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Electrodialytic Remediation of Copper Mine Tailing Pulps

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Abstract: This work compares and evaluates nine electrodialytic laboratory remediation experiments on copper mine tailings. Experiments in the past have applied this method on moist mine tailings, but can also be applied to mine tailing-liquid mixtures. The objective of this work was the treatment of mine tailing pulps. Different parameters were analyzed, such as current density, desorbing agents, and liquid–solid ratio over non-stirred and stirred mine tailings by air suspension. The results showed that the remediation action is improved using mine tailings in pulps. As expected, stirring of the pulp favors the process performance. For 7 days remediation the best results were obtained using air stirring of the pulp, citric acid addition, a liquid/solid ratio (L/S) of 4.0 [mL/g] and a current density of 0.9 [mA/cm^2] reaching a 15% removal of the total copper.

Keywords: Airlift, copper removal, electric field, electro remediation, mine tailings impoundments

INTRODUCTION

For many decades, mining of different metals in Chile has caused the generation of waste products. The mining of copper from sulfide ores resulted in large amounts of mine tailings that have to be deposited in impoundments. During 2006 (1), a mine production of 5.36 MMT copper

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content generated approximately 740 MMT of mine tailing pulps with 40% weight percent solids, considering copper ores with an average-grade of 1% and copper concentrates with 30% Cu. These mine tailings contain heavy metals such as copper, and to a lesser extent, lead, cadmium, zinc, and arsenic (2,3). At present, there are only physical procedures to stabilize the mining tailings in impoundments.

In the last 20 years, electrokinetic remediation has proved to be a possible way to remove heavy metals from fine-grained porous solids such as soil, clay, fly ash, and sludge (4–6). An improvement of this method is the electrodialytic remediation (EDR) method (7,8), where the introduction of ion exchange membranes optimizes the remediation process, in which remediation phenomena in the soil are isolated from the electrode reactions. Figure 1 shows the principle of the conventional electrodialytic remediation method, where the heavy metals during the remediation will be moved from the polluted compartment II to either compartment I (anions) or compartment III (cations) as a consequence of an electric DC voltage that acts as a remediation tool. The contaminants are either moved as ions (in the case of copper as Cu^{2+}) by electro-osmotic flow or by migration, by passing electric current through the media. The process of electrodialytic remediation can be improved by adding reagents (desorbing agents) to the contaminated medium before or during remediation (9–11).

The main problem is to dissolve the inert material surrounding the heavy metals in the solid waste and subsequently dissolve the heavy metals, too. The pulp remediation process would facilitate the dissolution by the contact of the solid with the desorbing agent in solution, by

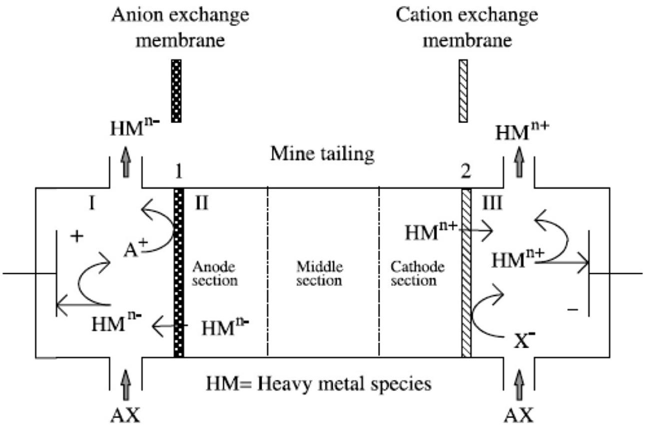

Figure 1. Principle of the conventional electrodialytic remediation method.

creating concentration gradients in the non-stirred or settled pulp experiments, therefore enhancing diffusion and the movement of ions into solution for migration to one of the electrode compartments. Diffusion is not a phenomenon in the stirred or aerated pulp experiments but due to mass transfer caused by convection, the ions would dissolve into the solution and then migrate towards the electrodes. Mechanical stirred pulps have been remediated using electric fields (12–15).

