Reactive Barriers for Mine Waters Treatment: an Approach using Alternative and Nature-Based Materials

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Abstract

This work aims to reduce the influence of Acid Mine Drainage in two mining areas in the Iberian Pyritic Belt, specifically the Caveira Mine System in Portugal, and the Trimpancho Mining Complex in Spain, which both stopped operations in the 1960s. Since then, acid drainage from exposed waste piles has released toxic elements into nearby waterways, causing widespread contamination. Laboratory tests were conducted to find the best materials for neutralization of the acid drainage and subsequently retain Potentially Toxic Elements (PTE). Water samples from both mines showed high levels of toxic metals like As, Fe, Cu, Pb, and Zn, with very low pH levels, so laboratory scale ponds were created where various byproducts and nature-based materials were used to test the ability to neutralize acid drainage from the mines. With these tests it was verified that paper sludge was a great pH neutralizer, increasing mine water pH from 1.64 to 6.23 in 11 days and that industrial activated carbon, biochar, three different sludges and two different clays had great PTE removal ratios for As, Cu, Pb, Mn and Zn. Therefore, column tests with different materials simulated reactive barriers to determine the best combinations for this PTE removal. The tests indicated that sludges and industrial activated carbon are effective for retaining PTE and that multilayered reactive barriers are recommended for large-scale field applications to remediate contaminated water after increasing pH with paper sludge-based ponds.

Keywords: Acid mine drainage, potential toxic elements, byproducts, reactive barriers, remediation

Introduction

Environmental wealth is increasingly a factor of concern for us, combined with the needs to explore the geological heritage, essential for modern industry. This work is mainly focused on testing byproducts and nature-based materials, which otherwise had no practical use, to remediate watercourses, and water sources, from the Caveira Mine System (CMS) in Grândola, Portugal, and Trimpancho Mining Complex (TMC) in Spain. These mining sites (Fig. 1), located in the Iberian Pyrite Belt (IPB) – a volcanogenic massive sulfide province, in the southwestern part of the Iberian Peninsula – were explored since the period of Roman occupation, with particular incidence in the last two centuries (Oliveira & Matos 2002; Matos & Sousa 2008; Salmerón *et al.* 2014). CMS is embedded in Palaeozoic formations, in the NW region of the IPB, about 10 km SE of Grândola, Portugal (Mateus *et al.* 2008; Reis *et al.* 2012). This local has sediments predominantly of sandy nature, with few presences of clays in samples collected around the exploring area (da Silva *et al.* 2025). TMC is located in the SE region of the IPB, more precisely in the Huelva Province, in the SW of Spain, where a stream, that crosses the complex, flows to the Chança river in Portugal (Pérez Ostalé 2014). In this region the sediments are mostly of coarse sandy nature with a very few silts and clays mixed in their composition (da Silva *et al.* 2025).

Both mining sites have not undergone any mining exploration work since the 1960s, when different companies ceased mining operations in several mines in the IPB, due to the collapse of the copper market worldwide (Oliveira & Matos 2002), leaving them without proper supervision, poor management and absence of policies to contain contaminants. After comprehending the level of contamination in both regions, the aim of this work is to contribute with essential understanding on selecting the best tools to be applied, such as the use of byproducts and nature-based materials, to retain Potentially Toxic Elements (PTE) present in the effluents, which are responsible for the contamination not only of the surrounding watercourses, but also of the sediments that comprise them (da Silva *et al. in press*).

Preliminary Study

Initially, element concentrations were quantified to understand the level of contamination in the watercourses. To do so, Partial Digestion with Aqua Regia was carried out on water samples collected from the effluents for total quantification (dissolved and particulate forms). The same samples were also filtered through 0.45 µm filters, to quantify the dissolved forms (Tab. 1). In addition to element concentrations pH and SO4 was also measured in the effluents. Both effluents were acidic with CMS (pH 1.64) being slightly less acidic compared to TMC (pH 1.1). CMS has an average of 1251.22 mg/L in SO4 concentration, ranging from 0 to 14967,46 mg/L, and TMC has an average of 3665,08 mg/L, ranging from 47,38 to 9598.03 mg/L.

