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5-years leaching experiments to evaluate a modified bauxite residue: Remediation of sulfidic mine tailings

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Abstract

The ALTEO company produces approximately 300,000 tons per year of bauxite residue after alumina extraction, which is washed and dried in a press filter to produce Bauxaline®. In this study, different ways for recovering and reusing this residue were explored, namely transformation into a vegetated soil, use in acid mine drainage depollution, and application in sulfide-mine tailings remediation. The Bauxaline® was therefore transformed into modified bauxite residue (MBR), resulting in reduced alkalinity, salinity and sodicity. To counterbalance the net acid generation potential of two sulfidic mine tailings with 1 mol H⁺ kg⁻¹ (1.5% sulfide) and 3.3 mol H⁺ kg⁻¹ (5.3 % sulfide), respectively, various treatments were applied. These treatments included the addition of 10% MBR or 10% MBR plus limestone, or by limestone only, within 40-liters lysimeters. Six lysimeters were monitored over a 5-year period to assess the long-term emissions from treated materials. Vegetation was tested under various conditions, and its impact on emission was evaluated. The emissions of mine tailings treated with MBR and limestone were very low. The mine tailings with limestone showed intermittent peaks of emission, probably due to the coating of calcite grain by ferric oxide, hindering contact with percolating water. Vegetation successfully grew in the treated tailings. This study demonstrated that the alkalinity of limestone can temporarily immobilize elements in sulfidic mine tailings, with a reduction factor of emissions of 300 and 40 for the two mine tailings, respectively. For long-term immobilization, the alkalinity provided by both limestone and MBR and the Al and Fe oxides of MBR are more effective and necessary for long-term immobilisation, with a reduction factor of 300 and 900, respectively.

Keywords: Red mud, bauxite residue, potentially toxic metals, revegetation, lysimeter, remediation, sulfidic mine tailing

Introduction

The economic and technical development necessitates mineral resources, leading to significant mining activity that generates a substantial amount of finely crushed rocks known as mine tailings. Unfortunately, these tailings pose severe environmental challenges. In recent decades, the generation of such waste has intensified, particularly due to the treatment of high-tonnage ores containing sulfidic minerals with contaminants (Elghali et al., 2019). When these tailings come into contact with oxygen and water, they produce acidic and contaminated drainage waters. This acidity results from the microbial oxidation and hydrolysis of sulfide minerals by atmospheric oxygen, leading to the formation of sulfuric acid which is a strong acid. Additionally, these drainage waters contain high levels of metallic species. The primary sulfide minerals found in mine wastes are pyrite and pyrrhotite, though others may also undergo oxidation, releasing elements like Al, As, Cd, Co, Cu, Hg, Ni, Pb, and Zn into the water (Blowes et al., 2014). As environmental concerns have grown, regulations have become more stringent to protect the environment. This necessitates the development of environmentally friendly processes for managing mine wastes sustainably (GISTM 2020), while continuing to support industrial activities.

Acid mine drainage (AMD) is usually at pH below 3.5, which enhances the dissolution of metallic species in water (Saria et al. 2006). A major concern with AMD is run-off into waterways, leading to environmental issues (Kaur et al. 2018). Therefore, the use of lime or limestone amendment has been considered as a viable solution for immobilizing metal and neutralizing acid mine tailings.

Several studies have tested the neutralization of AMD using limestone, with some demonstrating effectiveness in field-scale applications (Hedin et al., 1994; Potgieter-Vermaak et al., 2006; Daraz et al., 2022). This approach involves using lime (CaO), hydrated lime (Ca(OH)₂) or calcite (CaCO₃) to neutralize the AMD waters and precipitate metallic species. However, challenges such as the production of large amounts of sludge or pipeline plugging have been mentioned (Tolonen, 2014), along with a potential loss of efficiency over time.

As a result, alternative eco-friendly and cost-effective solutions utilizing industrial by-products as neutralizing agents have been proposed. Alkaline agri-food residues (e.g., eggshells, though large quantities are required) and industrial by-products containing high levels of calcareous species show promise as alternatives to limestone amendment for remediating acid mine tailing impoundments (Kastyuchik, 2016). Kaur et al. (2018) has experimented an alternative solution : Bayer precipitates obtained by the seawater neutralization of Bayer liquor waste (from bauxite residue) were shown to be quite effective for the remediation of acid mine drainage water, since the resulting material met discharge pH guidelines. However, the presence of manganese remains a challenge since high pH values would be required to remove it. The efficiency of the material used for neutralizing AMD depends on its long-term buffer capacity, which indicates its ability to reduce the pH of AMD, as well as the composition of the chemical tailings. Moreover, the quantity of material required for neutralization will also be influenced by this buffer capacity.

To reduce metal mobility, utilizing dry covers with various materials has emerged as an alternative to flooding sulfide-mine tailings methods (Lottermoser et al. 2010). Ideally, these cover materials should be non-reactive and natural, like clay or soil. However, the requirement for a large quantity of such materials raises environmental concerns. To address this issue, the concept of using waste residues as a substitute for natural materials has been proposed, which could overcome the challenge of availability. While employing waste to treat waste offers cost-effectiveness, it may introduce new environmental issues, such as metal leaching into groundwater. Numerous studies have explored this alternative solution. For instance, various alkaline residue materials (fly ash, green liquor dregs, and lime mud) generated from the pulp and paper industry were assessed for their efficacy in covering aged mine waste tailings (Alakangas et al. 2013). The study evaluated the mobility of Cr, Cu, Zn, and As. Leaching tests demonstrated that alkaline amendments effectively immobilized Cr, Cu, and Zn. However, the presence of As exceeded permissible limit values at L/S 10 L kg⁻¹ (Jia et al 2016). On the other hand, other studies reported less effective outcomes. In a field scale experiment over two years, Nason et al. (2014) compared uncovered sulfide-tailings to sewage-sludge biosolid amended tailings over 2 years, with and without the use of fly-ash. In this case, sludge-derived metals (Cu, Ni, Fe, and Zn) migrated and precipitated at the tailings-to-sludge interface.

Bauxite residue can be recycled in different ways (Tanez and Hurel 2019; Botelho Junior et al 2021), but above all stand out as a compelling material for neutralizing AMD. It is massively produced by alumina/aluminium industries (Chandra et al. 2020), around 120 millions of tonnes per year (Silveira et al. 2021). Although the chemical composition of bauxite residue, also called red mud, may vary depending on the bauxite ore source, it exhibits typical characteristics: a high alkalinity with a pH ranging from 10 to 13 and the presence of metallic species such as Fe, Al, Ti, and Si, constituting about 5 to 45% of its composition and whose oxides can effectively bind with various elements. In addition, bauxite residues can also contain other trace elements such as Cr, As, Cd, Cu, Pb, Mn, Ni, Zn, etc (World Aluminium 2015).