On the other hand, due to the semiconductor nature of the mine tailings, the electrical resistance in the conventional remediation cell increases quickly with time. This polarization phenomenon results in a continuous depletion of the current. The advantage of a liquid-solid mixture should reduce electrical resistance because of the conductive properties of water; therefore, polarization should be reduced. Table 1 summarizes characteristics of the transport phenomena present when applying electric fields to solid/liquid mixtures—with low (L/S) ratios

Table 1. Transport phenomena comparison

	Remediation technique	
Transport phenomena	Conventional systems (treatment of soils)	Pulp systems
Diffusion	Reaction/Dissolution in the solid–liquid interface. Diffusion through the solid–liquid interface.	Reaction/Dissolution in the solid–liquid interface. Diffusion through the solid–liquid interface, enhanced by stronger concentration gradients.
Convection	Not applicable.	Pulp can be stirred mechanically or by aeration.
Migration	Moist solid is more resistive than conductive. A voltage drop is generated through the solid. The flow of electric charge is very slow; therefore, the remediation process is slow.	The pulp is more conductive due to its water content. There is a smaller voltage drop through the solid. The flow of electric charge is better; therefore, the remediation process is faster.
Electro-osmosis	Produces cation concentration gradients across the solid towards the cathode. Is just as important as migration.	Concentration gradients are not as strong, and only applicable in non-stirred experiments. Only a secondary effect due to higher water content.

(like in conventional EDR) or high (L/S) ratios (in pulp remediation systems).

The objective of this work is the application of the electrodialytic remediation technique to mine tailing pulps, through the analysis of copper removal, evaluating the importance of different parameters on the efficiency of the remediation process: electric current density, liquid–solid ratio (L/S), desorbing agent and aeration, in consideration of the transport phenomena such as migration, convection, diffusion, and electro-osmosis. The remediation efficiency will be evaluated as the copper removal in the whole cell, in the case of stirred (aerated) experiments, and in three sections of the remediation cell: 1) anode, 2) middle, and 3) cathode in the case of non stirred (or settled) experiments.

EXPERIMENTAL DETAILS

Analytical Methods

The concentration of copper in the mine tailings was measured after pre-treatment as described in Danish Standard 259 "Determination of metals in water, sludge and sediments, general guidelines for determination by atomic absorption spectrophotometer." 1.00 g of dry mine tailings and 20.0 mL (1:1) HNO_3 were heated at 200 kPa (120°C) for 30 min. The liquid was separated from the solid particles by vacuum through a 0.45 μm filter and diluted to 100.0 mL. The elements were measured by AAS in flame. The units used in this paper are mg metal/kg dry matter.

The pH in the mine tailings was measured by mixing 3.0 g dry matter and 20.0 mL distilled water. After 1 h of contact time, the pH was measured using a Radiometer pH electrode.

The water content was found as the weight loss after heating a sample for 24 h at 105°C.

Experimental Mine Tailings

The mine tailings used for remediation experiments were sampled from the Caren impoundment at Codelco-El Teniente copper mine in VI Region of Chile. Table 2 gives the characteristics of the mine tailings used, determined by X-Ray Diffraction Analysis. The mine tailings sample was dry, and for each experiment a pulp was prepared according the L/S ratio, the pH was adjusted to 2 by sulfuric acid or citric acid addition.

Table 2. Main species in the mine tailings sample

Main mineral species	
Quartz	SiO_2
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$
Ferric clinochlore	$(Mg,Fe)_6(Si,Al)_4\ O_{10}(OH)_8$
Calcic albite	$(Na,Ca)Al(Si,Al)_3\ O_8$
Anorthite	$CaAl_2Si_2O_8$
Hydrated calcium sulfate	$CaSO_4 \cdot 0.6H_2O$
Copper sulfide species	
Chalcocite	Cu_2S
Brochantite	$Cu_4SO_4(OH)_6$
Chalcopyrite	$CuFeS_2$
Ramsbeckite	$Cu_{15}(SO_4)_4(OH)_{22} \cdot 6H_2O$
Wroewolfeite	$Cu_4(SO_4)(OH)_6 \cdot 2H_2O$
Guildite	$CuFe(SO_4)_2(OH) \cdot 4H_2O$

Experimental Remediation Cells

The experiments were carried out in two acrylic cells (see Fig. 2). A cylindrical cell of 83 mm diameter was used for non-stirred pulps experiments, divided in three compartments I, II, and III. A rectangular cell of 150 mm length and 80 mm square section, also divided in three compartments I, II, and III, was used for the stirred (aerated) experiments, in which air was introduced through the bottom of compartment II (Fig. 3).

The ion exchange membranes were from Membranes International Inc. (CMI-7000 cation exchange membrane and AMI-7001 anion

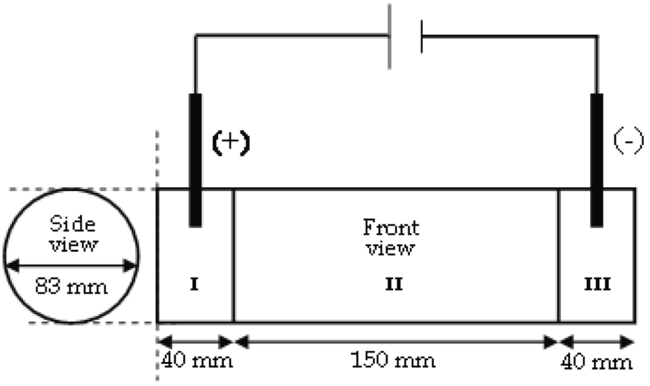

Figure 2. Cylindrical cell used for non-stirred pulps experiments.

