

Article

Laboratory Study on the Effectiveness of Limestone and Cementitious Industrial Products for Acid Mine Drainage Remediation

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Abstract: Acid mine tailings may affect several environmental matrices. Here, we aimed to stabilize acid-generated mine tailings using several alkaline and cementitious amendments, which were tested in columns for 361 days. The alkaline amendments consisted of 10 and 20 wt.% limestone, while the cementitious amendments consisted of different binders at a total dosage of 5 wt.% binder. The different formulations for the cementitious amendments were: 50% Kruger fly ash and 50% class F fly ash; 20% ordinary Portland cement, 40% Kruger fly ash, and 40% class F fly ash; 80% ordinary Portland cement and 20% Kruger fly ash; and 20% ordinary Portland cement, 40% Kruger fly ash, and 40% fly ash. Kinetic testing on the amendment formulations showed that the pH values increased from <2.5 to circumneutral values (~7.5). The mobility of various chemical species was greatly reduced. Cumulative Fe released from the unamended tailings was ~342.5 mg/kg, and was <22 mg/kg for the amended tailings. The main mechanisms responsible for metal(loid) immobilization were the precipitation of secondary phases, such as Fe-oxyhydroxides, physical trapping, and tailing impermeabilization.

Keywords: mine tailings; acid mine drainage; alkaline amendments; cementitious amendments; contaminant stabilization



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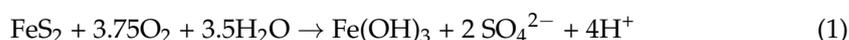
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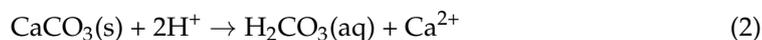
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1. Introduction

Mining activities generate large quantities of solid wastes such as waste rocks and tailings. Tailings are generated after ore treatment and processing, and are characterized by fine grain-size distributions and high specific surface areas [1–3]. The majority of tailings are stored at the surface in a tailing storage facility (TSF). Mine tailings often contain non-negligible amounts of iron sulfide minerals such as pyrite and pyrrhotite [4–6]. The oxidation of sulfide minerals occurs when they are exposed to water and oxygen, both in the presence or absence of microorganisms [5]. Sulfide oxidation can involve various and complex processes, including chemical, biological, and electrochemical reactions [7]. Sulfide oxidation increases the acidity of leachate waters, which can lead to the formation of acid mine drainage (AMD). The overall reaction of pyrite oxidation result produces four moles of H⁺ (Equation (1)).



Consequently, various metals and metalloids (e.g., As, Cd), iron, and sulfate could be released into the environment due to sulfide oxidation [8]. The mobility of metals is mainly influenced by pH conditions [9]. Depending on the mineralogical composition of tailings, acid production by sulfide oxidation can be partially neutralized by carbonate, hydroxide, and, to a lesser extent, silicate dissolution [10–13]. An example of acid buffering by calcite dissolution under acidic conditions ($\text{pH} < 6.3$) is illustrated in Equation (2):



Contamination of the environment caused by acid-generating tailings represents a serious global issue for the mining industry. Consequently, numerous techniques have been developed to prevent and mitigate AMD [14]. Stabilization/solidification (S/S) using cementitious and alkaline amendments is one method that was successfully used in various case studies related to contaminated geological materials, such as: (i) acid-generating tailings [15–26], (ii) contaminated soils and sediments [27–39], and (iii) mine backfills [4,40–44]. Various cementitious and alkaline materials were used as amendments to stabilize contaminated materials. The most used materials in the stabilization/solidification of hazardous wastes are presented in Table 1. Within alkaline amendments, limestone is one of the most used materials to neutralize and stabilize acid-generating materials. However, there are no specific formulations for either alkaline or cementitious amendments due to the wide range of geochemical and mineralogical properties of mine tailings. In the category of cementitious amendments, ordinary Portland cement (OPC) in combination with pozzolanic and industrial byproducts is widely used. Moreover, numerous studies were conducted to substitute OPC by industrial byproducts to reduce costs related to cement (Table 1).

Alkaline amendments consist of added materials with a high neutralization potential (NP) to buffer the acidity produced by tailing oxidation [15,22,45]. The main objective of alkaline amendments is to take tailings with a high acid-generating potential (AP) and add NP until the material is no longer acid-generating. When alkaline materials dissolve under acidic conditions, they provide alkalinity and neutralize acidity [46]. Consequently, contaminants such as arsenic (As), lead (Pb), iron (Fe), zinc (Zn), and copper (Cu) can be immobilized through mechanisms such as: (i) precipitation of low-solubility secondary phases like iron oxyhydroxides, (ii) coprecipitation of contaminants or their adsorption onto newly formed secondary phases, and (iii) reduction of sulfide oxidation under circumneutral conditions and their passivation.

Cementitious amendments consist of added cementitious materials to increase tailing cohesion and mechanical resistance. They are commonly used for the treatment of hazardous contaminated materials before their disposal. Cementitious additives reduce the hydraulic conductivity, porosity, and available surface area of the mixture. Consequently, many inorganic contaminants can be immobilized into the solidified matrix through a number of physical and chemical mechanisms [15,23,27,35,47]. Contaminant immobilization with cementitious amendments is ensured through the following processes: (i) the same chemical mechanisms as alkaline amendments; (ii) a reduction of the available surface area of the tailings, which decreases their reactivity; (iii) a physical encapsulation of contaminants due to the tailings' cementation; and (iv) a reduction of the contact between water and the tailings.

The main objective of this study was to stabilize highly oxidized acid-generating tailings from a closed mine site located in Quebec Canada. The effectiveness of alkaline and cementitious amendments was studied based on laboratory column tests. Limestone was used as an alkaline material, while ordinary Portland cement, fly ash (FA), Kruger fly ash (KFA), and class F fly ash (FAF) were used in various combinations as cementitious amendments. The effectiveness of the used amendments was tested in a laboratory column for 361 days. The geochemical behavior of each amendment's formulation was compared to that of oxidized tailings. Consequently, the reduction factor of each chemical element was calculated. At the end of column tests, the reduction of hydraulic conductivity was evaluated using infiltration tests. At the local scale, this technology studied in this paper can

be used as an option for the mitigation of the studied mine site. Moreover, this technique can be easily used for other problematic mine tailings in other countries.

Table 1. Some case studies of alkaline and cementitious amendments used to stabilize contaminated materials.

Problematic	Amendments	Country	Reference
Acid-generating tailings	5% and 10% limestone, 5% OPC, 5% (1/2 OPC-1/2 FA)	Canada	[15]
Contaminated mine soils	Sludges from a purification plant and a bleach plant	Spain	[16]
Acid-generating mine tailings	Alkaline phosphate wastes	Morocco	[17]
Contaminated mine tailings	Ordinary Portland cement and furnace slag	Korea	[18,19]
Synthetic-acid-generating tailings	Limestone and red mud	Greece	[20]
Acid mine drainage	Cement kiln dust	Canada	[21]
Sulfidic mine waste	Limestone	Canada	[22]
Acid-generating mine wastes	Cementitious materials	Review paper	[23]
Contaminated mine tailings	Sugar foam, lime-rich waste, drinking-water-treatment sludge, olive mill waste and paper mill sludge	Spain	[24]
Highly sulfidic mine tailings	MgO-activated ground granulated blast-furnace slag and ordinary Portland cement	Finland	[25]
Tailings and contaminated soils	Fly ash	Greece	[26]
Radioactive-contaminated soils	Portland cement and barite powder	Italy	[27]
Contaminated materials	Organic matter, alkaline material	Review paper	[28]
Waste materials	Ordinary Portland cement and pulverized fly ash	Not indicated	[29]
Wood-ash-contaminated grassland soil	Biochar	Not indicated	[30]
Municipal solid-waste incineration	Waste fishbone	Japan	[31]
Synthetic-contaminated materials	Ordinary Portland cement, clinker kiln dust modified OPC, cement kiln dust	South Korea	[32]
Fuel-biofuel fly ash	Ordinary Portland cement and alkali activation	Finland	[33]
Acidic and phytotoxic mine spoil	Lime and nitrogen (NH_4NO_3)	Hungary	[34]
Contaminated soils	Portland cement, MgO-based cement, ground granulated blast-furnace slag	United Kingdom	[35]
Contaminated soils	Portland cement, ground granulated blast-furnace slag, pulverized fuel ash, MgO, and zeolite	United Kingdom	[36]
Lead-zinc smelting slag	Geopolymerization	China	[37]
Contaminated soils	Superphosphate and calcium oxide	China	[38]
Mine soils	Lime, organic amendments	Spain	[39]
Mine backfill	Ordinary Portland cement, cement kiln dust, ground granulated blast furnace slag, waste glass, copper slag, wood bottom ash and coal fly ash	Canada	[44]
Synthetic-contaminated soils	Lime-slag	United Kingdom	[47]
Acid generating mine tailings	Carbonates	Sweden	[48]
Acid-generating mine tailings	2% Portland cement	Canada	[49]
Synthetic-contaminated soils	Ground granulated blast-furnace slag and hydrated lime	United Kingdom	[50]
Pyrite-waste-contaminated soil	Iron- and phosphorus-based amendments	Spain	[51]
Acid-generating mine tailings	Red mud bauxite	Canada	[52]
Contaminated sludge generated from common effluent treatment plant	Ordinary Portland cement, fly ash and sludge	India	[53]
Zinc mine tailings	Geopolymerization	China	[54]
Cadmium-spiked soils	Biochar and alkaline amendments	Ethiopia	[55]
Contaminated sediments	Limestone, MnO_2 , and natural zeolite	China	[56]