In response to the imperative to prevent discharging bauxite residues into the sea, various solutions have emerged to develop methods for recovering and reusing these materials. Such alternatives include applications in construction industries, glass ceramics, reinforcement for composite materials, rare earth element extraction,

geopolymer production, and more (Verma et al., 2017). Establishing a vegetation cover is an interesting way to managing bauxite residue disposal since it can mitigate atmospheric dust dispersion and aid in immobilizing metallic species (Wong et al. 1993; Mishra et al. 2017). However, due to its physical and chemical properties, the bauxite residue is phytotoxic, including due to its high alkalinity, salinity and sodicity, low hydraulic conductivity, presence of high pH soluble metal species, and organic matter and nutritive ions deficiencies (Xue et al. 2016). To address these limitations, various strategies have been explored. Incorporating coarse material such as sand can improve hydraulic conductivity (Courtney et al. 2005). Alternatively, saturating the cation exchange complex with calcium can enhance structural stability. Another common practice involves two steps: gypsum amendment to lower the pH and washing to reduce the salinity. By addressing both physical limitations and chemical composition, the red mud disposal site can be made more suitable for revegetation. However, it is crucial to thoroughly assess and control the risks associated with these remediation approaches. Specifically, long-term evaluation of metal leaching into groundwater and potential soil and plant contamination must be conducted to ensure effective and safe rehabilitation.

Dry cake disposal of bauxite residue requires therefore careful considerations, particularly when planning subsequent utilisation of the solids, due to potential environmental issues. Kinnarinen et al. (2015) proposed a treatment to improve the properties of bauxite residue. This treatment involves washing to minimize the amount of soluble soda, followed by the use of a horizontal membrane filter press. A similar process was used to produce the bauxite residue commercial product from ALTEO called Bauxaline® used in this study. It is a thickened red mud, washed and partially dried in a filter press, resulting in a shovelable material (Taneez et al. 2016).

Here the Bauxaline® pH was reduced from 11 to 8.5 through neutralization using atmospheric CO₂ with 5% gypsum in order to precipitate calcium carbonate. The resultant material was called “modified bauxite residue” (MBR). Initially, the immobilization of potentially toxic metals (PTEs) from effluents, wastes, contaminated soils and mine tailings by MBR was developed at the laboratory scale. Subsequently, sixteen lysimeters were established for a 5-year period to assess the long-term emissions from the treated materials in comparison to the untreated ones. Additionally, experimental revegetation of the MBR was carried out. The long-term behavior of materials resulting from our experiments can be categorized into three main themes: (1) Storage of modified bauxite residue and its potential for revegetation; (2) Immobilization of PTEs using Modified Bauxite Residue (MBR) in the treatment of acid mine drainage; (3) Remediation of sulfidic tailings using MBR and limestone, coupled with the prospects for revegetation. The present paper focuses on the third theme.

Material and methods

Lysimeters

Two groups of three 40-litres lysimeters each were used to measure emissions from two mine tailing residues: TF, from the Saint-Félix site, and T1, from a confidential site (Table 1). They include for each tailing type: untreated mining tailings (#9 and #12), mining tailings treated with MBR for TF (#10) and with MBR and limestone for T1 (#13), and mining tailings treated with limestone only (#11 and #14). The lysimeters were vegetated with success for treated mine tailings # 10, #11, #13, #14 and without success for untreated mine tailings # 9 and #12. These six lysimeters are part of a larger series of 16. At the bottom of lysimeters #9 to #14, a 5 cm layer of coarse silica sand was placed, topped with a commercial geotextile made of polypropylene. Each lysimeter, with a total volume of 60L, was filled to 40L.

Red mud or MBR have inherently a low hydraulic conductivity and a very poor structural stability (Feng et al. 2017). When watered, these materials turn muddy and impermeable, lacking the necessary cohesion to support young plants. To facilitate plant growth, compost and topsoil were added to the first 20 cm layer of the lysimeters (1% w/w for both). The revegetation was made with *Dactylis glomerata* (orchardgrass) and *Onobrychis sativa* (common sainfoin).

The bulk dry density of the material used in the lysimeters was measured using the modified Proctor test method (ASTM 2012). Mining residue without MBR has a 1278 kg m⁻³ dry density, against 1028 kg m⁻³ for the mining residue with MBR.

The experimental setup is presented in Fig. 1.

Table 1. Experimental setup of the 6 lysimeters. MBR: Modified Bauxite Residue ; T1 and TF are mine tailing from two origins.

Lysimeter number	Composition	Revegetation and watering	Weight (kg of dry material)	Experiment duration (year)
9	TF	Failure	45.49	5
10	TF + 10% MBR	Success	45.49	5
11	TF + 10.75 % limestone	Success	45.49	4
12	T1	Failure	37.44	4
13	T1 + 10% MBR + 13% limestone	Success	37.44	4
14	T1 + 13.75% limestone	Success	37.44	4



Fig 1 Lysimeters of TF mine tailings (left: control #9, treated with MBR #10, treated with limestone #11) and of T1 mine tailings (right: control #12, treated with MBR and limestone #13, treated with limestone #14). The orange color on the walls of the lysimeter #12 and in the bucket is iron oxide

Lysimeter management and chemical characterization

In the first year, leachate collection from the lysimeters was conducted for every 100 mm of rain. In the subsequent years, a composite sample was obtained proportionally to the volume drained for each rainfall event. There was one exception for lysimeters #13 and #14 in the 2 last years. Due to the pH drop in lysimeter #14 leachate, a sample was collected and analyzed after each rain during this period. Moderate watering was implemented during the summer to keep the plants in a vegetative state. Sowing was repeated each year in case of failure of revegetation.

At each sampling, pH, Eh and EC were measured and the samples were acidified with ultrapure acid and stored at 2°C until sent for analysis. These were performed by ICP-MS at the Eurofins certified laboratory.

Each sample was quantified by its volume, known by weighing, enabling the calculation of the liquid/solid ratio L/S in liter per kilogram of tailing residue. This ratio represents the volume of the leachate sample divided by the mass of the tailing residue. Concentration data were expressed in mg L⁻¹ while quantity data were expressed in mg kg⁻¹ by multiplying the concentration by the L/S ratio of the sample. The cumulative quantities were calculated by adding together the quantities of each sample. In all samples, measurements were taken for metal content, pH, conductivity, and redox potential.