The ability of different byproducts, to neutralize the acidic effluents, was then tested through kinetic tests, simulating small ponds in 250 ml Erlenmeyer flasks with different ratios between water and byproducts used,

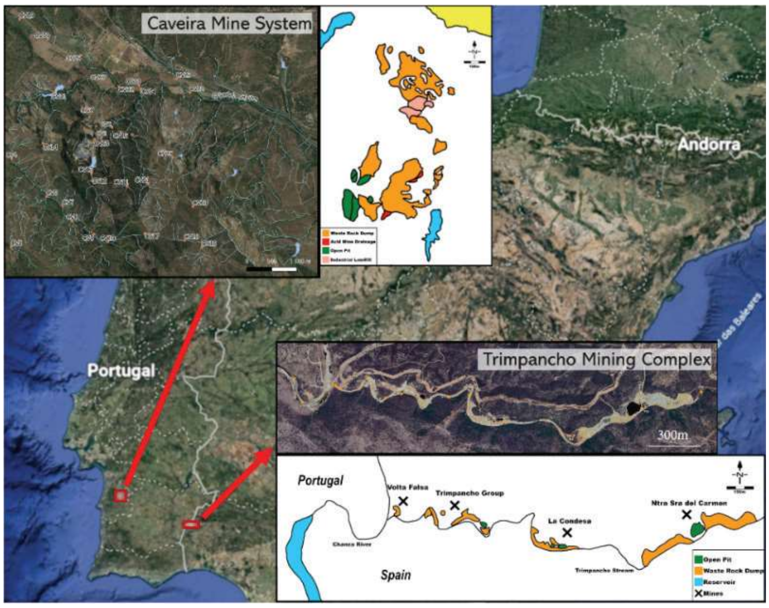


Figure 1 *Geographical representation of the CMS (adapted from: Ferreira da Silva* et al. *2015) and TMC (adapted from Grande* et al. *2017).*

Table 1 PTE in original waters from CMS and TMC – filtered and digested.

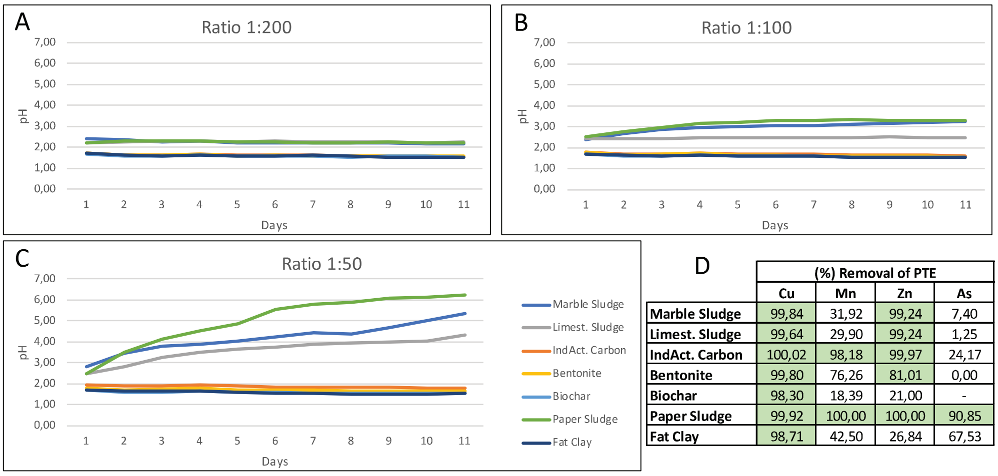
	Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
								mg/L							
CMS Filtered	583.3	17.66	123.3	0.5	1.0	0.3	33.1	2831.7	0.5	194.1	63.7	84.1	1.2	2.3	146.0
CMS Digested	604.6	15.6	101.1	0.8	1.0	0.4	29.2	2652.3	3.7	183.4	47.5	73.7	1.4	5.2	145.3
TMC Filtered	2507.9	<0.1	474.5	2.7	2.1	0.8	206.0	2958.0	0.6	1934.8	252.1	68.4	3.0	0.2	2402.1
TMC Digested	2300.0	<0.3	464.8	3.0	3.0	1.3	210.0	2691.0	4.9	1789.0	255.4	68.1	3.5	0.9	2207.3

such as paper, marble and limestone sludges, industrial activated carbon, biochar and two different clays. Tests lasted for 11 days until the pH of the waters stabilized to verify the best materials to increase pH (Fig. 2A-C) and to take the opportunity of carrying out preliminary analysis of the materials' PTE retention potential (Fig. 2D).

These preliminary tests showed us that paper sludge has great potential to increase pH in mine waters and that the byproducts can decrease the concentration of PTEs in the waters.

