

PRELIMINARY EVALUATION OF A PASSIVE TREATMENT FOR MINE TAILINGS IN PORTOVELO, EL ORO, ECUADOR

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Introduction

Tailings impoundments are an almost inexhaustible source of contamination from sulphide oxidation, mainly pyrite, which represents the main environmental challenge facing the mining industry worldwide. Abandoned mining areas and/or uncontrolled tailing dumps expose tonnes of sulphide-rich wastes to oxidation under atmospheric conditions, generating highly acid leachates with extreme concentrations of metals, metalloids and sulphates known as acid mine drainage (AMD) (Lowson, 1982; Parker and Robertson, 1999; Younger et al., 2002; Delgado et al., 2009).

In mine tailings, the mechanisms that control the oxidation process are mainly environmental parameters like climate conditions and precipitation (Dold, 2003; Acero, 2007). In addition, the potential for AMD generation depends on the following factors: i) bacteria control; ii) pH; iii) sulphide content; iv) the grain size of the waste material, including the crystallinity and morphology of sulphides; v) the type of storage or waste management; and vi) the capacity to neutralize acidity by means of carbonates present in the wastes. In order to reduce the environmental impact of mine tailings, several remediation strategies have been designed: a) addition and mixing of an alkaline reagent with the mining sludge to promote AMD neutralization (e.g. Mylona et al., 2000); b) physical treatment, which consists on the application of synthetic sealants on the tailings to prevent oxygen ingress and water infiltration (e.g. Romano et al., 2003); or c) combining aspects of the physical and chemical strategies, this method is based on the self-isolation of the mining waste by inducing the formation of a cemented layer by adding an alkaline cover (e.g. Chermak and Runnells, 1997; Quispe et al. 2013). Limestone is the most commonly used additive for the chemical neutralization of sulphide-rich wastes. Calcite (CaCO_3) and dolomite (MgCO_3) are the principal minerals providing alkalinity, so they can neutralize the acidity. According to the equation 1 (Cravotta et al., 1990), the potential generation of acid can be calculated by stoichiometry considering a ratio of 1:3.15, which means that per 1% of sulphide (FeS_2) in any given sample, 3.15% of calcite (CaCO_3) is required to neutralize the acidity generated by sulphide oxidation. In other words, any tailings or mine waste with 1% sulphide content needs 3.15

times more neutralizing minerals like calcite and dolomite to avoid generating acid drainages. Therefore tailings with only 1% of sulphide and a lack of neutralizing minerals will be susceptible to the generation of AMD. As such, any waste management methodology for mine tailings must first consider a detailed geochemical and mineralogical analysis.



One of the most important mining districts in Ecuador is Portovelo, located in El Oro Province. This district is mainly drained by the Amarillo River and the Calera River which are part of the Puyango watershed. Many authors have evaluated the impact of Portovelo mining on aquatic ecosystems (e.g. SGAB-Prodeminca, 2000; Tarras-Wahlberg, 2001; Tarras-Wahlerberg y Lane, 2003; Betancourt et al., 2005; Guimarães et al., 2011). These studies have demonstrated how mining activities have impacted negatively on water, soil, sediments, macro invertebrates and fish in the Puyango watershed.

Portovelo constitutes a complex system of deep veins in a zone of 50 km length, 10 km width, and a vertical profile around 1400m. Gold ore is associated with sulphides (mainly pyrite, chalcopyrite, sphalerite and arsenopyrite) in quartz veins. The host rock is formed by dacitic-andesitic volcanic rocks. Generally, the release of acid rock drainage is avoided due to the alkaline composition of host rocks which assures a low contribution of metals to rivers. However, once the ore body is exploited and minerals are processed, the oxidation of sulphide-bearing waste rock and tailings increases the potential for acid drainage.