The results by lysimeter, by year and by parameter are presented in the supplementary data (appendix 1 and appendix 2: average concentration in mg L⁻¹ of drain and annual cumulative quantity in mg kg⁻¹ of MBR or mining residue, according to the themes and given in the tables).

Results and discussion

Experiments with the Saint-Félix mine tailing (TF)

Characteristics of the TF mine tailings

The TF mine tailings remained naturally unvegetated for over 50 years. It was collected at 3 points and sieved on site at 10 mm. It contained 50,000 mg Pb kg⁻¹, 5,000 mg Zn kg⁻¹, 300 mg As kg⁻¹, 20 mg Cd kg⁻¹ and 15,000 mg kg⁻¹ of sulfur. It had a net acid generation potential (NAGP, sum of the current acidity and the potential acidity by sulfide oxidation minus any neutralization by the material) comprised in the 0.78-1.32 mol H⁺ kg⁻¹ range, 1.00 mol H⁺ kg⁻¹ in average, and a pH of 4 (L/S = 10 L kg⁻¹).

After treatment with 10% MBR, the NAGP of the tailings was 0.42 mol H⁺ kg⁻¹ in average. Such a decrease would correspond to a consumption of 0.58 mol OH⁻ kg⁻¹. However, the addition of 10% MBR was only likely

to produce $0.15 \text{ mol OH}^- \text{ kg}^{-1}$ at pH 7, which is insufficient to produce the effect observed at field. This indicates that the MBR was more effective in neutralizing acidity at field compared to limestone, even more so than its effectiveness measured in laboratory acid/base titration. Similar results have been reported in Maddock (2009) and Fergusson (2014) who used an MBR equivalent to that used in the present study, which had effects for several years (data available for 14 years), whereas limestone had an effect for 2-4 years. In the present study, the 10% dose of MBR was selected based on its ability to immobilize leachables, with no consideration given to the potential for acid generation. Due to regulatory requirements, it was decided to complement the MBR with limestone, to ensure that their cumulated acid neutralisation capacity (ANC) surpassed the acidity potential of the tailings. In an effort to gain further insights into the long-term behavior of both MBR and limestone in treating these tailings, a separate lysimeter was installed the second year with only limestone treatment applied at a dose of alkalinity equivalent to the NAGP of MBR.

Hydraulic properties

The cumulative volumes of water input and drainage, expressed in height of water in mm (equivalent to L m^{-2}), the drainage/water input ratio and the L/S ratio (litre per kg of MBR) are given on Fig. 2 and Table 2. Lysimeter #9, untreated and devoid of vegetation despite annual sowing every year, showed a saturated vertical hydraulic conductivity decreasing over time. While water stagnation was rare before year 4, it occurred regularly thereafter with rainfall of 10 mm and more. To investigate this, measurements of rain infiltration speed were conducted, even in year 6. In November of year 5, the K_{sat} (saturated hydraulic conductivity) was found to be 6.10^{-7} m/s , equivalent to 53 mm per day (for a hydraulic head of 1 m per m of material). In November of year 6, the K_{sat} reduced to 1.10^{-8} m/s , equivalent to 1 mm per day. As a consequence of these changes, the water stagnated in the lysimeter. Low permeability of acid mine tailings is frequent (Harris and Megharaj 2001). The clogging of the material was probably due to the closing of the porosity by the fine particles entrained by the percolation water, not compensated by a biological activity because there was no vegetation. The practical consequences visible on the ground are maximum surface runoff from rainfall, and therefore maximum surface erosion.

Lysimeters #10 and #11 exhibited a hydraulic conductivity that enabled efficient the drainage of rainwater, even during heavy rainfall, within a few hours. The presence of the vegetation enabled evapotranspiration, leading to a reduction in the leachate volume. For untreated material, leachate volume was approximately 65% of the water input, while for the treated material, it ranged between 35 and 40%.

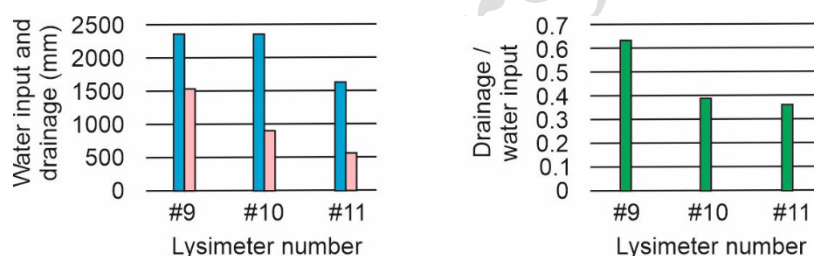


Fig. 2 Water input (rainfall + watering) (blue columns), drainage (pink columns) and drainage/water input ratio (green columns) of lysimeters #9, #10 and #11.

Table 2. Annual and cumulated L/S ratio (L kg^{-1} of MBR) of lysimeters #9, #10 and #11

	#9	#10	#11
Year 1	1.06	0.71	
Year 1 to 2	1.34	0.82	0.11
Year 1 to 3	1.76	1.11	0.41
Year 1 to 4	2.19	1.16	0.47
Year 1 to 5	3.00	1.90	1.19

pH and salinity

The pH of the untreated mine tailing leachate was acidic (average 3.8) while the pH of the treated mine tailing leachates was close to 7.5 (Fig. 3). The neutralization treatments, operating over a span of 5 years, effectively reduced the acidity caused by the continuous production of sulfuric acid. In the fall of year 6, the pH of the leachate from the treatment limestone alone dropped to pH 6.6 (result not included in this study). The

salinity was moderate but continuous, and was higher for the neutralization treatments, probably by the solubilization of Ca^{2+} by sulfate. The MBR treatment had the highest salinity emitted.

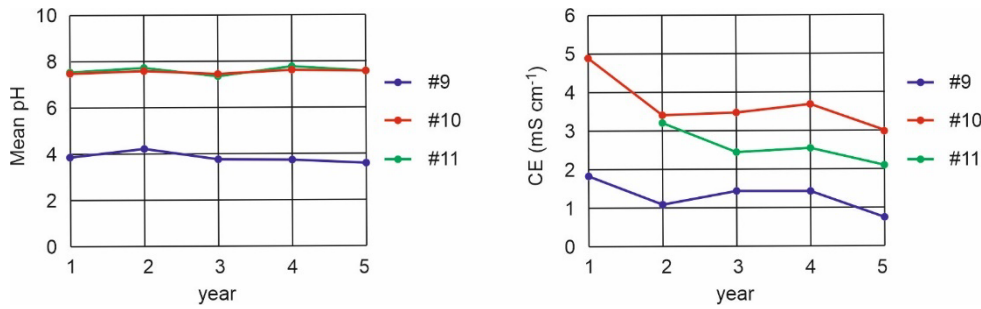


Fig. 3 pH and electrical conductivity (CE) of lysimeters #9, #10 and #11.