Lab-scale Testing Ponds and Reactive Barriers

Verifying that paper sludge had the best performance in increasing pH of mine waters, lab-scale ponds were constructed using inert plastic trays, holding 10 L of mine water (water from CMS was used to make this experiment, due to its higher concentration in PTE) with 200 g of paper sludge (Fig. 3). In the first pond experiment, paper sludge was used raw, conglomerated, in its original state. For the second pond, paper sludge was crushed before being combined with the mine water. The water in the first pond remained in contact with the byproduct for over two weeks, when it attained a pH value of 6,55. The water in the second pond attained a pH value of 7.52 just after 3 days. After neutralizing the pH, the water's clarity became practically translucent, losing its characteristic dark brownish colour and turbidity (Fig. 4). Then, after the water was separated from the residue at the bottom of the pond, samples were collected from both water and residue to be analysed by ICP-OES. The water was then used to perform the reactive barriers test, to



	(%) Removal of PTE			
	Cu	Mn	Zn	As
Marble Sludge	99,84	31,92	99,24	7,40
Limest. Sludge	99,64	29,90	99,24	1,25
IndAct. Carbon	100,02	98,18	99,97	24,17
Bentonite	99,80	76,26	81,01	0,00
Biochar	98,30	18,39	21,00	-
Paper Sludge	99,92	100,00	100,00	90,85
Fat Clay	98,71	42,50	26,84	67,53

Figure 2 A–C; Results of the first pH increment tests, with different ratios of water (200; 100; 50 ml) to 1 g of byproduct. D; results from the preliminary analysis on main PTE removal after pH increment tests for each byproduct.

Figure 3 Lab-scale Pond with mine water from CMS and paper sludge. First precipitation of iron oxides.

Figure 4 Mine water before (left) and after (right) Pond experiment.

check for the maximum PTE removal from these contaminated waters.

Therefore, for the last experiment, different columns were created (Fig. 5) simulating reactive barriers, with the following combinations:

- Column 1 – Marble Sludge + Biochar
- Column 2 – Marble Sludge + Fat Clay
- Column 3 – Limestone Sludge + Industrial Active Carbon
- Column 4 – Limestone Sludge + Bentonite

All byproducts were separated with fine gravel, to prevent direct contact between them, and water was pumped against gravity in each column through a peristaltic pump, at 1.20 rpm in a 4mm tubes, resulting in a flowrate of 2.77 ml/min. These combinations were created with insight from the preliminary study, to understand which byproduct would make the best combination to attain a total, or close to a total, PTE removal from the contaminated waters. In the end, and for each column, samples were taken from the four final waters and for each byproduct, to be chemically analysed.

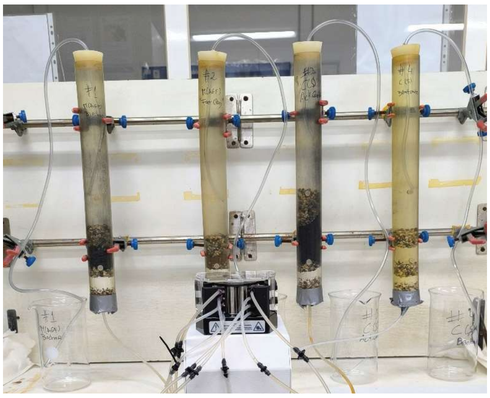


Figure 5 Reactive Barriers experiment with 4 different byproducts combinations.

All collected samples, waters and byproducts, were digested through Partial Digestion with Aqua Regia, and then analysed by ICP-OES, allowing us to verify that PTE were mostly retained in the pond residue (iron hydroxide film over the paper sludge) after the 11 days of contact, between the water and paper sludge, and yet, that some of the other byproducts still managed to retain PTE during the reactive barrier experiment, after the pond (Fig. 6).

In the end of the whole experiment, most PTE were removed from the mine water. As, Cu and Pb reached minimum values in all experiments and Fe reached very low amounts after passing through the columns with marble sludge. Zn and Mn were considerably retained at the end of all experiments, although with a lower performance compared to the other elements (Fig. 7).

In a first instance, it was noticed that the paper sludge has a great potential to increase pH in mine waters, influencing a greater retention of PTE by other materials. With just the contact of mine water with paper sludge, in the pond experiment, it made Fe precipitate by 95%, and then it was still retained after passing through the reactive barriers. Best results were attained in the first two columns, with marble sludge, and also with biochar and fat clay, attaining a removal over 99% of this element, going from an initial amount of around 2800 mg/L to just around 20 mg/L by the end of the whole experiment. Same happened for Cu and Pb, in which most part of each element was retained in the pond experiment, by the paper sludge. In the end, values decreased from around 30 mg/L (Cu) and 5 mg/L (Pb) to