High concentrations of metals may be released in mine tailings and mine waste water due to inadequate and inefficient recovery methods. In Portovelo, liquid and solid wastes from processing plants are usually released into rivers or deposited on the surrounding soil without any security measure, which constitutes a great impact to the environment. However, highly alkaline processes like cyanidation and flotation are applied in the processing plants for gold and bulk of metals recovery, respectively, generating tailings with alkaline properties. Nonetheless, inappropriate tailings management strategies could enhance oxidation of the tailings, increasing the potential for the development of acid drainage. Indeed INIGEMM (2014) reported environmental liabilities in Portovelo which are already generating AMD.

A pilot-scale experimental plot (Figure 1) has been initiated for the remediation of mine tailings in the Portovelo district. This study's hypothesis is that the different nature of mining wastes, acids or neutro-alkalines, can be a factor to reduce the environmental impacts of mine tailings. The implementation of this experimental plot allows the oxidation of disseminated sulphides in tailings to be studied. In addition, potential treatment mechanisms for tailings or mine wastes in Portovelo can be tested, and waste management plans for reducing the probability to generate acid mine drainage and wastewater can be proposed.

Methodology

In June 2014, according to preliminary chemical/mineralogical data provide by SGAB-Prodeminca (2000), tailings samples were collected from three sites located in Portovelo (EMICOR, LOS AGAPITOS, and SAN JOSÉ). From each sample, bulk analysis and mineralogy were done by ICP-OES (Perkin-Elmer Optima 8300) and XRD (Bruker D.8 advanced), respectively.

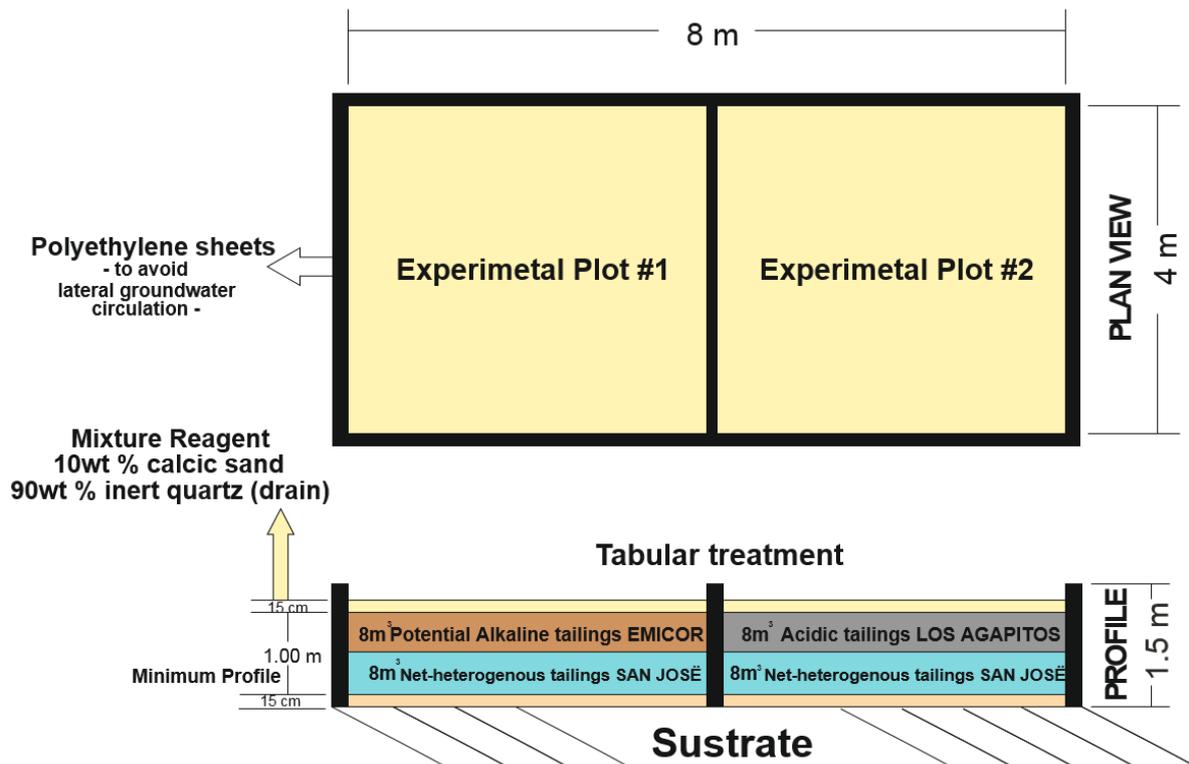


Figure 1. Pilot-scale treatment system scheme, showing the disposition of tailings in each experimental plot.