Elements concentrations in leachates

Table 3 give the average concentration of elements in the leachates. The leachates contained S, most likely in the form of sulfate SO_4^{2-} coming from the oxidation of pyrite, Ca^{2+} , from partial or total neutralization with the limestone present in the initial or added material, with in addition for the lysimeter #10 of Na^+ coming from the MBR as well as gypsum. The elements Cd, Pb, and Zn, which were emitted by the mining residue at an average concentration greater than 0.1 mg/l over 5 years, were effectively immobilized by the two treatments.

Table 3: Average concentrations (mg L^{-1}) of elements emitted by the TF lysimeters

Measured parameter	Lysimeters		
	#9	#10	#11
S	352	845	390
Ca	297	453	622
Na	39	634	76
Zn	34	0.050	0.042
Si	31	28.44	31.18
K	15	3.3	3.1
Al	10.21	0.07	0.05
Mg	8.8	8.6	9.0
Pb	3.050	0.098	0.140
Mn	0.52	0.01	0.01
P	0.45	0.02	0.03
Cd	0.289	0.005	0.004
Fe	0.084	0.038	0.033
Ni	0.048	0.007	0.009
Ce	0.042	0.023	0.023
Se	0.038	0.033	0.034
As	0.016	0.021	0.023
Sb	0.013	0.033	0.024
Cu	0.011	0.004	0.005
Co	0.010	0.002	0.007
Cr	0.009	0.008	0.007
V	0.004	0.004	0.005
Mo	0.003	0.004	0.003

Fig. 4 illustrates the behavior of potentially toxic elements (PTEs) in the three lysimeters over the five-year period, based on decreasing emission in the untreated material. For the untreated material, the three most emitted PTEs (Zn, Pb, Cd) showed quantities that were not exhausted, indicating behavior controlled by the solubility of one or more sparingly soluble mineral phases known as “solubility controlled” (Yao et al. 2023). On the other hand, the other PTEs exhibited depleting amounts (availability controlled) or were emitted in very low quantities. In the third year, emissions of most elements were higher compared to the second year, possibly due to a significant increase in the L/S ratio, ranging between 1.5 and 2.7 times higher in the third year when compared to the second year, depending on the lysimeter. Treatments proved to be effective. The higher emission in the third year than in the second year may be related to a L/S more high between 1;5 and 2.7 fold the third year than the second year.

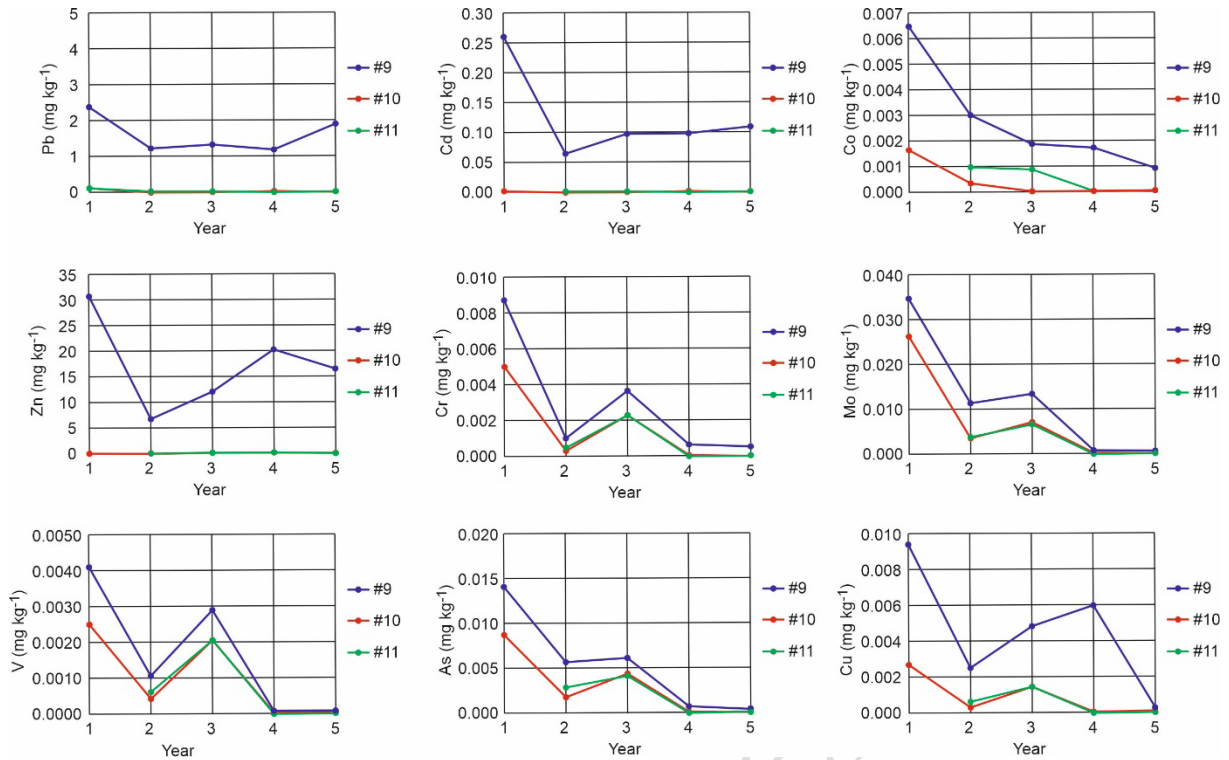


Fig. 4 Emission of some selected elements (Pb, Cd, Co, Zn, Cr, Mo, V, As, Cu) by leachates expressed in mg kg⁻¹

Figure 5 presents the cumulated quantities of elements emitted for the three treatments over 5 years, arranged in decreasing order of untreated TF lysimeter (#9) leachate. All elements emitted by the treated mine tailings are in a lower quantity compared to the untreated material, with the exception of S, Ca, Na and Sb, the latter being in a very low quantity (< 0.05 mg kg⁻¹ over 5 years).

