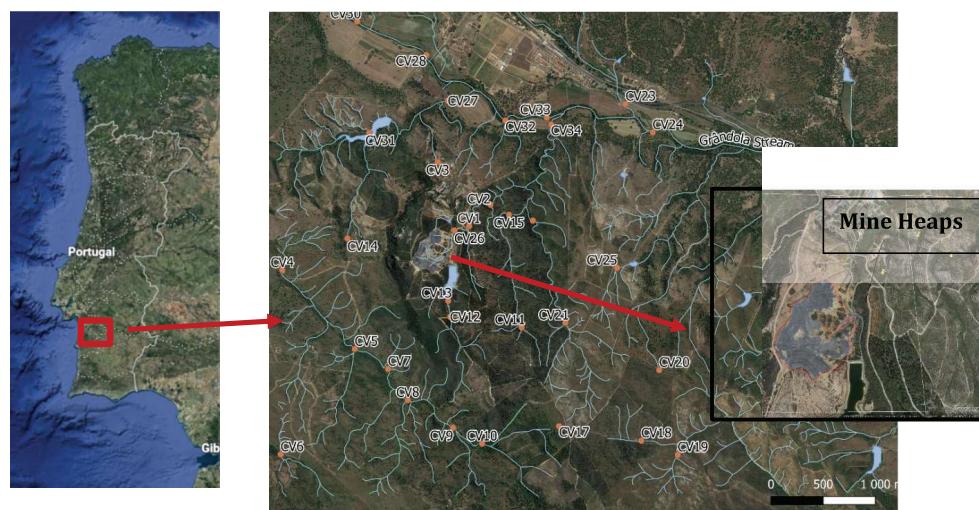


Figure 1 Location of the mine heaps of Cunha and sampling design in the macrocourses affected by the AMD.

containers, using a mercury analyzer (NIC MA-3000) based on thermal decomposition, gold amalgamation, and cold vapor atomic absorption spectroscopy detection. The accuracy and analytical precision of all the analyses were checked through the analysis of reference materials and duplicate samples in each analytical set.

To better control and prevent the excess of Hg found in watercourses, a bench-scale evaluation of the effectiveness of twelve nature-based and waste materials was carried out, considering their retention capacity for Hg. The goal of these tests is to identify the most appropriate materials to be used in the upstream sections of waterways to restore water quality. The selected materials have different mineralogical composition, always following the principle of easy availability and low cost: powders of carbonate rocks (limestone and marble), terra rossa, iron oxides, clays (bentonite and illitic clay with quartz, K-feldspar, kaolinite, goethite), cellulose wastes, acacia biochar, activated carbon from coconut shell in powder and pellets. Before contact with the mining water, all the materials were analysed for: 1) contents of the chemical elements in extractable forms through partial digestion with bi-acid hydrochloric and nitric solution in a high-pressure microwave digester, followed by ICP-OES analyses; 2) determination of their retention capacity by analysing the cation exchange capacity; 3) Hg content. The evaluation of the effectiveness of these materials, included:

1. kinetic tests: The main objective was to determine the rate and capacity of adsorption of excess Hg in mine waters, for each material, and the most suitable chemical and physical conditions for its adsorption. These tests were carried out by shaking each material with a mono elemental solution of the same concentration as the sample with the highest level (CV1: 10mg/L) with a pH adjusted to pH5.5. Each material, in contact with the Hg solution at a ratio of 10g material/1L Hg solution, was placed in an orbital shaker at room temperature in distinct containers corresponding to different time intervals: t_1 -5 min, t_2 -15

min, t_3 -30 min, t_4 -1h; t_5 -2h; t_6 -5h; t_7 -10h and t_8 -24h. At the end of each time interval, the samples were analyzed in the mercury analyzer. Based on the concentrations found, the adsorption capacity of each material was calculated for each element.

2. Simulation of retention ponds: Ponds were simulated in which the 12 natural/waste materials set in laboratory beakers, were covered with water collected in the point closer to the mine heaps (CV1), characterized by critical PTE levels including Hg, and very low pH (pH1.64), in order to evaluate their ability to increase pH, just by being in contact with it for 10 days. The materials were tested individually under the same conditions, varying only two parameters: i) different proportions of materials: mine water (1:50, 1:100, 1:200), ii) different conditions of contact with atmospheric oxygen (direct contact vs. isolation). Throughout the contact period, pH and conductivity were measured daily and the water was analyzed for Hg content after the 10 days of contact with the materials. These values were compared with the actual Hg concentration in the mining water before contact, and the percentage of element removal was calculated.