2. Materials and Methods

2.1. Materials and Study Site

The tailings used in this study were collected from the Joutel mine site, which is an inactive mine site located in Quebec, Canada. During operation, the Joutel mine extracted gold via floatation and cyanidation [57], with the waste tailings from this process being deposited in a 120 ha TSF. Operations at Joutel ended in 1994, which has allowed for significant oxidation and acid generation to occur in some localized areas of the TSF [58]. The tailings used in this study were collected from an acidic oxidized zone in the TSF. The samples were homogenized in situ and shipped to the laboratory.

The materials used as amendments in this study were limestone (LS); fly ash (FA) that was collected from the Boralex thermal energy station in Sennterre, Quebec; ordinary Portland cement (OPC); Kruger fly ash (CVK) that was collected from the biomass cogeneration power plant at the Kruger paper mill in Brompton, Quebec; and class F fly ash (FAF), which was provided by LafargeHolcim Canada. Limestone was formed mainly by calcite and dolomite [15]; fly ash was mainly composed of plagioclases and carbonates [15]; FAF contained mainly quartz [59], plagioclase, and mullite; and CVK was composed of lime, gehlenite, quartz, and calcite.

2.2. Physical, Chemical, and Mineralogical Material Characterizations

The grain-size distribution (GSD) of all samples was analyzed using a laser analyzer (Malvern Mastersizer, Malvern Panalytical, Rouyn-Noranda, Quebec, Canada). The chemical composition of the solid samples was evaluated using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin Elmer Optima 3100 RL, USA) following complete digestion by $\text{HNO}_3/\text{Br}_2/\text{HF}/\text{HCl}$ (HF and HCL to dissolve silicates; HNO_3 and Br_2 to oxidize sulfur). The ICP-AES was calibrated using an international standard (SY-4). The detection limits of ICP-AES are variable and depend on the analyzed element (60 ppm for Al and Ca, 15 ppm for Mg, 5 ppm for Mn, 1 ppm for Na and K, 10 ppm for Fe, 5 ppm for Li, Pb, As and Cr, 10 ppm for Cu and 55 ppm for Zn). Total carbon and sulfur were analyzed in pulverized samples to $<74 \mu\text{m}$ via infrared spectroscopy following combustion in an induction furnace (ELTRA CS-2000; detection limit = 0.09%). During sulfur and carbon (S/C) analysis, blank samples consisted of samples containing only iron and tungsten. Calibration of the induction furnace was done using four standards: low carbon standard ([C] = 0.5 wt.%), high carbon standard ([C] = 11.97 wt.%), low sulfur standard ([S] = 0.28 wt.%), and high sulfur standard ([S] = 18.03 wt.%).

The mineralogical composition of tailings was investigated thoroughly using mineral liberation analysis (MLA). MLA is technique based on scanning electron microscopy with an energy dispersive spectrometer (SEM-EDS) that uses special software to automate mineral abundance quantification [60]. This technique also enables quantitative analyses of mineral liberation, mineral association, and elemental department. In this study, MLA was used to quantify modal mineralogy; calcite and pyrite liberation; and Ca, Mg, Fe, and S departments.

2.3. Toxicity Characteristic Leaching Procedure and Kinetic Column Tests

Toxicity characteristic leaching procedure (TCLP) was used as preliminary test to evaluate metal(loid) mobility within the different amendment formulations (Table 2). TCLP was primarily designed to simulate the release of heavy metal(loid)s and organics from municipal wastes [61], but is frequently used on mine tailings. In brief, around 20 g of each sample was added to 400 mL of a leaching solution composed of acetic acid [62]. Each mixture was then placed in a high-density polyethylene (HDPE) bottle, and the bottles were tumbled for 18 h at a 30 ± 2 rpm. Samples were filtered through a $0.45 \mu\text{m}$ nylon filter, and the leachates were analyzed for their pH, electrical conductivity (EC), and chemical composition (by ICP-AES).

Table 2. Formulations used for the alkaline and cementitious amendments.

Column	Amendment Type	Formulation
C1	Reference	Mine tailings
C2	Alkaline amendment	20 wt.% LS
C3	Alkaline amendment	10 wt.% LS
C4	Cementitious amendment	5 wt.% (50%FAF-50%CVK)
C5	Cementitious amendment	5 wt.% (20%OPC-40%CVK-40%FAF)
C6	Cementitious amendment	5 wt.% (80%OPC-20%CVK)
C7	Cementitious amendment	5 wt.% (20%OPC-40%CVK-40%FA)

Kinetic column tests (KCTs) are widely used to predict the environmental behavior of mine tailings, as well as to test different reclamation scenarios for acid-generating tailings [63]. Column tests are recognized as reproducible tests [64], and under the right conditions, they may be able to provide insight into the environmental behavior of wastes under field conditions. The column tests were monitored for more than 365 days. The long-term geochemical monitoring of columns presents several advantages, such as: (i) considering the possible dynamic changes, (ii) using a large quantity of sample (around 10 kg in this study), and (iii) allowing possible precipitation reactions. Seven amendment formulations were selected based on laboratory batch tests and tested in KCTs as indicated in Table 2. Each sample was placed in an acrylic column with a diameter of 14 cm and a height of 100 cm. Each column's inner wall was covered with grease to avoid the creation of preferential flow paths during the flushing of the samples [65]. Column C1 contained a reference sample of pure mine tailings. Columns C2 and C3 contained alkaline amendments based on the LS addition.

The limestone dosage was about 20 wt.% for C2 and 10 wt.% for C3. All the cementitious amendments were added to mine tailings at a total dosage of 5 wt.%. Column C4 contained 50%FAF-50%CVK, C5 contained 20%OPC-40%CVK-40%FAF, C6 contained 80%OPC-20%CVK, and C7 contained 20%OPC-40%CVK-40%FA.

The leachates from each column were analyzed for pH and EC using individual probes, while the acidity and alkalinity were analyzed using an automated titrator (Metrohm Binkmann, 716 DMS Trinitro, Rouyn-Noranda, Canada). The chemical composition of the leachates was determined by ICP-AES for samples filtered to 0.45 µm and acidified to 2% *v/v* HNO₃. The chemical quality of the leachates from the column tests was integrated in Visual Minteq (Version 3.1) to calculate the saturation indexes of the ferrihydrite and goethite [66]. Saturation indexes were calculated using the standard database of Visual Minteq.

3. Results and Discussion

3.1. Physical and Chemical Characteristics

The GSDs and chemical characteristics of the studied samples are presented in Table 3. Grain-size distributions were relatively heterogeneous. The D₉₀ values, which correspond to the diameter at which 90% of particles pass on the cumulative grain-size distribution curve, were about 30.4, 4500, 46.7, 1500, 104.2, and 89.1 µm for the mine tailings, LS, OPC, FA, CVK, and FAF, respectively. The mine tailings had a similar GSD to that of the OPC.

Table 3. Grain-size distribution and chemical composition of the studied samples (MT = mine tailing, LS = limestone, OPC = ordinary Portland cement, FA = fly ash, CVK = Kruger fly ash, FAF = fly ash class F, and DL = detection limit).