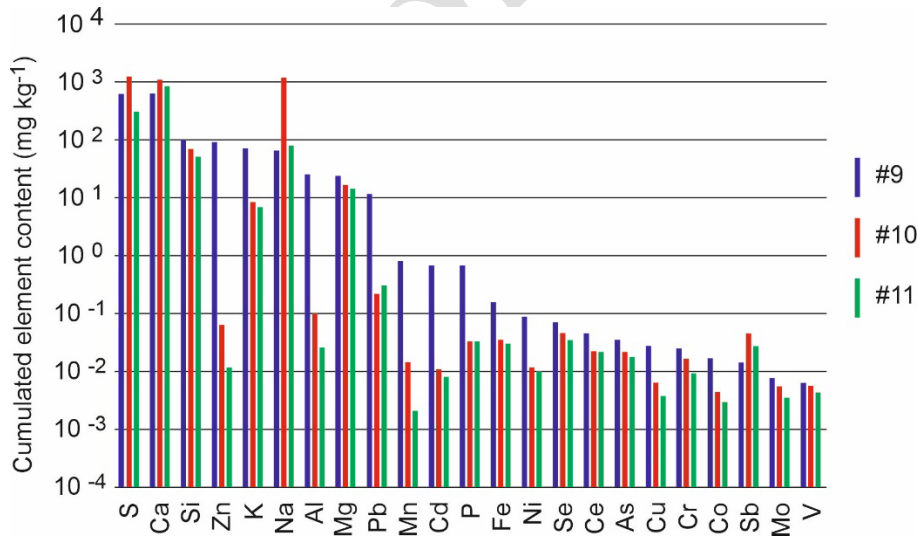


Fig. 5 Cumulated element quantities (mg kg⁻¹) emitted by the lysimeters

Table 4 gives lysimeter cumulated emission, ratio of emission between treatments and regulatory requirements for admission to an inert waste storage facility (IWSF) and a non-hazardous waste storage facility (NHWSF). The emission ratio obtained for lysimeters #9 and #10 (#9 value/ #10 value) and from lysimeters #9 and #11 (#10 value/#11 value) allowed to estimate the efficiency of the treatment using MBR + limestone (lysimeter #10) and limestone only (lysimeter #11). At the leaching rate of 3 L kg⁻¹, the untreated mining residue did not meet the eligible criteria for NHWSF due to emitted Pb and Zn. Their emission would probably have

increased with the L/S ratio. While the treated residues did not meet the requirement for IWSF due to the quantities of sulfates emitted, they demonstrated a significant reduction in all metals by an average factor of 300.

Table 4: Lysimeters cumulated emissions and comparison with the concentration limits of leachable elements for admission to an inert waste storage facility (IWSF) and a non-hazardous waste storage facility (NHWSF). Values are shown in red or purple if they exceed the IWSF or NHWSF limits, respectively.

	#9	#10	#11	#9 value/ #10 value	#9 value/ #11 value	IWSF	NHWSF
L/S (L kg ⁻¹)	3.0	1.9	1.2			10	10
pH	3.8	7.5	7.5				
Soluble fraction (mg kg ⁻¹)	3042	4978	2105			4000	60000
Sulfates	1863	3469	877			1000	20000
Calculation 1: all values below the Limit of Reporting (LOR) were set to 0 for the calculation							
As (mg kg ⁻¹)	0.01	0.002	0.003	4	3	0.5	2.0
Cd (mg kg ⁻¹)	0.65	0.001	0.000	627	1605	0.04	1.00
Co (mg kg ⁻¹)	0.01	0.001	0.001	18	14		
Cr (mg kg ⁻¹)	0.01	0.005	0.000	3	59	0.5	10.0
Cu (mg kg ⁻¹)	0.02	0.002	0.001	14	29	2.0	50.0
Mo (mg kg ⁻¹)	0.00	0.001		3		0.5	10.0
Ni (mg kg ⁻¹)	0.07	0.000	0.000	667	219	0.4	10.0
Pb (mg kg ⁻¹)	10.76	0.200	0.305	54	35	0.5	10.0
Sb (mg kg ⁻¹)	0.00	0.044	0.022	0	0	0.06	0.70
Se (mg kg ⁻¹)	0.03	0.000	0.000	248	88	0.1	0.5
V (mg kg ⁻¹)	0.00	0.000	0.001	6	1		
Zn (mg kg ⁻¹)	86.86	0.049	0.003	1758	29671	4	50
Calculation 2: all values below the Limit of Reporting (LOR) were set to the LOR for the calculation							
As (mg kg ⁻¹)	0.04	0.028	0.020	1	2	0.5	2.0
Cd (mg kg ⁻¹)	0.65	0.011	0.008	59	81	0.04	1.00
Co (mg kg ⁻¹)	0.01	0.004	0.003	4	5		
Cr (mg kg ⁻¹)	0.02	0.016	0.011	1	2	0.5	10.0
Cu (mg kg ⁻¹)	0.03	0.007	0.004	4	6	2.0	50.0
Mo (mg kg ⁻¹)	0.01	0.006	0.003	1	3	0.5	10.0
Ni (mg kg ⁻¹)	0.08	0.018	0.014	5	6	0.4	10.0
Pb (mg kg ⁻¹)	10.76	0.200	0.305	54	35	0.5	10.0
Sb (mg kg ⁻¹)	0.02	0.044	0.029	0	1	0.06	0.70
Se (mg kg ⁻¹)	0.07	0.049	0.048	1	1	0.1	0.5
V (mg kg ⁻¹)	0.01	0.008	0.006	1	2		
Zn (mg kg ⁻¹)	86.86	0.069	0.014	1254	6209	4	50

Remediation of the T1 (confidential site) sulfidic mine tailing

Characteristics of the T1 mine tailings

Like TF, T1 tailings have remained naturally unvegetated for more than 50 years. The T1 mining tailings contained a high content of sulfides (5.3%) and various metals, including Cu (> 1%), Pb (100 mg kg⁻¹), As (75 mg kg⁻¹), Mo (10 mg kg⁻¹), and Zn (10 mg kg⁻¹). The pH was measured at 2.6 (L/S 10 L kg⁻¹). The current acidity was 0.26 mol H⁺ kg⁻¹, with an NAGP of 3.29 mol H⁺ kg⁻¹, equivalent to 165 kg CaCO₃ per ton of mining residue or 2200 kg MBR per ton of mining residue (at pH 7). This substantial acidity cannot be effectively neutralized by MBR at a reasonable dose alone. Therefore, a combination of MBR and the limestone is necessary to capitalize on the benefits of MBR, such as the fixation of elements on iron oxides, the formation and stabilization of the structure, and water retention, while ensuring that the generated acidity will be adequately neutralized. The contribution of MBR was set at 10%, and its calcareous complement at 13%. Limestone treatment alone contains 13.75% limestone.