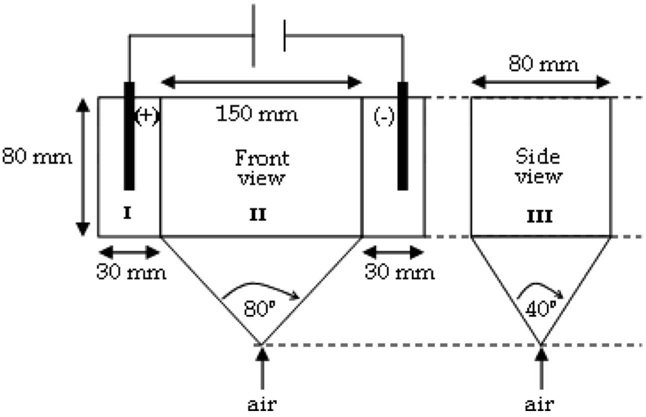

Figure 3. Rectangular cell used for stirred pulps experiments.

exchange membrane). The electrode solutions were initially distilled water, and in the cathode compartment dilute sulfuric acid was added in order to maintain pH 2 and avoid precipitation. The electrode solutions were stirred. The tailing pulps were placed in compartment II in both cases; decanting in the cylindrical cell (Fig. 2), and forming a watery suspension in the rectangular cell by aeration (Fig. 3).

After the experiments, liquid was separated from the humid solid. The mine tailings remaining in compartment II in the case of the non-stirred experiments were segmented into six slices: two slices (bottom and top) in three sections of the remediation cell, anode, middle, and cathode. In this work the anode section is defined as the slice closest to the anode, the middle section the slice in the center, and the cathode section the slice closest to the cathode. The copper concentration in the stirred tailings was assumed uniform. A conventional experiment with 20% of water was additionally carried out as a reference. Here, the mine tailings remaining in compartment II were segmented into three slices with a thickness of 5 cm.

In all the experiments, copper concentration and pH were measured.

Experimental Remediation Plan

Nine remediation experiments were carried out with conditions given in Table 3. All experiments were conducted during a seven day period. The current density throughout the experiment was constant, therefore the voltage was variable. The experiments are classified in two according

Table 3. Experimental conditions

Experiment	Acid agent	i [mA/cm^2]	L/S [mL/g tailing]	Stirring (Yes/No)	Voltage at SS [a] [V]
1	Sulfuric Acid	0.9	7.5	No	4.6
2	Sulfuric Acid	0.4	7.5	No	3.6
3	Sulfuric Acid	0.9	4.0	No	5.7
4	Sulfuric Acid	0.4	4.0	No	4.2
5	Citric Acid	0.9	4.0	No	–
6	Sulfuric Acid	0.9	7.5	Yes	5.7
7	Sulfuric Acid	0.9	4.0	Yes	–
8	Citric Acid	0.9	4.0	Yes	7.2
Reference	Sulfuric Acid	0.05[b]	0.25	No	30[c]

[a] Steady state (SS): Stable value reached after 30 hours.

[b] Average value.

[c] Constant voltage.

to whether the pulp is non-stirred/settled (experiments 1 to 5) or stirred by air suspension (experiments 6 to 8). A reference (experiment 9) was conducted to compare these experiments with conventional electrodialytic remediation.

In the first four experiments, the effect of current density (mA/cm^2) and liquid–solid ratio (L/S, mL/g dry tailings) was evaluated considering values in the range used previously with other solid waste materials (14,15). Since copper removal was better with higher current density, experiments with aeration were conducted applying 0.9 mA/cm^2 only. Citric acid was added (experiment 5) due to its copper complexing capacity, to compare with sulphuric acid addition (experiment 3) in order to determine the importance of stable complexes in the remediation.

The aerated tailings experiments 6, 7, and 8 stirring were conducted to simultaneously analyze the L/S ratio and desorbing agent type.

RESULTS AND DISCUSSION

General remediation results of the experiments are given in Table 4. Results are reported as relative copper concentrations ($C/C_0 < 1$ implies copper removal, $C/C_0 > 1$ implies copper accumulation). In this study only the total copper concentrations (both soluble and insoluble) in mine tailings are considered. The pH was maintained constant around 2 in pulp systems adding either sulfuric or citric acid, and for this reason no precipitation was observed during the experiments.