		Units	DL (ppm)	MT	LS	OPC	FA	CVK	FAF	
Chemical composition	Al		60	1.73	0.30	2.75	4.69	3.84	11.91	
	Ca		60	3.00	33.82	49.07	7.58	34.88	2.87	
	Mg		15	0.27	2.35	1.18	1.05	1.56	0.58	
	Mn		5	0.231	0.03	0.06	0.42	0.12	0.02	
	Na		1	0.972	0.125	0.16	1.96	0.45	0.45	
	K		1	0.267	0.245	0.43	1.85	0.32	1.38	
	Fe		10	19.30	0.483	2.23	2.24	3.31	13.43	
	Li	%	5	≤DL	≤DL	≤DL	0.002	≤DL	≤DL	
	Pb		5	0.042	≤DL	≤DL	≤DL	0.05	≤DL	
	As		5	≤DL	≤DL	0.005	≤DL	0.006	≤DL	
	Cr		5	0.01	0.004	0.007	0.006	0.014	0.02	
	Cu		10	0.001	≤DL	0.007	≤DL	0.031	≤DL	
	Zn		55	0.007	≤DL	0.049	0.070	0.15	0.19	
	S (total)		200	4.36	NA	1.737	0.431	3.33	0.38	
	S (sulfates)				4.20	NA	NA	NA	3.33	0.38
C	900		0.2	NA	NA	NA	1.29	2.69		
Physical characteristics	D ₁₀		μm		1.8	50	4.2	82	5.78	6.07
	D ₃₀				4.7	250	11.3	180	14.3	12.8
	D ₉₀				30.4	4500	46.7	1500	104.17	89.12

Chemical compositions of the bulk samples are shown in Table 3. The aluminum content was about 1.73, 0.30, 2.75, 4.69, 3.84, and 11.91 wt.% for the mine tailings, LS, OPC, FA, CVK, and FAF, respectively. Calcium concentrations were between 2.87 wt.% for the FAF and 49.07 wt.% for the OPC. Magnesium concentrations were below 2.5 wt.%, with the highest concentration of about 2.35 wt.% found within the LS sample. Iron concentrations were about 19.30 wt.% and 13.43 wt.% for the mine tailings and FAF, respectively, and <3.5 wt.% for all other samples. Total S contents were <4.5 wt.% for all samples. Concentrations of other species, including K, Na, Mn, Li, Pb, Cr, Cu, and Zn, are presented in Table 3.

3.2. Mineralogical Composition of the Mine Tailings

The mineralogical composition of the highly oxidized mine tailings was investigated using mineral-liberation analysis. The tailings' modal mineralogy and mineral-liberation degrees are presented in Figure 1. The tailings sample contained approximately 31 wt.% of secondary iron oxides, 20 wt.% of quartz, 16 wt.% of albite, 11 wt.% of chlorite, and 9 wt.% of gypsum. Secondary iron oxides were present as a cementitious material that coated various minerals, especially pyrite and silicates (Figure 2A–D). Other minerals were detected in varying concentrations, such as pyrite, chalcopyrite, and calcite. The pyrite content was about 0.44 wt.%, despite a total S content of about 4.36 wt.%. This suggests that a major part of pyrite was oxidized in situ and that the resulting sulfate precipitated as gypsum. As a result of sulfide oxidation, carbonates dissolved to buffer the produced acidity. Thus, residual calcite was present in trace amounts of about 0.19 wt.%. Comparing the sulfide content with the carbonate content allows prediction of the acid-generating behavior for the mine tailings, since it is recognized that the balance between acid-forming and acid-consuming minerals can inform on the environmental behavior of mine tailings (acid-generating or not) [13,67,68]. However, the reactivity of these minerals is influenced by several parameters, such as their available reactive surface area [69–73]. Therefore, the degree of liberation for calcite and pyrite was analyzed by MLA, as shown in Figure 1B. The degrees of liberation for calcite and pyrite were only slightly different. Free (liberation degree = 100%) calcite and pyrite represented around 47.6 and 55.5% of the total calcite and pyrite, respectively, which meant that the completely available reactive surface of pyrite was slightly higher than that of calcite. The locked part of calcite and pyrite was about 23 and 20%, respectively. Around 7.5% of calcite and pyrite were mid-liberated (between 20 and 70%).

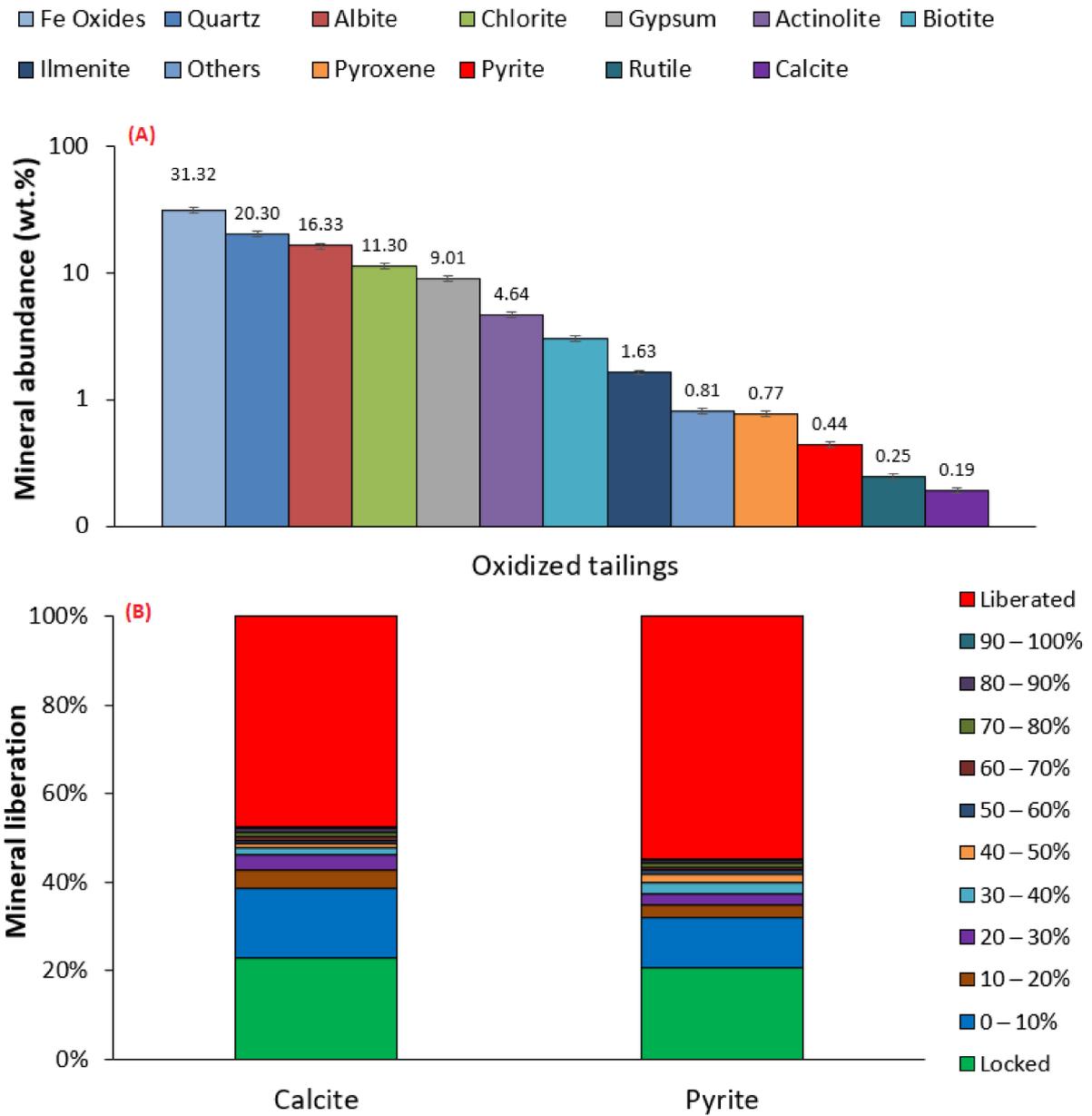


Figure 1. (A) Mineralogical composition of mine tailings; (B) calcite and pyrite liberation degrees.