Hydraulic properties

The cumulative volumes of water input and drainage, expressed in height of water in mm (equivalent to L m⁻²), the drainage/water input ratio and the L/S ratio (litre per kg of MBR) are given on Fig. 6 and Table 5. These

materials exhibited a hydraulic conductivity that enabled efficient the drainage of rainwater, even during heavy rainfall, within a few hours. However, they lacked structural stability prior to revegetation. As for the TF lysimeters, the presence of the vegetation led to a reduction in the volume of leachate, from around 65% of the water input for the untreated material to 20% to 40% for the treated materials.

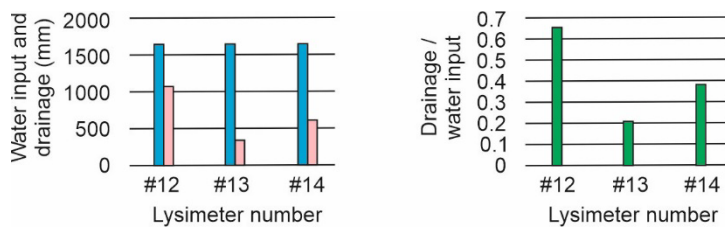


Fig. 6 Water input (rainfall + watering) (blue columns), drainage (pink columns) and drainage/water input ratio (green columns) of lysimeters #12, #13 and #14.

Table 5. Cumulated L/S ratio (L kg⁻¹ of MBR) of lysimeters #12, #13 and #14

	#9	#10	#11
Year 1			
Year 2	0.22	0.12	0.16
Year 2 to 3	0.71	0.17	0.20
Year 2 to 4	1.28	0.17	0.21
Year 2 to 5	2.62	0.85	1.52

pH and salinity

The pH of the leachate of the untreated T1 tailing was extremely acidic (average 2.0) whereas the pH of the leachates of the tailing treated with MBR and limestone was around 8, and that treated with limestone alone varied, with drops to pH 3 and then rising to pH 8 (Fig. 7). At times, the alkalinity of the limestone no longer effectively neutralized the acidity, while at other times, the chemical balance was restored. This erratic behavior is no clear relationship with time or drainage intensity. This erratic behavior has not been explained to date, as the limestone used was finely crushed (< 1 mm) and intimately mixed with the dried T1, reduced to powder. Furthermore, the quantity of limestone added corresponded, as for lysimeter 13, to 1.1 times the potential for acid generation. This effect could be due to limestone coatings by precipitated iron oxides, although in the presence of bauxite residue, this phenomenon did not occur, leaving reasons for further exploration. This transient effect of limestone (2 to 3 years) has been observed at several sites in Australia (Maddock 2009; Fergusson 2014), and has been attributed in the literature to the loss of part of the alkalinity as bicarbonate at neutral pH and an effect of grain coating by precipitated iron and aluminum oxides. This observation is confirmed here.

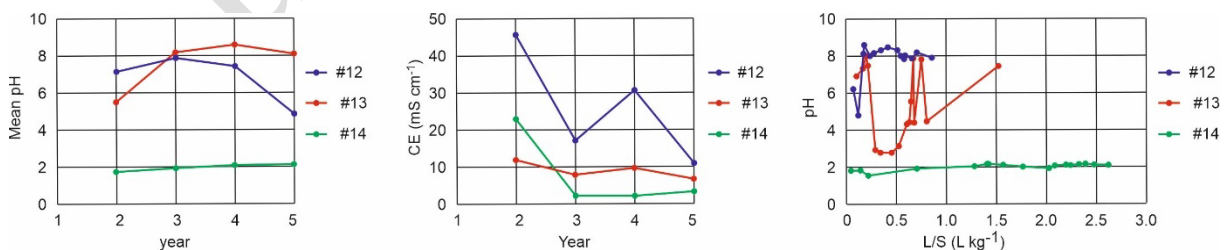


Fig. 7 pH, electrical conductivity (CE) and relationship pH with L/S of lysimeters #12, #13 and #14.

The alkalinity of limestone is a dependant on pH (Lindsay, 1979). At pH < 5, the dominant form of carbonate is H₂CO₃ (dissolved and undissociated carbonic acid), corresponding to the attachment of two protons H⁺ to the carbonate anion CO₃²⁻ from limestone. At pH 6.36, the soluble carbonate is distributed between H₂CO₃ and HCO₃⁻. Between pH 6.36 and 10.33, the HCO₃⁻ form dominates, that corresponds to the fixation of one proton on the carbonate anion from limestone, utilizing only half of the functional groups of the carbonate anion. At pH 10.33 and above, the carbonate form dominates, and the fixation of protons gradually becomes zero, rendering

the limestone alkalinity-less. Thus, the alkalinity of limestone is completely consumed by protons below pH 5, while the bauxite residue has a various mineralogical species with acid/base couples (aluminosilicates, oxides) whose pKa are staged from pH 11 to pH 4 or lower.

Elements concentrations in leachates

Table 6 give the average concentration of elements in the leachates.

Table 6. Average concentrations (mg L⁻¹) of elements emitted by the T1 lysimeters. PTE values greater than 0.1 mg/l are shown in red.

Measured parameter	Lysimeter		
	#12	#13	#14
Fe	5634	0.24	132
S	2044	985	738
Al	944	0.35	66.52
Ca	350	489	729
P	329	0.04	0.37
Cu	316	0.388	15
K	203	3.9	2.8
Si	44	14.23	37.67
Mg	26	106.8	116.5
As	15	0.020	0.025
Zn	11	0.042	1.262
Na	8	1632	74
Co	1.15	0.035	1.029
Se	1.102	0.497	0.210
Cr	1.06	0.05	0.10
Mn	0.96	0.13	2.31
Ni	0.847	0.017	0.559
Pb	0.61	0.021	0.025
Mo	0.57	0.006	0.003
Ce	0.40	0.02	0.04
V	0.39	0.005	0.009
Cd	0.27	0.008	0.009
Sb	0.03	0.012	0.012

The first element emitted was Fe, followed by S, at several grams per litre, which is characteristic of acid mine drainage. Subsequently, Al and Ca showed intense mineral weathering. Silicon was not emitted, as silica is poorly soluble. Additionally, the concentrations of P and K were exceptionally high. As the material was processed, the emission of Fe decreased or ceased altogether, while S and Ca, and Na for MBR processing, continued to be emitted.

In the untreated material, Cu, As and Zn were emitted in concentrations greater than 10 mg L⁻¹, and nine other PTEs were emitted in concentrations greater than 0.1 mg/l. However, when the material was treated with MBR and limestone, only Cu and Se exceeded 0.1 mg L⁻¹ on average over 4 years. When the material was treated with limestone alone, the emission of Cu increased sharply, and there was also an emission of Zn, Co and Cr in an average concentration greater than 0.1 mg L⁻¹.