An experimental plot (Figure 1) for storage of the three tailings samples was built as a pilot-scale treatment system. The plot installation was completed in June 2014 and consisted of a plot of 8x4x1.50m in size, divided into two sub-plots of 16m². Each plot was waterproofed to avoid lateral chemical diffusion and potential pollution of adjacent areas. Quartz sand was put in the plots as a substrate or drainage material, and a collection system for effluents was also implemented. Finally, depending on the mineralogy and bulk analysis composition, tailings were disposed in each plot covered with a 15cm mixture reagent as reactive layer (Figure 1). This top layer was composed of a mixture of 10 wt% limestone sand and 90 wt% inert quartz sand as a drainage material. Due to viability reason and to ensure reactivity, 0.01 to 2mm, high purity (94%), limestone sand (Mocoral gravel) acquired in LACEC (Quito) was used in the top layer.

Once experimental treatment was implemented, sampling campaigns were conducted every three months. Each campaign consisted on taking a down-core by

means of 1m-long polyethylene tube. In the laboratory, specific subsamples taken from interphases between the reactive layer and the upper tailings, and the upper tailings and the heterogeneous one were collected from each experimental plot down-core. In addition, other samples were collected every 10 cm in order to monitoring the metal vertical fluxes. All of the samples were dried at 30 °C, disaggregated, homogenized and convenient storage to future conventional geochemical and mineralogical analysis. In situ, subsamples were analysed by Field Portable XRF (Thermo Scientific Niton XL3t) and by Field Portable XRD/XRF (Terra). To date, two sampling campaigns have been completed in the dry season (July and October 2014). In July, one sample of water from the drainage system of the experimental plots was collected, but, in October, there was no evidence of drainage because of the dry season. This water sample was sent to the INIGEMM Chemical Laboratory to determine chemical composition by ICP-OES and sulphate concentration by titration.

Results and discussion

Results from the preliminary analysis are shown in Table 1. From this table, the EMICOR tailings have a greater alkaline mineral (calcite, hydrotalcite, actinolite, and dolomite) content (18%) than the LOS AGAPITOS (2.6%) and SAN JOSÉ (13.5%) tailings. The EMICOR tailings also have the highest concentration of Ca (13.95%), and the lowest concentration of S and Fe (1.67 % and 4.42%) in comparison with the two other tailings. The EMICOR tailings can be considered as net-alkaline; this is consistent with the findings of previous studies. On the other hand, the SAN JOSÉ tailings contain the highest concentration (8.7%) of sulphide minerals (pyrite, arsenopyrite, chalcopyrite and gypsum), the lowest concentration of Ca (2.13%), and the highest concentration of S (11.5%) and Fe (13.7%). However, from previous studies, the SAN JOSÉ tailings had lower concentrations of sulphide minerals (2.90%), higher concentration of alkaline minerals (21.2%), 12.4% of Ca, 2.39% of S and 3.9% of Fe. Therefore, in this study, the SAN JOSÉ tailings material is considered heterogeneous tailings since it comes from a processing plant that works with ore from different sources every day. Finally, the LOS AGAPITOS tailings contained 2.3% of sulphide minerals which cannot be neutralized by only 2.6% of alkaline minerals. Moreover, these tailings contained 5.77% of Ca, 3,34% of S and 5,33% of Fe. With this composition, the LOS AGAPITOS tailing has been considered as acidic tailings in this study.