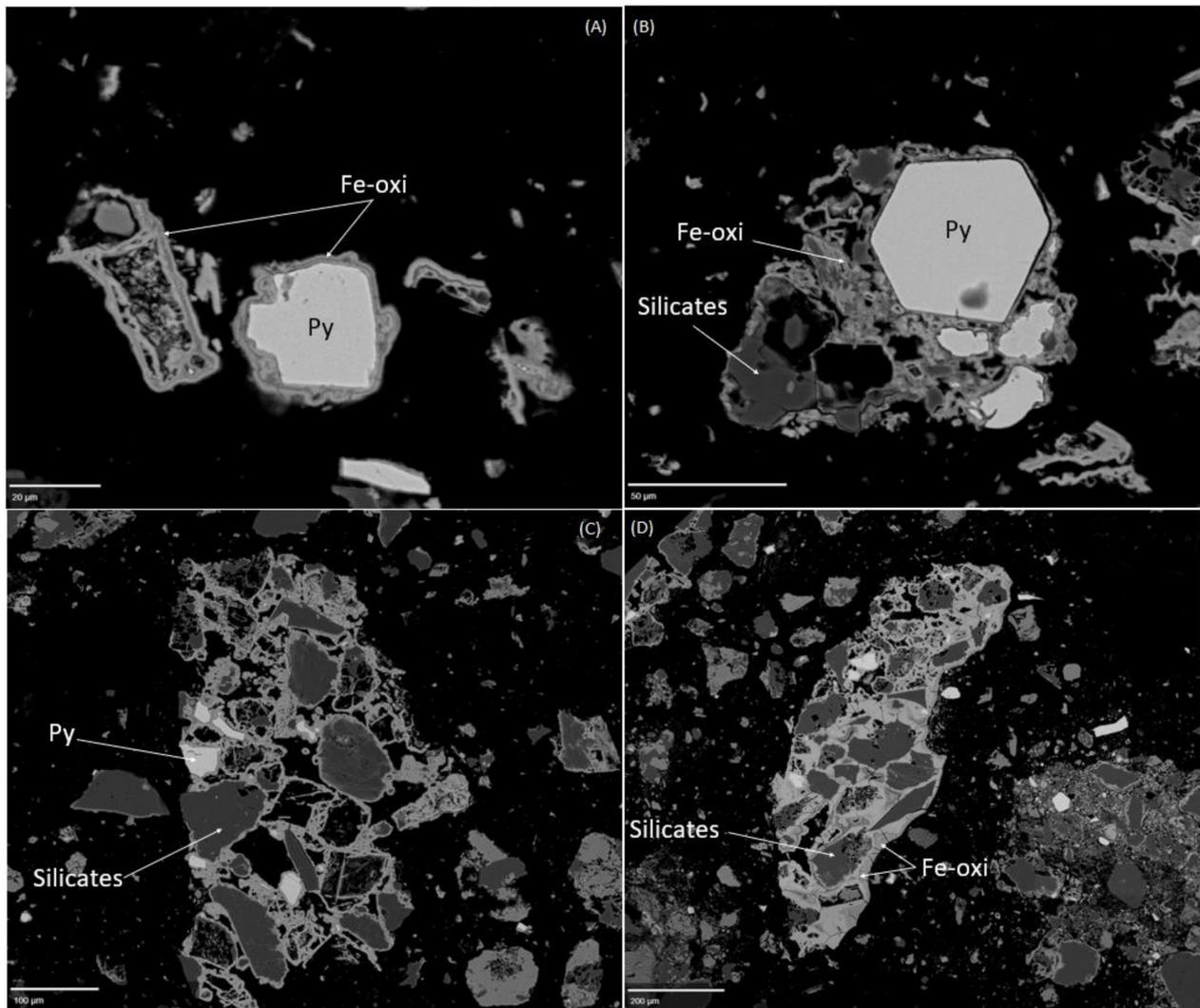


Figure 2. Backscattered electron (BSE) images showing the precipitation of secondary iron oxides on the surfaces of pyrite and silicates (Py = pyrite, Fe-oxi = iron oxides). (A–D) examples of pyrite and silicates coated by iron oxides.

Calcium, iron, magnesium, and sulfur deportments within the tailings sample are presented in Figure 3. The mineralogical composition of the studied sample showed Ca mainly occurring in three minerals: calcite [CaCO_3] $\text{—}3\%$, gypsum [$\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$] $\text{—}81\%$, and actinolite [$\text{Ca}_2(\text{Mg}, \text{Fe}^{++})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$] $\text{—}15.5\%$. Iron occurred mostly in iron oxides, followed by chlorite, actinolite, and pyrite. Around 84% of iron was present in iron oxides, 11% came from chlorite, and small amounts of iron were associated with actinolite and pyrite ($<2\%$). Magnesium mainly occurred in chlorite and actinolite; 74% of magnesium came from chlorite, and 26% came from actinolite. Sulfur was mainly associated with gypsum and pyrite; 87.5% of S came from gypsum, and 12% of S came from pyrite. Small amounts of S were also associated with chalcopyrite ($<0.2\%$).

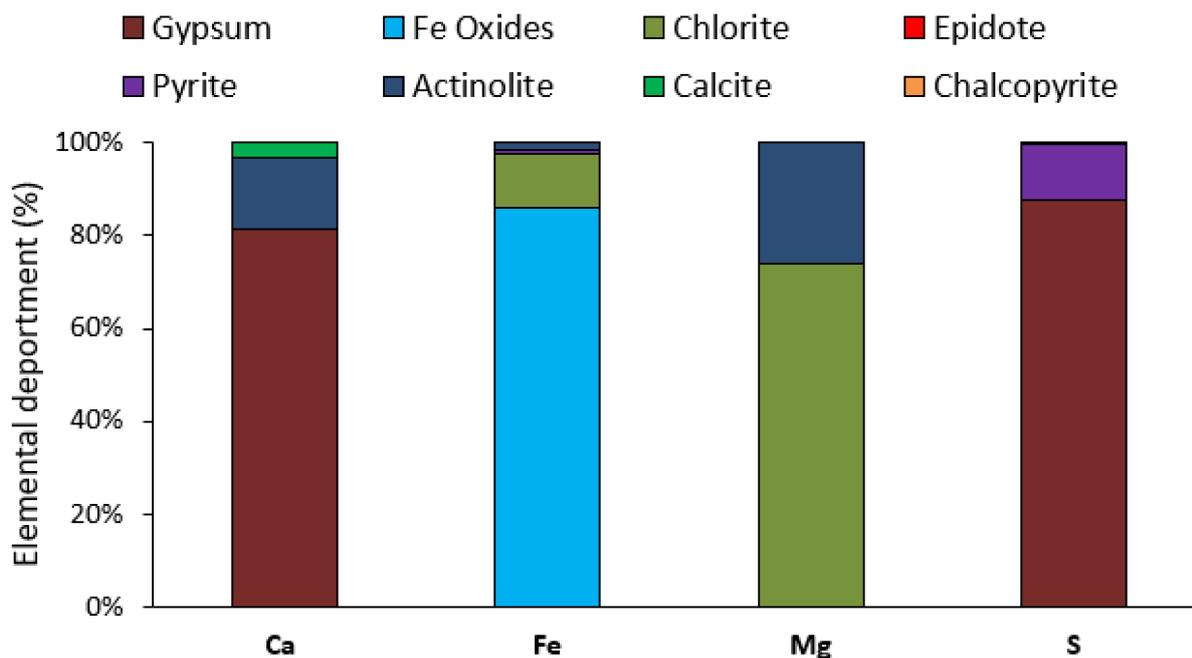


Figure 3. Elemental department of Ca, Fe, Mg, and S within the Joutel mine tailings.

3.3. Comparison of the Geochemical Behavior of Unamended and Amended Tailings

3.3.1. Results of Toxicity Characteristic Leaching Procedure

Table 4 presents results of TCLP tests that were carried out to evaluate metal(loid) mobility following different amendment treatments. The performance of each amendment formulation was slightly different. Both alkaline (C2 and C3) and cementitious formulations (C3, C4, C5, C6, and C7) increased the pH of the leachates compared to the unamended tailings, indicating the dissolution of alkaline phases that buffered the produced acid. The pH of the leachates from the unamended tailings was about 2.5, while pH values of that from amended tailings ranged from 4.92 for C6 (80%OPC-20%CVK) to 6.46 for C2 (20 wt.% LS). The analyzed EC was similar for all samples, ranging between 7.81 mS/cm for C1 and 9.37 mS/cm for C2.