Fig. 8 illustrates the behavior of potentially toxic elements (PTEs) in the three lysimeters over the five-year period, based on decreasing emission in the untreated material.

In the untreated material, most of PTEs (Cu, As, Zn, Co, Cr, Pb, Ni, Mo) showed quantities that did not deplete, indicating a solubility controlled behavior. The other PTEs showed much lower amounts, erratic behavior, or depleting quantities (availability controlled). The treatments were effective, except for the lime treatment in the last year, which showed an increase in Cd, Co, Cr, Cu, Ni, Pb, V, and Zn emissions. This indicates that the treatment with limestone alone was not sufficient starting from the fourth year. During this period, the pH of the leachates periodically dropped (reaching pH 3) (Fig. 7), resulting in an immediate increase in cationic metal emissions.

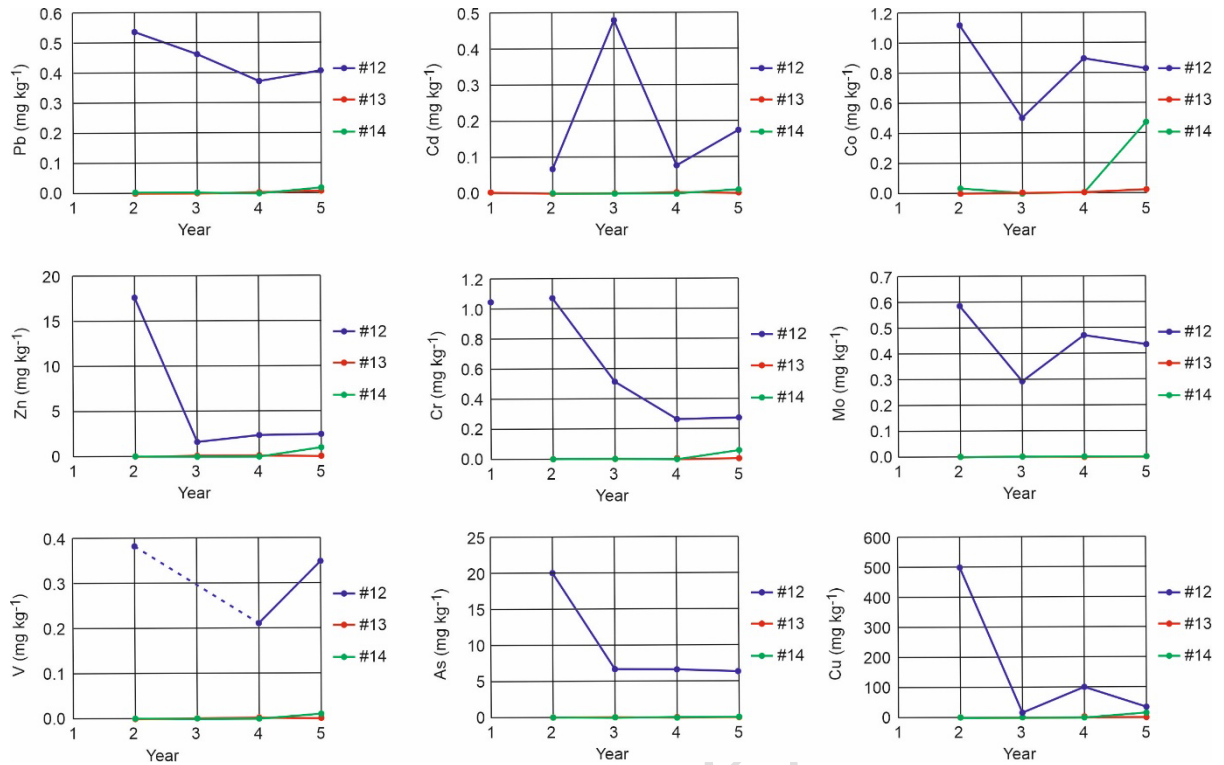


Fig. 8 Emission of some selected elements (Pb, Cd, Co, Zn, Cr, Mo, V, As, Cu) in leachates expressed in mg kg⁻¹. There is a dotted line where the annual value is unreliable.

Figure 9 presents the cumulated quantities of elements emitted for the three treatments over 4 years, arranged in decreasing order of untreated T1 lysimeter (#12) leachate. The oxidation of sulfides was intense in the untreated mining residue: 1.6% of the mass of the material was emitted as Fe, 1% as S (representing 4% of sulfate) and 0.3% as Al in just 4 years. For the treated mine tailings, all elements were emitted in lesser to much lower quantities compared to the untreated material with the exception of Na in the MBR + limestone treatment. Treatment with MBR and limestone proved to be more effective than treatment with limestone only.

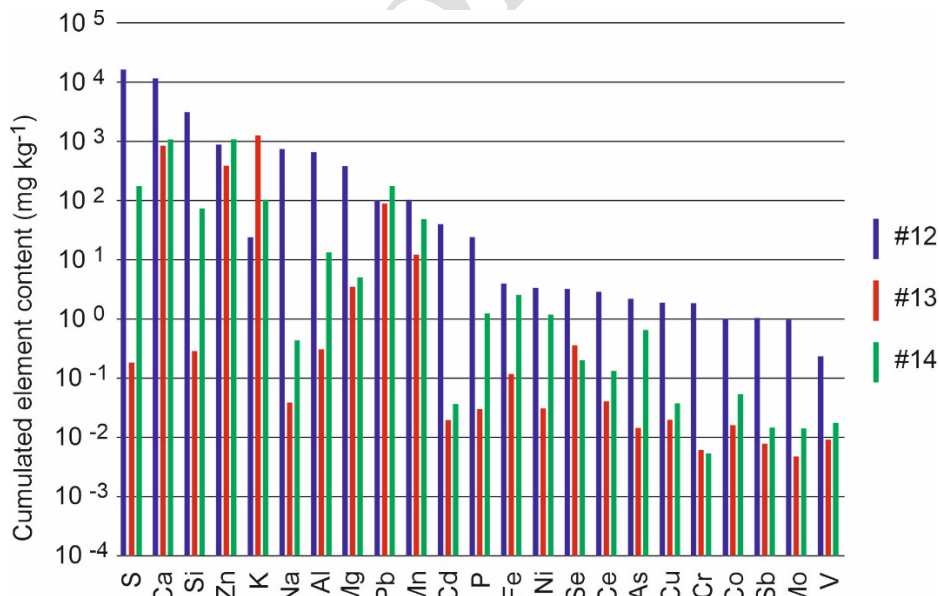


Fig. 9 Cumulated element content (mg.kg⁻¹) emitted by the lysimeters of topic 3 related to T1 tailing (number 12, 13, 14)

Table 7 gives lysimeter cumulated emission, ratio of emission between treatments and regulatory requirements for admission to an inert waste storage facility (IWSF) and a non-hazardous waste storage facility (NHWSF). At the leaching of 2.6 l kg⁻¹, the untreated mining residue did not meet the criteria for NHWSF due to

its emissions of sulfates, As, Cd, Cu and Se. Additionally, it did not meet the criteria for IWSF due to its emissions of Cr, Ni, Mo, Pb, Sb and Zn. These quantities are likely to continue increasing with the L/S ratio.