Table 1. Mineralogy and Bulk Analysis Composition of tailings previously collected for plant installation in June 2014

Plant		LOS AGAPITOS	EMICOR	SAN JOSÉ
	X	652084	651691	650623
Location	Y	9589730	9589573	9585578
Mineralogy				
Quartz	%	60,6	36,8	42,2
Albite-Anortite	%	4,20	12,1	6,20
Muscovite	%	13,1	8,10	10,9
Clorite	%	12,3	7,20	6,40
K-Feldesphate	%	2,20	9,30	x
Kaolinite	%	x	7,10	x
Calcite	%	1,50	13,2	5,90
Hydrotalcite	%	x	2,30	0,40
Dolomite	%	1,10	x	7,20
Actinolite	%	x	2,5	x
Pyrite	%	1,60	1,00	6,90
Chalcopyrite	%	0,70	0,20	0,30
Arsenopyrite	%	x	x	1,50
Gypsum	%	x	x	x
Magnetite	%	0,40	x	x
Sylvite	%	0,40	x	x
Dravite	%	1,90	x	x
Bulk analysis composition				
Ca	%	5,77	13,95	2,13
Na	%	0,55	0,30	0,29
K	%	1,32	1,99	2,33
Mg	%	3,88	1,23	1,74
Al	%	9,52	9,90	11,3
S	%	3,34	1,67	11,5
Fe	%	5,33	4,42	13,7
Mn	ppm	1405	3529	2262
As	ppm	916	1229	12970
Cd	ppm	12,9	2,46	12,2
Co	ppm	19,1	15,6	47,6
Cr	ppm	49,8	39,1	102
Cu	ppm	1541	908	2045
Ni	ppm	55,76	52,7	78,4
Pb	ppm	1153	676	5927
Zn	ppm	91,7	4,47	4454
Ag	ppm	19,3	76,4	30,2

Three conventional Cu K α XRD spectra are shown in Figure 2. The blue spectrum corresponds to subsamples taken at 20cm from the surface in both experimental plots; in other words, these subsamples are part of the net-alkaline EMICOR tailings and the acidic LOS AGAPITOS tailings, respectively. The orange spectrum represents subsamples taken in the interphase (reactive surface) existing in each plot. Finally, the grey spectrum represents subsamples taken at 70cm from the surface, corresponding to the heterogeneous SAN JOSE tailings.

From Figure 2A, in LOS AGAPITOS diffractogram, there are peaks of quartz and ferrihydrite. In the SAN JOSÉ diffractogram, there are peaks of quartz, calcite, ferrihydrite, hematite and noise that may correspond to formation of amorphous complexes due to the heterogeneity of this tailings material. While, in the interphase, ferrihydrite and hematite peaks are also present.

From Figure 2B, in the EMICOR diffractogram, there are peaks of quartz and a great peak of calcite which corresponds to the initial composition of the tailing. On the other hand, apparently in the SAN JOSÉ diffractogram, there are only peaks of quartz and no peaks of pyrite or any other sulphide minerals. While, in the interphase, ferrihydrite and hematite peaks can be seen.