Table 4. Results of the TCLP tests performed on unamended and amended tailings. Concentrations are presented in ppm. <DL indicates concentrations lower than the detection limit of the method.

	pH	EC (mS/cm)	Al	Fe	Ni	S	Zn
C1	2.50	7.81	0.40	0.50	0.01	766	0.60
C2	6.46	9.37	0.01	0.06	<DL	567	0.34
C3	5.58	8.84	0.01	0.05	<DL	608	0.33
C4	5.00	8.15	0.04	0.05	<DL	664	0.30
C5	5.05	8.25	0.02	0.05	<DL	669	0.60
C6	4.92	8.17	0.03	0.08	<DL	696	0.31
C7	4.93	8.05	0.05	0.04	<DL	695	0.30

The application of the different amendment formulations reduced Al, Fe, Ni, and Zn releases compared to the unamended tailings. Aluminum release from the unamended tailings was about 0.4 mg/L, but did not exceed 0.05 mg/L in any of the amended tailings. Iron releases were reduced from 0.5 mg/L from the unamended tailings to a maximum of 0.08 mg/L from C6. Nickel releases were around 0.01 mg/L for the unamended tailings and less than the detection limit of the analytical method for all amended tailings. Zinc concentrations were about 0.6, 0.34, 0.33, 0.30, 0.60, 0.31, and 0.30 for C1, C2, C3, C4, C5, C6, and C7, respectively. Finally, S releases were between a minimum value of 567 mg/L from C2 to a maximum value of 766 mg/L from the unamended tailings.

3.3.2. Kinetic Column Tests

The water quality of leachates from the KCTs are presented in Figures 4–6. The evolution of pH in the leachates from the KCTs (Figure 4A) varied widely among the tested samples. The mine tailings showed an acidic behavior characterized by pH values ranging between 2.1 and 2.8. Thus, there was a relatively small variation in pH values from the beginning to the end of the tests. However, the amended formulations raised pH values to circumneutral values. Average pH values were about 7.7, 7.2, 7.7, 7.4, 7.7, and 7.5 for C2, C3, C4, C5, C6, and C7, respectively, and these values were stable throughout the duration of the KCTs. Average EC values (Figure 4B) were about 4.2, 4.24, 4.93, 5.7, 6.8, 5.3, and 5.2 mS/cm for C1, C2, C3, C4, C5, C6, and C7, respectively. At the beginning of the leaching tests, EC values were notably higher than at the end of the tests. This is likely due to the redissolution and release of secondary mineral phases that are naturally present in preoxidized tailings. Acidity and alkalinity values were in stark contrast between the amended and unamended materials (Figure 4C,D). Acidity in leachates from unamended tailings started at around 1400 mg CaCO₃/L, then stabilized at around 300 mg CaCO₃/L. However, average acidity values in the amended tailings were 23, 60, 33, 45, 31, and 42 mg CaCO₃/L for C2, C3, C4, C5, C6, and C7, respectively. The results for acidity were mirrored by the results for alkalinity (Figure 4D). Leachates from the unamended tailings (C1) showed negligible alkalinity values. The amended tailings showed leachates with non-negligible values. Average alkalinity values were about 144, 141, 359, 232, 307, and 264 mg CaCO₃/L for C2, C3, C4, C5, C6, and C7, respectively. In general, the cement-based amendments showed higher alkalinity values compared to the limestone-based amendments.

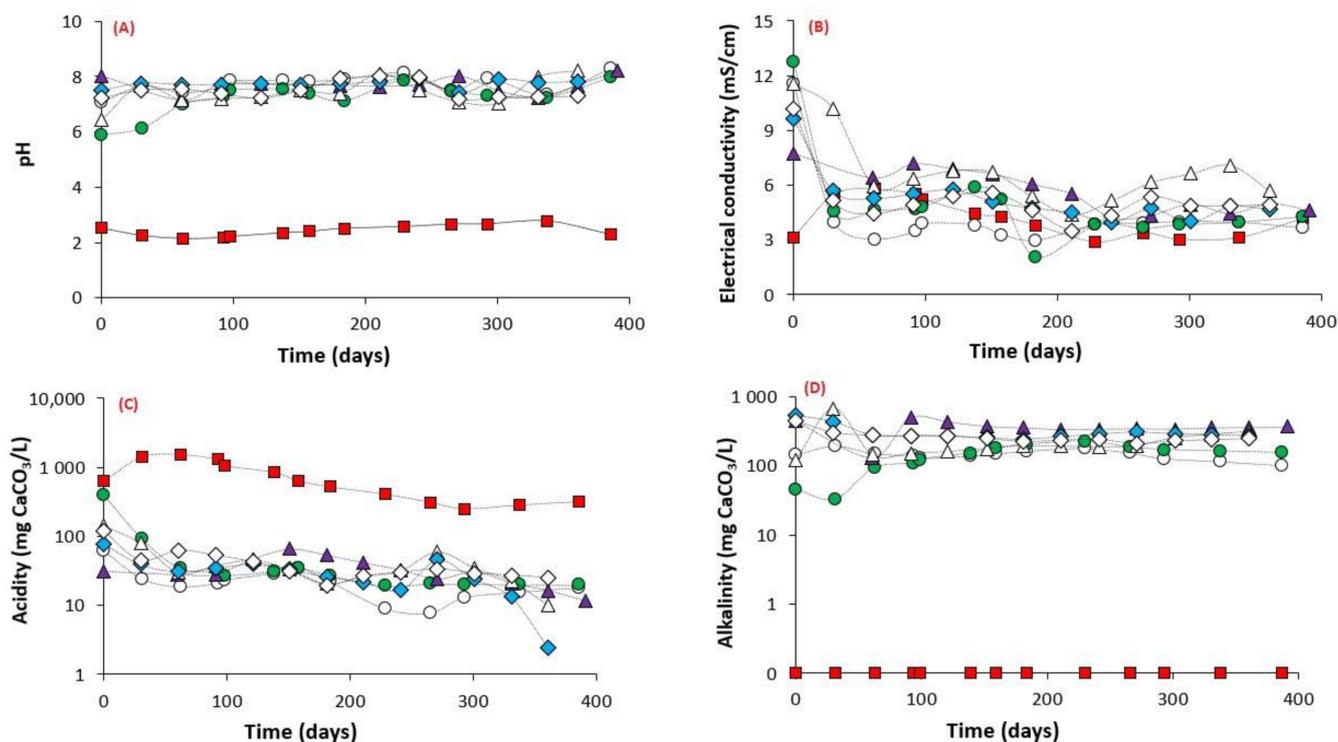


Figure 4. Evolution of (A) pH, (B) electrical conductivity, (C) acidity, and (D) alkalinity within the leachates from the kinetic column tests.