The treated residues were not eligible for IWSF due to the quantities of sulfates emitted. Material treated with MBR and limestone was also ineligible for IWSF due to its Se emissions, while material treated with limestone was ineligible due to its emissions of Cu, Ni and Se. However, these treatments demonstrated a significant reduction of all the metals by an average factor of 900 and 40, respectively. In particular, they allowed an effective reduction of the emission of anionic compounds (As and Mo) difficult to immobilize (Taneez and Hurel, 2019).

Table 7. Lysimeters cumulated emissions and comparison with the concentration limits of leachable elements for admission to a inert waste storage facility (IWSF) and a non-hazardous waste storage facility (NHWSF). Values are shown in red or purple if they exceed the IWSF or NHWSF limits, respectively.

	#12	#13	#14	#12 value/ #13 value	#12 value/ #14 value	IWSF	NHWSF
L/S (L kg ⁻¹)	3.02.6	0.8	1.5			10	10
pH	2.0	7.8	5.5				
Soluble fraction (mg kg ⁻¹)	30152	4265	5981			4000	60000
Sulfates	30045	2247	2996			1000	20000
Calculation 1: all values below the Limit of Reporting (LOR) were set to 0 for the calculation							
As (mg kg ⁻¹)	39.82	0.005	0.016	8244	2441	0.5	2.0
Cd (mg kg ⁻¹)	1.06	0	0.003		349	0.04	1.00
Co (mg kg ⁻¹)	3.37	0.029	1.135	115	3		
Cr (mg kg ⁻¹)	2.72	0.040	0.132	67	21	0.5	10.0
Cu (mg kg ⁻¹)	650.95	0.302	13.607	2157	48	2.0	50.0
Mo (mg kg ⁻¹)	1.79	0.003	0.001	551	2454	0.5	10.0
Ni (mg kg ⁻¹)	2.07	0.007	0.626	278	3	0.4	10.0
Pb (mg kg ⁻¹)	1.81	0.002	0.014	743	133	0.5	10.0
Sb (mg kg ⁻¹)	0.23	0.000	0.000	94454	25282	0.06	0.70
Se (mg kg ⁻¹)	2.94	0.342	0.164	9	18	0.1	0.5
V (mg kg ⁻¹)	0.94	0.002	0.008	452	119		
Zn (mg kg ⁻¹)	24.38	0.021	1.257	1147	19	4	50
Calculation 2: all values below the Limit of Reporting (LOR) were set to the LOR for the calculation							
As (mg kg ⁻¹)	39.82	0.018	0.037	2166	1081	0.5	2.0
Cd (mg kg ⁻¹)	1.06	0.007	0.014	154	174	0.04	1.00
Co (mg kg ⁻¹)	3.37	0.029	1.135	115	3		
Cr (mg kg ⁻¹)	2.72	0.041	0.133	67	21	0.5	10.0
Cu (mg kg ⁻¹)	650.95	0.303	13.607	2150	48	2.0	50.0
Mo (mg kg ⁻¹)	1.79	0.005	0.005	334	351	0.5	10.0
Ni (mg kg ⁻¹)	2.07	0.014	0.626	147	3	0.4	10.0
Pb (mg kg ⁻¹)	1.81	0.019	0.037	96	48	0.5	10.0
Sb (mg kg ⁻¹)	0.23	0.009	0.017	24	13	0.06	0.70
Se (mg kg ⁻¹)	2.94	0.342	0.197	9	15	0.1	0.5
V (mg kg ⁻¹)	0.94	0.004	0.013	212	75		
Zn (mg kg ⁻¹)	24.38	0.029	1.260	832	19	4	50

Conclusion

For both types of tailings, the treatments led to successful revegetation and a significant reduction in leachate volumes. Without treatment, leachates represent approximately 65% of water supply; however, with treatment, this is reduced to 20-40%, primarily due to evapotranspiration facilitated by vegetation.

The pH of the leachates rised from 4 to 7.5 for TF and from 2 to 6-8 for T1. While the emission of sulfates was not modified by the treatments for TF, it was reduced by 40 to 50% for T1. Additionally, for both tailings, the emission of PTEs was greatly reduced. In the case of TF, the emission values of PTEs were lower than the admission limit in IWSF for both treatments. For T1, with regard to the MBR + limestone treatment, only the emission of Se remained above this standard; however, with the limestone treatment alone, the emissions of Se, Ni, and Cu remained above the standard despite a significant reduction, by a factor of 15, 3, and 48 for these three elements, respectively.

Furthermore, treatment with limestone alone is not durable enough over time. From the fourth year onwards, its buffering power is no longer sufficient, leading to acidity peaks in leachates, with pH dropping to 3, and an immediate correlative increase in PTE emissions. The better performance of the limestone + MBR treatment can be attributed to a lower loss of alkalinity through leaching of the bicarbonates at a neutral pH, as well as the fixation of the elements on the surface of the oxides.

As a result, the limestone treatment alone cannot be recommended, but the MBR + limestone treatment should be favored. When applied in situ on mine tailings, it allows for effective revegetation and, in most cases, the successful immobilization of PTEs, in particular those likely to be in the form of anionic species (Mo, As, Se) which are difficult to immobilize. Long-term monitoring will, of course, remain necessary on the treated sites.

Glossary

AMD: Acid Mine Drainage

EC: Electric conductivity (in mS/cm)

IWSF: Inert waste storage facility

L/S: liquid/solid ratio (in l kg⁻¹)

MBR: Modified bauxite residue ie Bauxaline® plus CO₂ and gypsum)

NHWSF: Non-hazardous waste storage facility

TF: St-Félix mine tailings

T1: Confidential site mine tailings

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Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

Authors Contributions

Patricia MERDY: conceptualization, investigation and writing—original draft preparation. Pierre HENNEBERT : conceptualization, investigation, methodology, resources, formal analysis, writing, review, and editing. Chen CHEN and Alexandre PARKER :investigation.

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Availability of data and materials

Data are available on request.