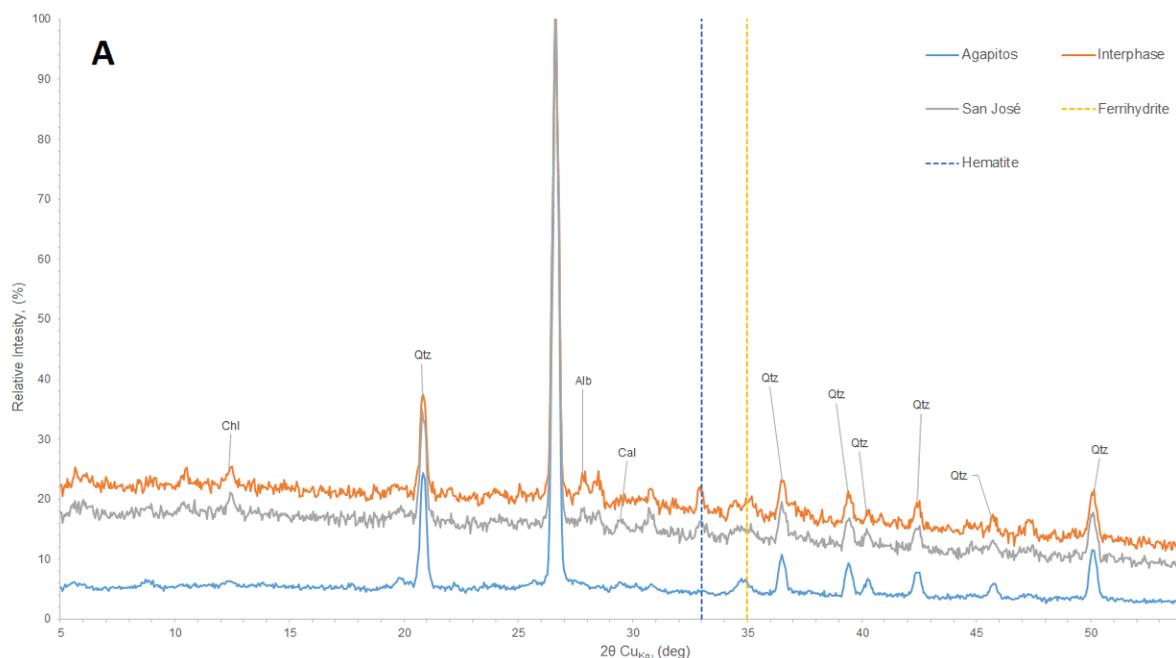


Figure 2. Conventional Cu K α XRD spectra of the bulk sample obtained in both wastes: A) Experimental plot 2 – LOS AGAPITOS and B) Experimental plot 1 - EMICOR. Chl: Chlorite, Qtz: Quartz, Alb: Albite, Cal: Calcite, Hem: Hematite, Fh: Ferrihydrite).