Results and Discussion

The physicochemical parameters of the water column show slight differences in the two periods (Table 1): a decrease in the lowest pH values is observed at points located nearest the heaps, ranging from 1.10–3.30 during the drier period (2022) and 1.42–4.53 during the wetter period (2023), while an inverse variation pattern is observed in relation to the higher pH values, observed at points further away from the heaps, with the highest values occurring during the wetter period (6.26–8.33). The extreme acidification (pH1–3) rich in metals is typical for the mining areas of the IPB, resulting from the oxidation of metal sulfides, producing metal(loid)s, sulfate ions, sulfuric acids, precipitates of Fe-Al-Ca-Mg (Mn, Co), sulfates and Fe-Al oxyhydroxides (Valente *et al.*, 2013). In the Caveira area, this acidification comes from the leaching



of the tailing piles, which is higher during the rainy season, but with a greater impact in the streams during the driest periods due to the lower dilution effect. This effect is also noticeable in the 2022 campaign, where the waters, especially those closer to the tailings, have higher conductivity values (median: 889 $\mu\text{S}/\text{cm}$) when compared with the values in 2023 (median: 583 $\mu\text{S}/\text{cm}$). The variation of these two parameters reflects the complex interaction between mining wastes and hydrogeochemical conditions, showing a deterioration of the water quality in the drier year 2022, and a leaching and dilution effect in 2023, which slightly improves its quality.

The analysis of metals (Fe, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) in water samples from both periods, carried out in previous studies (Araújo *et al.* in *litt.*), showed that these metals are mainly present in dissolved form. This increases metals mobility in watercourses and, consequently, their bioavailability and environmental hazard. At sampling points near the heaps, elements such as As, Al, Cd, Ni, Mn, Cu, Pb and Zn exceed the regulatory limits established by Portuguese legislation

(Decree-Law No. 236/98), classifying the water as extremely polluted. Concentrations of the more mobile elements, such as As, Cd, Mn, Cu and Zn, are higher during the period of increased precipitation, in the points close to the heaps, due to an extensive leaching and runoff of metals from the waste material.

The Hg levels in the waterways are very similar in both sampling campaigns (2022: 16–18 $\mu\text{g L}^{-1}$, 2023: 26–28 $\mu\text{g L}^{-1}$), following the same distribution pattern, with higher values in areas located near the Caveira waste pile, gradually decreasing with distance. For all the other metals, there is also evidence of a plume migration between the two sampling periods. These results suggest that the large waste dump in the area, rich in metal sulfides, is the main source of pollution affecting these waterways and the entire surrounding area.

The increase of several metals in the water column during the wetter period is also observed in relation to the sediments of the watercourses, especially those closest to the Caveira mine tailings. In these areas, the sediments are classified as contaminated to very contaminated for As, Cu, Pb and Hg,

Table 1 Variation of pH, conductivity and mercury levels in the waters of the waterways affected by the Caveira Mine, in the 2 study periods, 2022 and 2023.

2022				2023			
Samples	pH	Conduct. $\mu\text{S}/\text{cm}$	Hg $\mu\text{g}/\text{L}$	Samples	pH	Conduct. $\mu\text{S}/\text{cm}$	Hg $\mu\text{g}/\text{L}$
CV1	1.23	8250	10,000	CV1	1.58	23.22	27.320
CV2	1.10	8315	15.175	CV2	1.68	19.26	2.19
CV3	3.31	4761	18.185	CV3	4.53	2539	28.310
CV5	6.64	789	11.975	CV4	6.68	816	<0.01
CV10	7.29	490	0.79	CV5	6.73	822	<0.01
CV13	8.33	673	0.17	CV6	6.57	1075	<0.01
CV15	5.76	156	3.665	CV7	6.55	720	<0.01
CV22	8.25	1315	0.45	CV8	6.45	764	<0.01
CV23	6.96	896	0.215	CV9	6.59	748	<0.01
CV24	6.26	1008	0.835	CV10	6.61	573	<0.01
CV26	1.33	85.46	7.985	CV11	5.48	220	3.230
CV27	7.24	1752	0.365	CV12	5.6	91	<0.01
CV28	7.19	870	0.065	CV13	7.04	691	<0.01
CV29	7.45	863	0.78	CV15	5.77	403	<0.01
CV30	7.92	882	0.045	CV16	4.94	935	<0.01
CV31	8.28	749	0.095	CV18	6.21	391	<0.01
CV32	7.23	929	0.055	CV19	6.5	271	<0.01
CV33	7.28	930	<0.01	CV20	6.17	84	<0.01