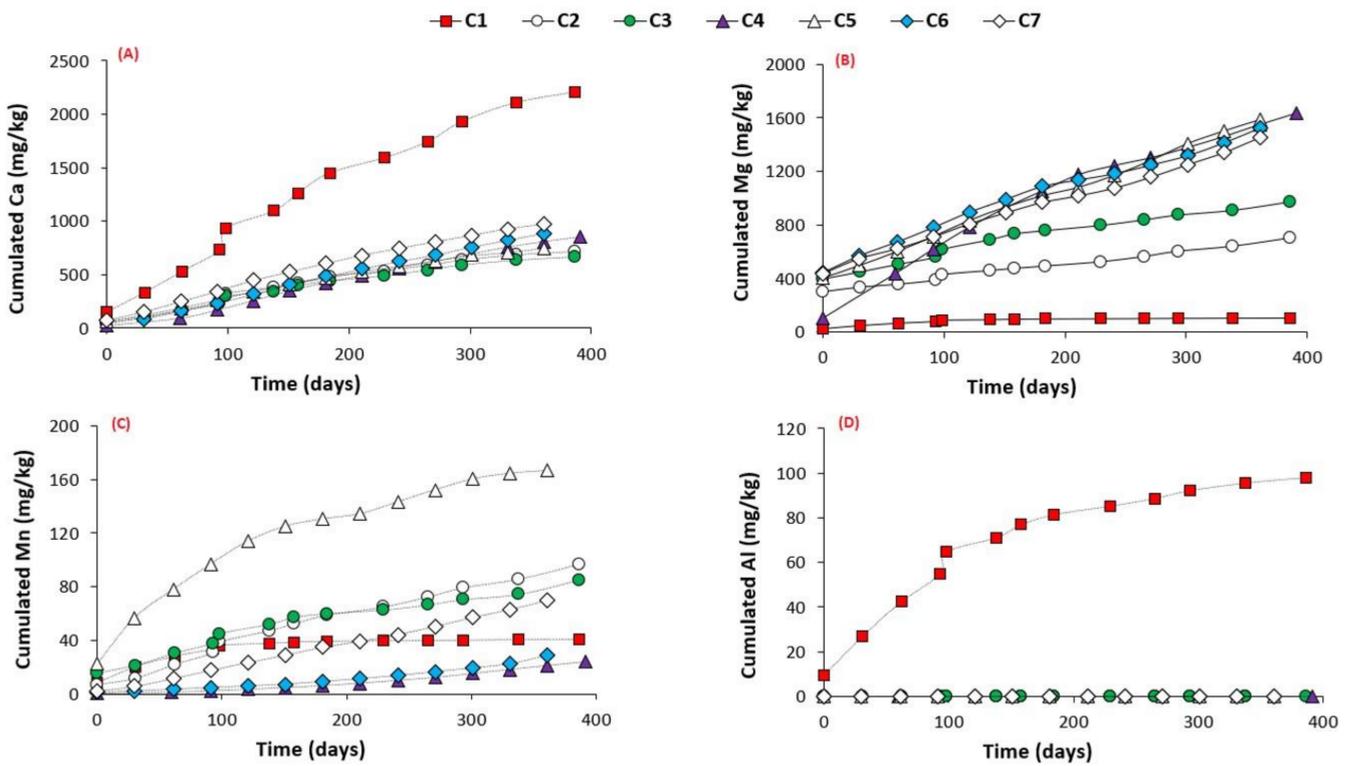


Figure 5. Evolution of cumulative concentrations of (A) Ca, (B) Mg, (C) Mn, and (D) Al.

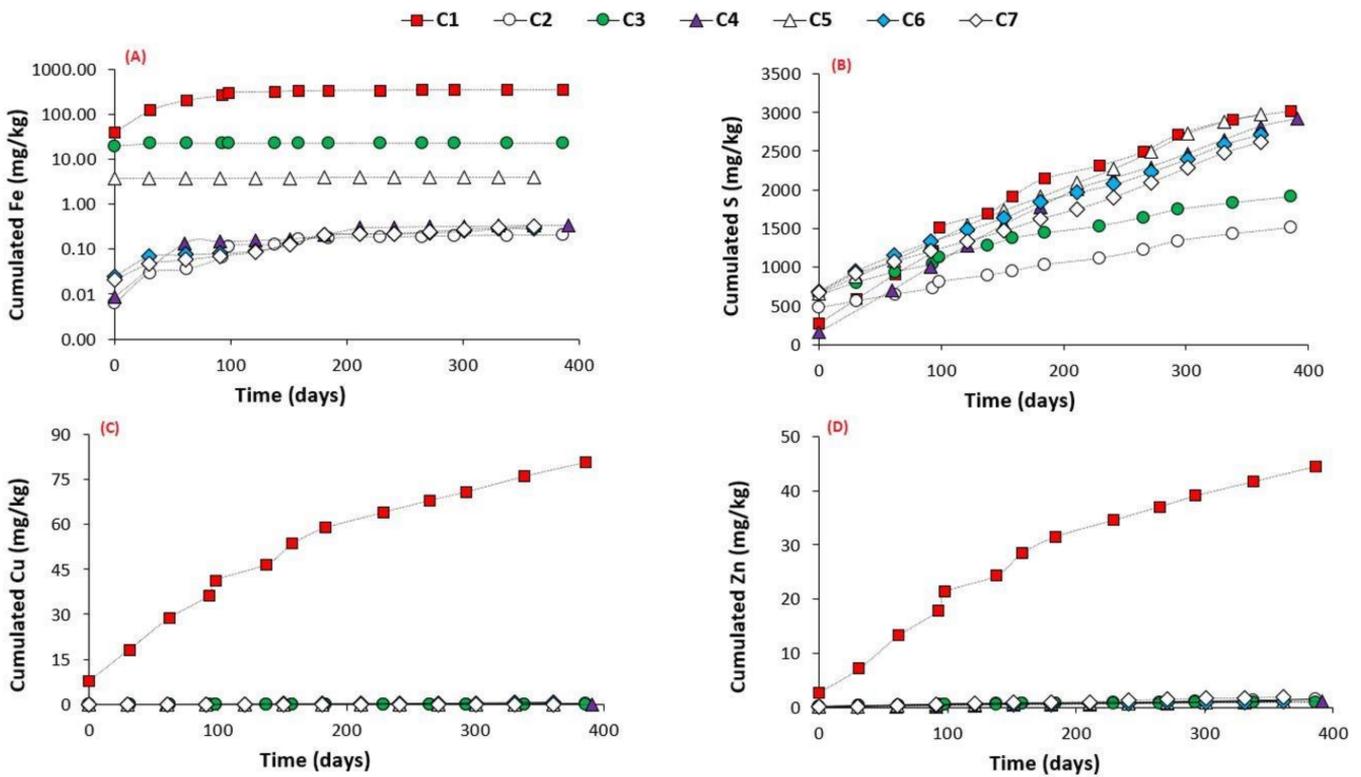


Figure 6. Evolution of cumulative concentrations of (A) Fe, (B) S, (C) Cu, and (D) Zn.

Concentrations of the chemical species in Figures 5 and 6 are presented as cumulative, mass-normalized releases (mg/kg) to avoid effects due to leachate volumes and the samples' initial weights. Calcium, magnesium, and manganese were chosen to indicate

dissolution of neutralizing minerals [74], and aluminum was chosen to indicate aluminosilicate dissolution [74]. Calcium releases (Figure 5A) were variable among the KCTs. The unamended tailings released higher concentrations of Ca compared to the amended tailings. Over 361 days, cumulative Ca release was about 2203, 713, 664, 849, 750, 937, and 969 mg/kg for C1, C2, C3, C4, C5, C6, and C7, respectively. Magnesium release was the lowest for the unamended tailings (~105.5 mg/kg). In contrast, Mg release was about 699, 972, 1634, 1588, 1524, and 1456 mg/kg for C2, C3, C4, C5, C6, and C7, respectively. Manganese releases were similar in all columns, being about 41, 97, 85, 24, 167, 29, and 70 mg/kg for C1, C2, C3, C4, C5, C5 and C7, respectively. Aluminum releases were negligible for the amended tailings, not exceeding 0.5 mg/kg. However, for the unamended tailings, Al release was about 98 mg/kg.

Iron (Figure 6A) was released more from the unamended tailings compared to the amended tailings. Iron release was about 342.5, 0.2, 22.2, 0.4, 3.9, 0.3, and 0.3 mg/kg for C1, C2, C3, C4, C5, C6, and C7, respectively. In general, Fe release is greatly influenced by pH/Eh conditions. Under circumneutral conditions, Fe precipitates as Fe-oxyhydroxides, thus explaining the low Fe concentrations observed in leachates from the amended tailings [75]. Sulfur was the most released element (Figure 6B). Cumulative S concentrations were about 3022, 1511, 1912, 2915, 2981, 2721, and 2616 mg/kg for C1, C2, C3, C4, C5, C6, and C7, respectively. Copper and zinc concentrations were negligible for the amended tailings, suggesting that they were largely immobile under these conditions (Figure 6C,D). Copper and zinc releases from the unamended tailings were about 81 and 44.50 mg/kg, respectively.

At the end of the KCTs, water-infiltration speed was measured for the different column tests. The main objective was to compare the hydraulic conductivity reduction of the different formulations. The results from the water-infiltration tests are presented in Figure 7. Samples C1, C2, and C3 drained water more quickly than the other samples. At 4000 min, about 68 mL was drained from C1, 69 mL was drained from C2, and 60 mL was drained from C3. In contrast, 30 mL was drained from C4, 49 mL was drained from C5, 48 mL was drained from C6, and 38 mL was drained from C7. In general, the cementitious amendments decreased water-infiltration rates through the tailings the most. This is likely explained by tailing cementation and cohesion processes that reduced the hydraulic conductivity of the amended materials [76].