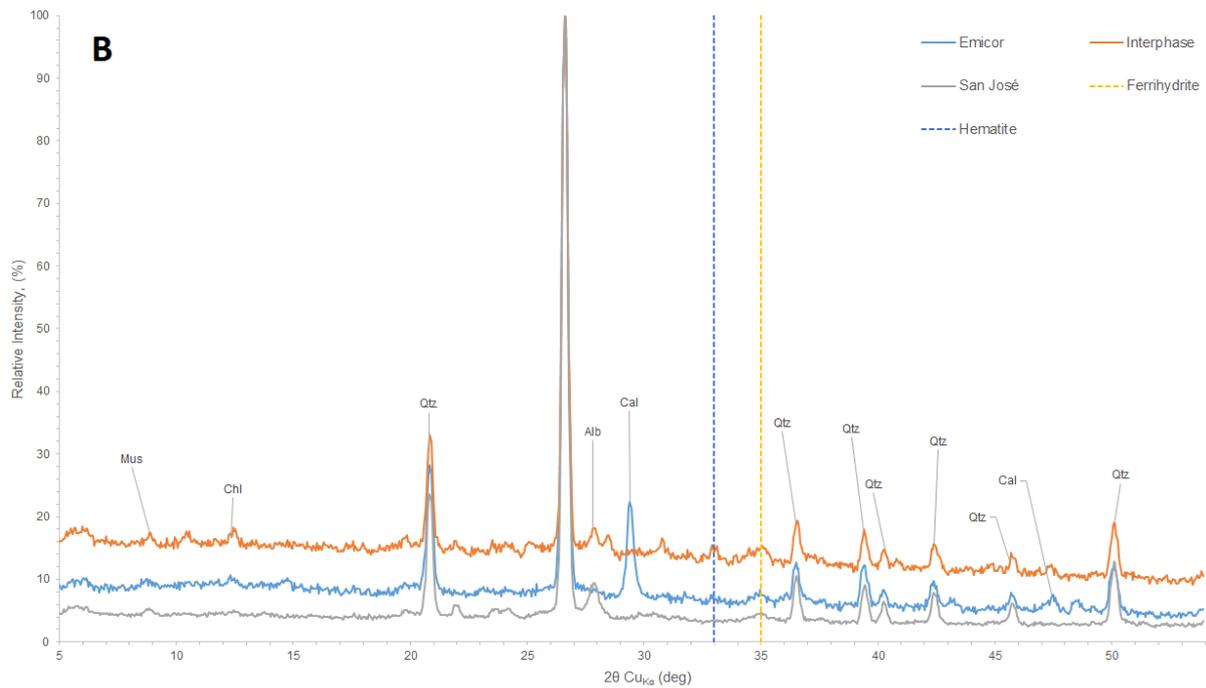


Figure 2 (Continued). Conventional Cu K α XRD spectra of the bulk sample obtained in both wastes: A) Experimental plot 2 – LOS AGAPITOS and B) Experimental plot 1 - EMICOR. Chl: Chlorite, Qtz: Quartz, Alb: Albite, Cal: Calcite, Hem: Hematite, Fh: Ferrihydrate).

From the results, it can be inferred that the alkaline cover layer may activate a reactive surface over the acid material due to vertical flows caused by a difference in gradient and an increase of pH in the interphase. According to the literature, in this reactive surface, geochemical processes like the precipitation of poorly crystalline Fe oxyhydroxysulfates (e.g. schwertmannite and jarosite), will occur. These Fe-oxyhydroxide will become in crystalline iron oxides (e.g. Ferrihydrate and goethite) and sulphates (Lottermoser y Ashley, 2006; Graupner et al. 2007; Kohfahl et al., 2011), which will develop a cemented surface known as “HARDPAN” in the future. This hardpan will act as a sealing material (or low-permeability barrier) that will inhibit oxygen diffusion into the tailings and the infiltration of runoff water, mitigating tailings oxidation and encapsulating the acid materials. Moreover, the acid/base chemical reactions that occur in the formation of the hardpan will neutralize the acidity of tailings and retain pollutants from solution (Quispe et al., 2013). In addition, the precipitation of a coating of iron oxyhydroxides on the surfaces of pyrite grains may prevent further oxidation (Pérez-López et al., 2007).

The in-situ portable XRF analyses taken in October 2014 from down-hole cores in the experimental plots (Figure 3) agree with the preliminary data. The vertical profile of Ca (Figure 3A, down h=20) confirms the alkaline capacity of the EMICOR tailings, and shows the lowest concentrations of potentially toxic elements (except Mn, Figure B). In fact, this consideration confirms the potential use of the EMICOR tailings to reducing environmental impacts by mitigating the down-acid

tailing oxidation. In addition, these profiles confirm the high potential of acidity and metals release capacity from the SAN JOSÉ tailings (Figure 3A, B, down h=55cm).

The results for experimental plot 2 (Figure 3A') show a different trend compared to experimental plot 1. In this case, the higher Ca concentrations correspond to below placed tailings (SAN JOSÉ). However, these tailings contain elevated toxic element concentrations (Zn 4454 ppm, As 12970 ppm, Pb 5927 ppm, Cu 2045 ppm, Cd 12,2 ppm and Mn 2262 ppm), and therefore the proposed storage with the EMICOR tailing and reactive barrier up to it, seems the best way to avoid adverse effects to the environment.