according to the Portuguese legislation for dredged sediments (Regulation 1450/2007). For Hg, the concentrations range from 2 to 12 times higher than the critical limit established by the Portuguese legislation (10 mgkg^{-1}) and high concentrations were also found in the pore water of these sediments ($1600\text{--}4000 \mu\text{gL}^{-1}$), with much higher levels than those analyzed in the water column. Given the dynamic behavior of Hg in these watercourses, as evidenced by the fractionation analysis of this element in the sediments (Fonseca *et al.*, 2025), the very high concentrations in the soluble fraction, and its high mobility and toxicity, it became clear that this element should be considered as one of the highest priorities to be included in the remediation strategies to be proposed for this mining area.

A large number of bench scale tests have been conducted using twelve low-cost and readily available nature/waste materials, to identify the most suitable for the remediation of this contaminated water system for a range of PTE, including Hg. The chemical characteristics of these materials were evaluated by analyzing the contents of Hg and of other metallic elements in extractable forms (Table 2). The retention capacity of the materials in terms of PTE was determined by analyzing their cation exchange capacity

(Table 2). Except for mineralized iron oxides (ORA2) with low exchange capacity and three other materials – biochar, marble sludge (M(AGF)) and limestone sludge (C(S)), with adsorption capacity within normal values, the remaining materials have high to very high adsorption and cation exchange capacity. This group includes activated carbon in powder and in pellets, bentonite clay and ferrihydrite.

Regarding the adsorption capacity for the 5 elements found above the critical limits in the Caveira mine water (Cu, As, Mn, Zn, Hg), the 12 materials behave differently for each element, due to their mineralogical and chemical characteristics and the chemical behavior of the elements, namely their greater or lesser solubilization capacity and the conditions necessary for their retention and the chemical form in which they occur in solution. This paper presents only the Hg retention tests.

The kinetic tests carried out with a mono elemental solution of Hg at a concentration of 10 mg/L show that, except for limestone sludge (retention of 13.7%) and marble sludge (retention of 2.79%), all the other materials were able to retain Hg, although activated carbon in powder and in pellets, were the only ones able to retain almost 100% (respectively 99.99% and 94.38%) after 15 minutes of contact with the synthetic Hg-solution,

Table 2 Characterization of the “pure” geo and waste materials before contact with mine water: contents of Hg and other metals found above the critical limits in Caveira mine water (Portuguese legislation, Decree-Law No. 236/98), and Cation exchange capacity.

Pure natural/waste materials						
Samples	Description	Hg $\mu\text{g/Kg}$	As mg/Kg	Cu mg/Kg	Pb mg/Kg	Mn mg/Kg
C(S)	Limestone sludge	5.41	<2.50	8.16	1.70	14.72
M(AGF)	Marble sludge	14.23	<2.50	6.94	2.07	158.63
BVV	<i>Terra Rossa</i>	66.51	2.50	3.77	5.858	177.15
B#2	Bentonite	5.91	<2.50	0.20	<0.50	113.37
ORA2	Fe-oxides	22.12	<2.50	<0.50	14.39	311.44
Lagoa	<i>Terra Rossa</i>	47.03	<2.50	23.96	3.01	203.02
Fat clay	Illitic clay	29.11	<2.50	6.49	3.32	1650.04
Celulose	Waste of Celulose	38.88	<2.50	128.32	16.11	5300.21
CF03	Ferrydrite	50.11	11,907.9	4.93	43.11	353.95
Biochar	Acacia Biochar	13.20	4.90	3.95	3.67	129.63
Pellets carbon	Activated Carbon in Pellets	21.50	<2.50	31.62	2.96	107.64
Powder carbon	Activated Carbon in powder	7.29	<2.50	17.00	2.35	29.67
						87.31