Table 4. General remediation results

Experiment	$C_{anode}/C_{initial}$	$C_{center}/C_{initial}$	$C_{cathode}/C_{initial}$	$C_{global}/C_{initial}$
1	0.88	0.90	1.06	0.95
2	0.90	0.96	1.09	0.99
3	0.87	0.95	1.12	0.95
4	0.90	0.96	1.03	0.96
5	0.92	0.99	1.07	0.98
6[a]	–	–	–	0.89
7[a]	–	–	–	0.94
8[a]	–	–	–	0.85
Reference	0.94	1.01	1.05	1.00

[a] Stirred (aerated) tailings experiments.

According to copper mineral processing, after the concentration process (flotation) in the tailings, the copper is present mainly as insoluble sulphides. In the mine tailings impoundments, the solid waste is inhomogeneous due to various factors:

1. difference in copper grades according to the date of disposal,
2. the time of aging of the tailings in the pond, and
3. the physical-chemical changes due to weathering and bacterial actions during the period of disposal.

This has resulted in different levels of oxidation of the minerals, making copper more soluble and therefore more susceptible to remove by electric fields.

The results of the reference experiment show copper removal in the anode zone (6%), accumulation in the center (1%) an in the cathode (5%), and the final global concentration the same as the initial, indicating no copper was effectively removed, the ions only migrated across the tailings. However, all the tailing pulp experiments showed global copper removal, as well as partial removal in the anode and in the middle.

Table 5 shows the stratification effect in non-stirred experiments. The experiments show two kinds of stratification: horizontally, due to copper migration towards the cathode, and vertically, due to diffusion towards the solution. This effect is eliminated by stirring the pulp.

Evaluating the stirring-L/S ratio effects, the smaller the L/S ratio, global copper tends to be the same for non-stirred and stirred pulp experiments: Comparing experiments 3 and 7, a 1% difference was observed. At a larger L/S ratio (i.e., less solid, more liquid) a difference

Table 5. Stratification effect in non-stirred/settled experiments

	Anode section		Middle section		Cathode section	
Experiment	$C_{final}/C_{initial}$ Bottom	$C_{final}/C_{initial}$ Top	$C_{final}/C_{initial}$ Bottom	$C_{final}/C_{initial}$ Top	$C_{final}/C_{initial}$ Bottom	$C_{final}/C_{initial}$ Top
1	0.92	0.85	0.94	0.89	1.14	0.96
2	0.95	0.85	1.00	0.92	1.15	1.03
3	0.92	0.86	0.98	0.92	1.24	1.02
4	0.92	0.89	0.98	0.95	1.08	0.99
5	0.99	0.85	1.04	0.92	1.18	1.03

of 6% resulted between experiments 1 and 6. Comparing non-stirred and stirred pairs, the removal was better in experiments with more solid. This can be explained because mass transfer is improved by stirring of the pulp, and the concentration gradients are stronger.

Analyzing the effect of the current density shows that it was found less important at lower L/S ratio. Copper removal is better when the L/S ratio is higher, and experiment 3 being the best case with 5% overall copper removal. It can be concluded that migration is better when there is more liquid, as it is an excellent electrical conductor.

On the other hand, in case of pulps the electric field reached a steady state level between 0.2 and 0.5 V/cm after around 30 hours. This value is considerably lower than the 2 V/cm applied in the conventional EDR reference experiment.

There is higher copper removal in the stirred experiments than non-stirred experiments. In non-stirred experiments, better results were shown with sulfuric acid experiments (even though the difference is small), and in case of the stirred experiments, citric acid showed better results. This can be explained because the copper-citric acid complex is more stable and favors the dissolving process previous to the removal.

The experiment with the best overall results was number 8, conducted with the following conditions L/S 4.0 [mL/g], current density 0.9 [mA/cm^2], stirring and citric acid as desorbing agent showing a removal of 15%, for the seven day period.

For future investigations, it is recommended to carry out experiments with prolonged remediation periods. Due to the fact that desorption and diffusion are key transport phenomena to enhance copper removal, it is also recommended to leach the tailings before applying DC (as a form of pre-treatment), trying out different types of desorbing agents.

CONCLUSIONS

The electrodialytic remediation of pulps is more effective than the conventional method applied to moist solids, for the conditions studied in this investigation.

In general the experiments conducted with stirring of the pulps (uniform concentration) were better than the non-stirred ones.

In the experiments with non-stirred pulps, the copper concentration increases towards the cathode due to migration and electro-osmosis, and decreases vertically upwards towards the solution due to diffusion.

The experimental conditions that gave the best results were those that used stirring of the pulp, with no concentration gradients. The best overall experiment included citric acid as desorbing agent. The experimental conditions here were: L/S 4.0 [mL/g] and current density 0.9 [mA/cm^2], obtaining a 15% copper removal for a 7 day remediation.

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