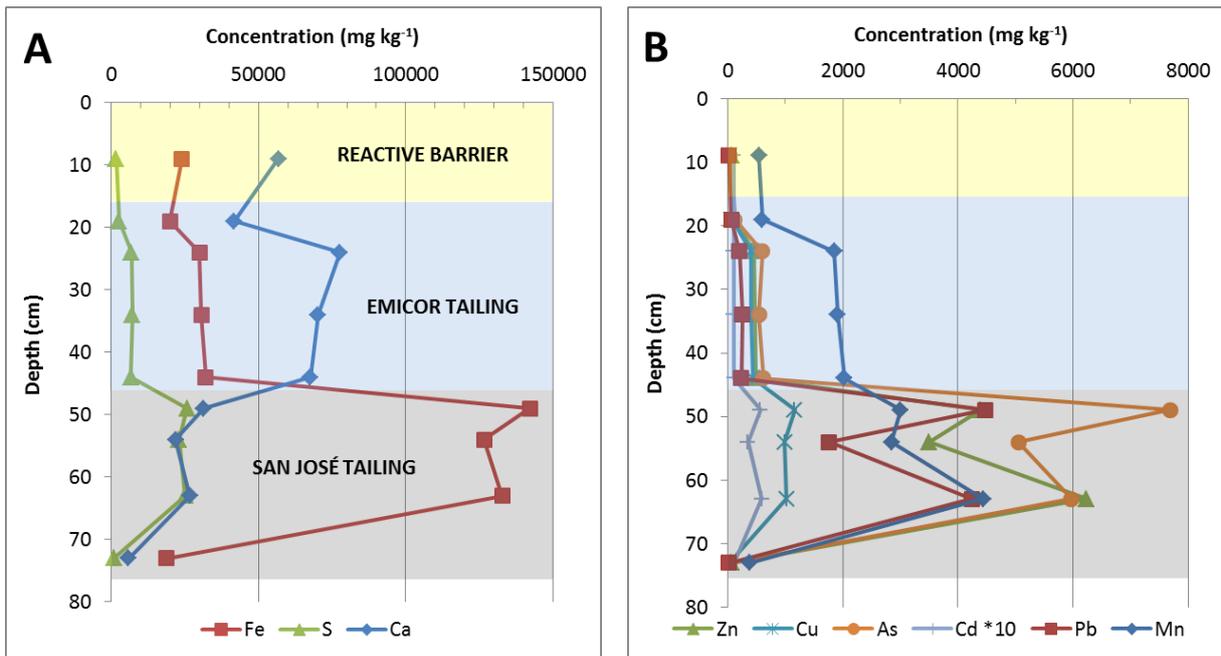


Figure 3. Vertical profiles for Fe, S, Ca, As, Cd, Cu, Pb, Zn and Mn obtained for each subplot. A, B experimental plot 1 and A', B' experimental plot 2. Yellow, blue and grey band represent reactive layer, Emicor tailing and San José tailing, respectively.