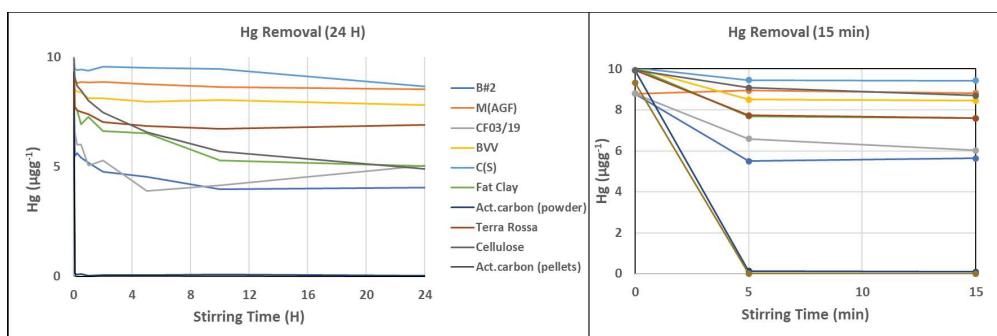


Figure 2 Hg removal from the mine water, by nature and waste products

followed by bentonite (53.83%) and cellulose (50.64%). The amount of Hg removed by each material is shown in Fig. 2.

Mercury in solution forms mainly anionic complexes but can also occur as the free cation Hg^{2+} . It is therefore preferentially retained by positively charged materials but can also be adsorbed by electronegative materials. This behavior is confirmed by the adsorption capacities of the 12 materials tested. A pond simulation evaluated the ability of the materials to (1) increase the initial pH (1.56) to reduce element solubility and (2) retain excess Hg after 10 days of contact with mine water at three material-to-water ratios (1:50, 1:100, 1:200). The results showed that:

- Cellulose, limestone, and marble sludges were most effective in raising water pH, increasing it from 1.56 to 6.6 after 7 days. The highest increase occurred at the lowest water/material ratio (50 mL:1g) in both oxic and anoxic conditions, with similar values. For example, cellulose, the most efficient, raised pH to 6.80 in an anoxic pond and 6.23 in an oxic pond.
- In Caveira mine water, with low initial conductivity, this parameter decreases at first and remains lower only in three geo-materials (limestone and marble sludge, ferrihydrite). In others, it stays unchanged or slightly increases, likely due to the high ion exchange capacity and exchange bases that most materials have (e.g., cellulose: Na, Mg, K) transferring to the water.
- Analysis of Hg in the water after the contact with these materials, showed a greater efficiency in reducing the original levels ($461\mu\text{g L}^{-1}$) for limestone, marble, activated carbon and cellulose ($2\mu\text{g L}^{-1}$ - $3\mu\text{g L}^{-1}$).

The slight difference in the Hg retention compared to the kinetic tests is due to: (1) some materials significantly increased the water pH when in contact, while others did not (e.g. activated carbon) and (2) chemical competition at the adsorption sites of materials between Hg and other elements also present in excess (As-Fe-Cu-Zn-Pb).

Conclusions

Contamination control of waterways affected by the Caveira Mine should occur only after intervention upstream of the tailings and dumps. Based on our studies, it is proposed to intervene in drainage water to reduce particle transport with high metal content and discharge of highly acidic water (pH 1–2) with dissolved metals. This intervention should occur where runoff water converges before entering watercourses, in two ways:

1. *Pond to increase pH:* In extreme acidity, metals cannot be adsorbed by any material. Depending on their availability at the remediation sites, any of the 3 materials that have shown good efficacy in raising the pH, cellulose and limestone and marble sludges (1:50 ratio) can be placed at the pond bottom in contact with air. These industrial waste materials have no economic value, and costs relate only to transport and placement. Though pH increase is somewhat slower in contact with oxygen, an open pond is more economical and aids iron oxidation, which is highly concentrated in these waters.
2. *Further treatment before discharge:* With improved pH and lower iron concentration, water should be pumped to

selected structures based on topography, before being discharged to watercourses: 1) a pond in flat terrain, or 2) a reactive barrier, preferably permeable, in rugged areas. The bottom should be capped with a layer of effective Hg-removing geomaterials, like activated carbon. Since these waters contain other harmful metals (Fe, Cu, Zn, Pb, As), a multi-layer coating can be applied, including cellulose and/or limestone and marble sludges, which have shown good efficacy in retaining these elements (Araújo *et al.*, 2025), in addition to activated carbon. In ponds, layers can be arranged sequentially controlled by zig-zag baffles, to direct the water flow and increase retention time of water for decontamination.

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