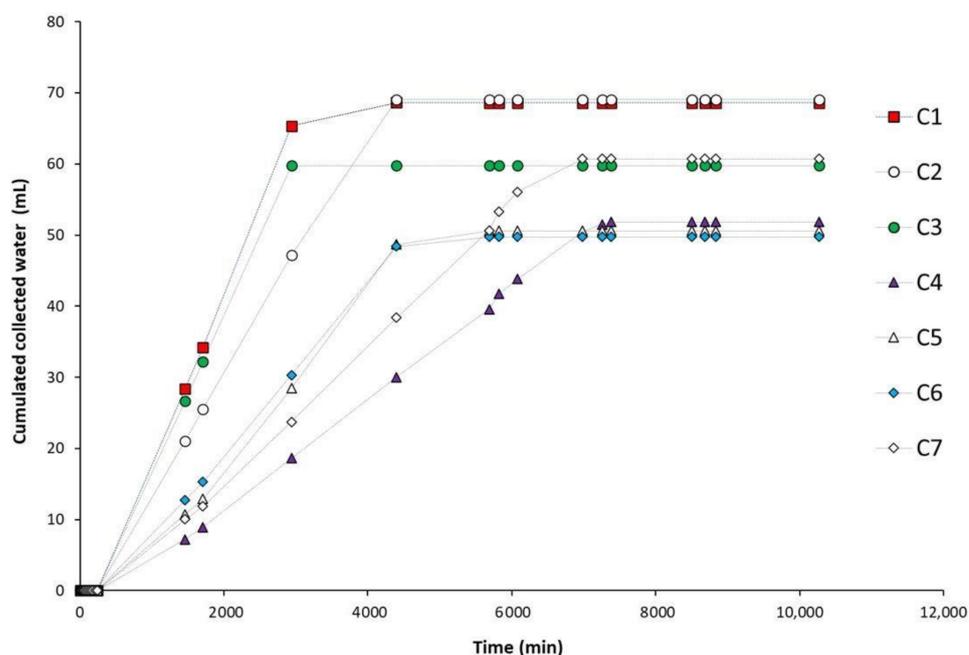
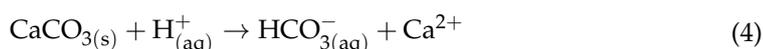
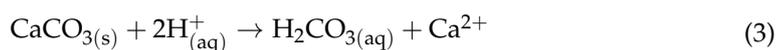


Figure 7. Results of water infiltration through the different kinetic column tests.

4. Discussion

The unamended tailings (C1) showed an acidic behavior; pH values were lower than 3 from the very first stages of leaching (Figure 4). Consequently, the acidity of the leachates from the unamended tailings reached high levels compared to that of the amended tailings. This could be explained by the mineralogical composition of the mine tailings. Their carbonate content was lower than 0.2 wt.%, and the calcite liberation degree was around 50%. This meant that the reactive surface of calcite was reduced by half, as suggested by several authors who demonstrated that a mineral's reactivity is influenced by its liberation degree [69–72,77]. Consequently, the tailings' neutralization potential was likely negligible, assuming that the NP was influenced mainly by its carbonate content [5,11]. Mineralogical analyses of the mine tailings revealed that the acidity could be from two sources: (i) pyrite oxidation and (ii) latent acidity due to the release of exchangeable Fe [65,78,79]. Exchangeable Fe explains the high concentrations of Fe released within the unamended tailings during the first stages of the leaching tests. Moreover, considering environmental regulations in Canada, such as Directive 019 in Quebec [80], the mine tailings used in this study are considered as problematic and require a reclamation scenario to prevent environment contamination. Instantaneous Fe concentrations in leachates from the unamended tailings were around 78 mg/L, which exceeded the regulatory limit of 3 mg/L set by Directive 019 (Quebec, Canada). The same tendency was observed for Cu, Pb, and Zn, which also exceeded regulatory limits. Average instantaneous concentrations of Cu, Pb, and Zn were 20.3, 1, and 11.35 mg/L, respectively; while their average concentrations should not exceed 0.3, 0.2, and 0.5, respectively.

The geochemical behavior of limestone- and cement-based amendments (Table 2) enabled the neutralization of acidity in the Joutel mine tailings. Following the amendment, pH values were maintained at circumneutral values (around 7.5), and the leachates of the amended tailings were less concentrated in several significant, toxic metals. The two categories of amendments used in this study were: (i) alkaline amendments (10% and 20% limestone) and (ii) cementitious amendments (based on OPC, FAF, CVK, and FA). Acid buffering by all amendments was performed through carbonate dissolution [48,81–83]. Depending on the pH of the system, two reactions of calcite (carbonate) dissolution could occur (Equations (3) and (4)):



For the cement-based amendments, cement hydration and the precipitation of hydrated phases could produce additional alkalinity [23,43]. For example, the dissolution of two moles of tricalcium silicate (C₃S) produced by cement hydration produces 8 moles of OH[−] following the reaction (Equation (5)):



The mobilities of the chemical species, including Al, Cr, Cu, Fe, Pb, S, and Zn, were greatly reduced through the use of both the alkaline and cementitious amendments. Reduction factors, calculated using Equation (6), are presented for Al, Cr, Cu, Fe, Pb, S, and Zn in Figure 8. The reduction factor for each element was calculated based on its average concentration in leachates from the unamended and amended tailings [15]:

$$\text{RF}_i = 100 \times \left(1 - \frac{C_a}{C_0} \right) \quad (6)$$

where RF_i is the reduction factor for element i; C_a is the cumulative concentration (mg/kg) for the element i from amended column (C2 to C7); and C₀ is the cumulative concentration (mg/kg) for the element i in the leachates from oxidized tailings (control column; C1).

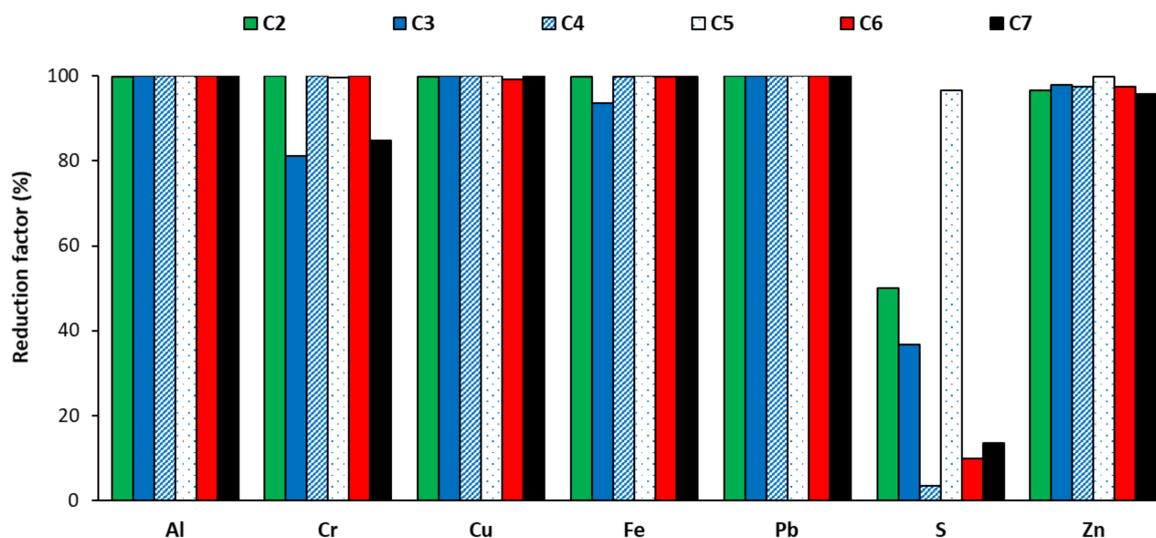


Figure 8. Reduction factors for selected elements in comparison to initial concentrations within unamended tailings.