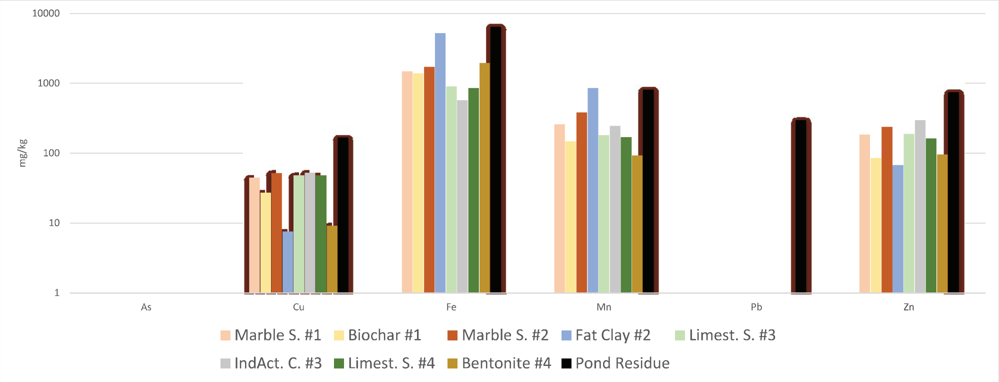


Figure 6 *Results, in logarithmic scale, from Partial Digestion with Aqua Regia analysed through ICP-OES in byproduct samples from the after-pond and after-reactive barriers experiments.*

8 mg/L and 0,40 mg/L, respectively. Meaning that Cu was removed by about 73% and Pb by about 92%. Arsenic was 100% removed from the water, going from about 15 mg/L to near 0 (all analysis were under the detection limit of the ICP-OES) and, Zn and Mn had a removal of 37,93% and 60,53%, dropping from 145 mg/L to 90 mg/L (Zn) and 190 mg/L to 75 mg/L (Mn).

Discussion

After performing the digestion of all samples collected from the pond/reactive barriers experiment, it's noticeable that PTE were mainly retained during this process, in which it was possible to reduce the amounts of As, Fe, Cu, Mn, Pb and Zn, in water contaminated by the influence of the mine and its wasting piles, to values below those recommended by the Decree-Law 236/98 (Portugal) on surface water quality.

The absence of arsenic values in all analyses during, and after the whole experiment, may indicate that this element may have undergone complexation, binding to iron oxides and precipitating with them during contact with paper sludge. The values of Mn and Zn may show a lower retention rate, compared to the other elements, this may be because paper sludge has high levels of these elements in its composition (4631,94 mg/Kg and 97,76 mg/Kg, respectively), which may have influenced its retention capacity.

Also, it was noticed that crushing the paper sludge before mixing with mine waters show better results, that may be because of the increment of specific area of the byproduct, leading to a pH increment within fewer days

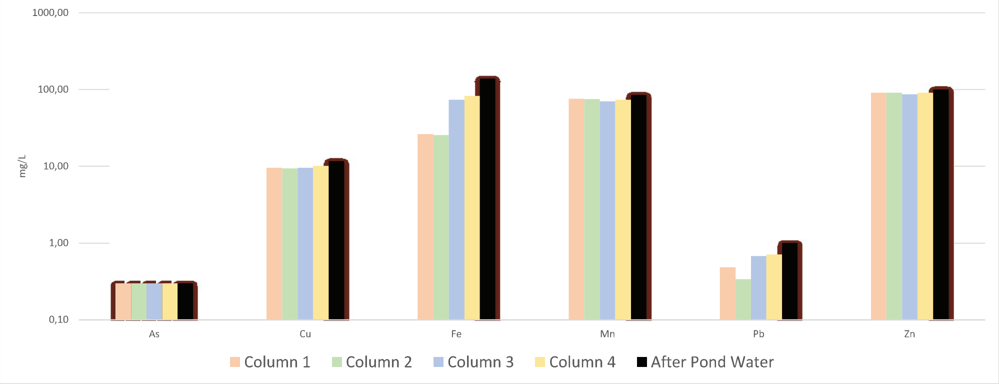


Figure 7 *Results, in logarithmic scale, from Partial Digestion with Aqua Regia analysed through ICP-OES in CMS water samples from the after-pond and after-reactive barriers experiments.*

of contact. And a slower speed when pumping water to the columns should also be tested to see if it can enhance PTE retention, allowing the water to remain in contact with the materials for longer periods of time, giving more time for retention to occur.

Conclusions

This shows that some byproducts and nature-based materials can be repurposed as a cost-effective material for environmental remediation in cases of Acid Mine Drainage, to increase water pH and remove PTE from it. According to this study, paper sludge was the best material for pH increment and a prior PTE removal, such as Fe, Cu and Pb. After pH increment using paper sludge, other materials such as industrial activated carbon, fat clay and marble sludge, showed high potential for retaining PTE. Furthermore, their homologous (Biochar, Bentonite and Limestone Sludge), despite having also performed well, they did not prove to be as good as the first ones in relation to PTE removal. However, it may be scientifically interesting to combine each homologous material and check if the potential for PTE removal improves. In conclusion, the experiment proved to be valid in the treatment of contaminated water affected by acid mine drainage in mining environments in a controlled laboratory-scale environment. Further experiments are underway to verify the removal potential, real-scale applicability and retention capacity of the materials that will determine the lifespan of the barriers.

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