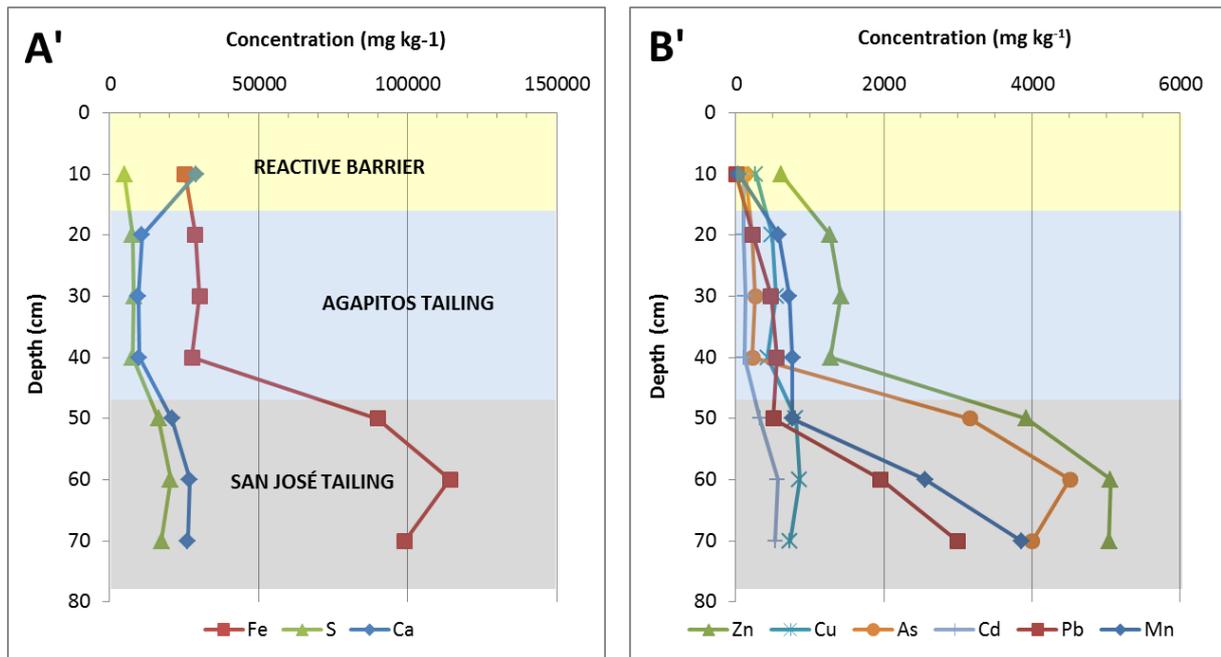


Figure 3 (Continued). Vertical profiles for Fe, S, Ca, As, Cd, Cu, Pb, Zn and Mn obtained for each subplot. A, B experimental plot 1 and A', B' experimental plot 2. Yellow, blue and grey band represent reactive layer, Agapitos tailing and San José tailing, respectively.

In addition, the behaviour of Ca concentrations in both plots decreases with depth between two first data points (Figure A and A'), representing the reactive barrier and the upper tailings. This fact indicates a precursor process of vertical fluxes induced by the different chemical gradient among the tailings. In addition, the presence of and iron oxyhydroxide precipitate coating on the surfaces of several grains has been observed. This fact links to the crystalline Fe oxyhydroxydes identification in the interphase zone by preliminary mineralogical analyses, suggesting an initial stage of sulphide oxidation mitigation. Probably, the lower chemical gradients observed during the early months of the treatment, could be due to the important control that the climatic conditions have upon sulphide oxidation process.

From the analysis done in the water sample collected in July, the chemical analysis correspond to a drainage with presence of alkaline elements (Ca: 69.42 ppm, K: 6.96 ppm, Mg: 11.29 ppm and Na: 134.6 ppm). In addition, this drainage had low concentrations of sulphate (56 ppm) and iron (0.02 ppm). Finally, elements associated to sulphur oxidation like As, Cd, Co, Cr, Cu, Ni, Pb, Zn are below the detection limit (<0.01 ppm). From these results, it can be seen that this drainage does not show AMD contamination. However, it is necessary to monitor this drainage in a time scale frame to confirm that there is no risk of AMD contamination in a passive treatment like the one implemented in this study.

A detailed geochemical and mineralogical study is necessary on a seasonal timescale for a better understanding about the sulphide oxidation process in equatorial tailings. Moreover, low cost materials rich in alkalis, like industrial wastes (carbon combustion, paper fabrication, and steelwork, among others), could be used in the treatment as the superior reactive layer. The use of volcanic ashes (Manz, 1997) and zeolites (Penilla et al., 2006) as reactive layers have also been seen in the treatment of sulphide waste from mining around the world (Pérez-López et al., 2007). This proposal evidently reduces the cost of treatment implementation and proposes a sustainable use for other residues derived from industrial activities.

Conclusions

An experimental plot to mitigate the sulphide oxidation of tailings was implemented in Portovelo. Thanks to this research project, technical guidelines based on scientific evidence can be given for a proper storage of mine tailings in Portovelo and other mining districts in Ecuador.

In summary, this type of passive treatment looks forward to benefiting from the own natural characteristics of tailings to mitigate and control pollution sources. Adequate tailings storage and the use of low cost alkaline materials (mine tailings) will allow encapsulation of acid materials that are potentially dangerous to the environment.

The results obtained in this ongoing pilot-scale experiment are encouraging and justify the need for the upscaling to a seasonal timescale monitoring and the need to develop detailed geochemical studies prior to a future full-scale treatment system. Management of tailings in this way could help to solve the mining environmental problem that exists in equatorial mining areas.

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