The RF_{Al} was around 100% for all amendments tested in this study. The RF_{Cr} was about 100%, 81%, 100%, 100%, 100%, and 85 % for C2, C3, C4, C5, C6, and C7, respectively. RF_{Cu} , RF_{Fe} , RF_{Pb} , and RF_{Zn} values were >95% for all amendment formulations tested in this study. Sulfur was immobilized less compared to other elements. Indeed, S immobilization was only about 50%, 37%, 4%, 97%, 10%, and 13% for C2, C3, C4, C5, C6, and C7, respectively. Metals immobilization within cementitious and alkaline amendments is ensured by several chemical and physical mechanisms [15,27,48,84]:

- i. Alkaline amendments: adding alkaline materials, such as limestone, enhances the neutralization potential of the mixture. This shifts the balance between the acid-generating potential and neutralization potential in a given tailing [20,85]. Acid buffering is reflected by an increase in the alkalinity and pH of the leachates (Figure 4). Changing the geochemical conditions of the system influences the elemental department. This means that a number of secondary phases may precipitate [13], the most notable of which are Fe-oxyhydroxides such as ferrihydrite and goethite, and sulfates such as jarosite [68,86]. Although several mechanisms are responsible for metal(loid) attenuation, the most discussed mechanisms are Fe-oxyhydroxide precipitation, and sorption mechanisms [87–89]. Moreover, saturation indexes for ferrihydrite and goethite calculated using Visual Minteq (V3.1) showed that these two minerals will likely precipitate (saturation index >0) for the amended tailings (Figure 9A,B). However, for the unamended tailings, these two mineral species will remain in solution (saturation index <0). Dissolution for Fe-oxyhydroxides within the unamended tailings and their precipitation within the amended tailings explains the high concentrations of Fe analyzed within the leachates from the Joutel tailings (Figure 6A).
- ii. Cementitious amendments: the same mechanisms discussed within alkaline amendments also occur within cementitious amendments, as they also neutralize acid and increase pH (Figure 4). However, the use of cementitious additives also improves the mechanical properties of the mixtures [23,47,50]. The use of cement and industrial byproducts increases the cohesion and the long-term impermeabilization of the mixture [15]. Consequently, contaminant mobility and diffusion are significantly limited by (i) physical trapping, and (ii) reducing the reactive surface area of the mixture. Tailing solidification reduces the available surface area of sulfide minerals, and thus their reactivity [35,36].

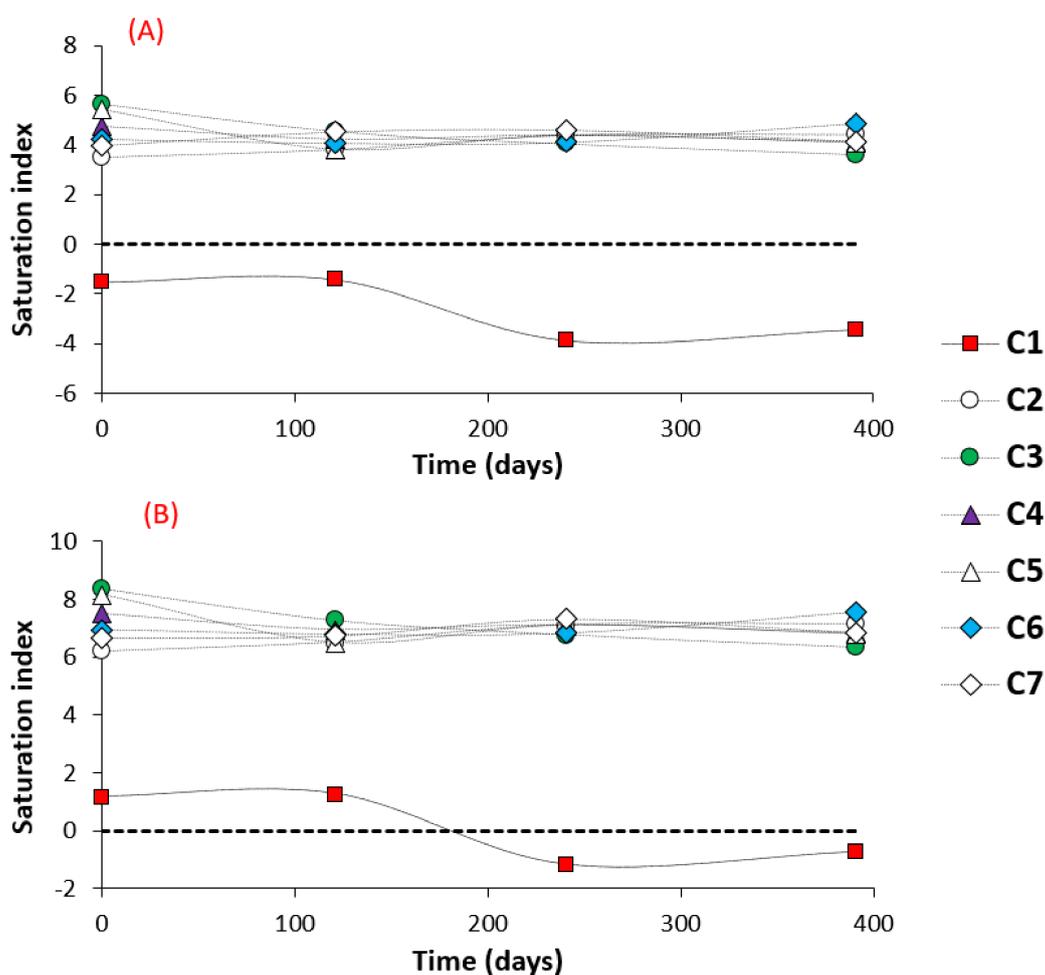


Figure 9. Saturation index for (A) ferrihydrite and (B) goethite.

Performances of the tested amendments were significantly different considering results of the TCLP tests and KCTs. Column tests are more realistic than TCLP tests due to several factors: (i) sample size—within column tests, higher sample masses (>10 kg) are used compared to those used in TCLP tests (20 g); (ii) liquid/solid ratios (LSR)—the LSR in TCLP tests is about 20, while in column tests it is around 0.2; thus, dilution of elements may occur within the TCLP tests; (iii) test duration—KCTs and TCLP tests are performed on different time scales (18 h for TCLP tests and 361 days for columns); and (iv) leaching solutions—the solution used for the KCTs was deionized water, and that used for the TCLP tests was acetic acid. Therefore, the reactivity of the mineralogical phases will be different. For these reasons, KCTs may represent more accurate tests for evaluating the performance of amendments to stabilize acid-generating tailings. Moreover, Ghosh, Mukiibi [90] showed that TCLP tests may underestimate leaching of some chemical species such as arsenic.

Considering metal(loid) immobilization, both the alkaline and cementitious amendments showed relatively similar effectiveness. However, several factors make the formulations based on industrial byproducts better. The formulations based on limestone require a quarry for carbonate extraction. This represents an additional environmental impact to resolve another environmental problem (AMD). Consequently, the formulations based on industrial byproducts (e.g., fly ashes) could be more interesting. Substitution of byproducts for OPC could also reduce costs related to cement production and valorize some industrial wastes. Teixeira, Mateus [91] showed that the substitution of cement with fly ashes is a viable alternative because it allows the reduction of the environmental footprint of cement production. The use of industrial byproducts in the S/S technology is an ecofriendly option,

but it must not affect the contaminants stabilization. This study proved that acid-generating and contaminated tailings can be stabilized using limestone and cementitious additives. Similarly, the use of industrial by-products in the stabilization of mine tailings needs more considerations during the rehabilitation of mine sites. Moreover, a technical and economic study is required to select the best scenario among those tested in this study. Additionally, geochemical modeling of the leachates from the different columns can be useful to predict the long-term efficiency (>10 y) of the tested formulations. Similarly, field tests are required to test the in situ effectiveness of the formulations used in this study. However, Elghali et al. (2019) [15] have already demonstrated that alkaline and cementitious amendments are efficient to neutralize acid-generating tailings and prevent contaminants release by AMD.

5. Conclusions

The reclamation and management of tailing storage facilities is a crucial step in the life cycle of a mine. The objective of TSF reclamation is to reduce or eliminate the risk of environment contamination due to acid and/or metal(loid) release. The mine tailings characterized in this study were acid-generating. Their neutralization potential was negligible due to carbonate depletion (calcite content <0.2 wt.%). Consequently, kinetic tests showed that the mine tailings generated AMD with no lag time. The mine tailings presented the risk of releasing Al, Cr, Cu, Fe, Pb, and Zn into the environment. Iron concentrations were significantly higher (78 mg/L) than the limit set by current regulations (3 mg/L). To stabilize these acid-generating tailings, amendments based on limestone, ordinary Portland cement, and fly ash were tested. All amendments showed promising results with respect to immobilizing potentially harmful chemical species. Indeed, pH values of the amended tailings immediately increased to circumneutral values (around 7.5). Moreover, the reduction factors of Al, Cr, Cu, Fe, Pb, and Zn releases were all higher than 80%. Application of this technique in the field at full scale will require a thorough economic evaluation of individual amendment formulations.

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