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Electrodialytic Remediation of Copper Mine Tailings: Sulphuric and Citric Acid Addition

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Electrodialytic Remediation of Copper Mine Tailings: Sulphuric and Citric Acid Addition

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Abstract: Decades of mining activities in Chile have generated large amounts of solid waste, which have been deposited in mine tailing impoundments. These impoundments cause concern due to dam failures or natural leaching to groundwater and rivers.

This work shows the laboratory results of 11 electrodialytic remediation experiments on copper mine tailings with the addition of sulphuric and citric acid. Comparing this to electrodialytic remediation with watery tailing, both acids enhanced the process. However, with citric acid addition the process was further enhanced because besides the pH decrease a formation of copper citrate complexes occurred.

The maximum copper removal reached in the anode side of the remediation cell was 53% with sulphuric acid in 504 h and 35% with citric acid in only 40 h, both experiments at 20 V treating approximately 1.7 kg mine tailing on dry basis.

Keywords: Copper removal, ion exchange membranes, electro dialysis, mine tailing impoundments, electric field, sulphuric and citric acid

INTRODUCTION

Mining of different metals is one of Chile's key industries because of the high concentration of metal ores in the Andes Mountains. This exploitation has generated large amount of waste products. The mining of copper from sulphide ores especially produces tailings that have to be deposited in

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impoundments. On the other hand, natural leaching from these impoundments has contaminated rivers and the soil close to the deposits. In the rivers, the metals precipitate in the sediments downstream.

The majority of the heavy metal contamination is caused by copper, and to lesser extents, lead, cadmium, zinc, and arsenic (1, 2). At present there are only physical procedures to stabilize the mining tailing impoundments. Untill now no methods existed that can remove the heavy metals from the tailing.

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 (3–6). An improvement of this method is the electrodialytic remediation process (7, 8), where the introduction of ion exchange membranes optimizes the remediation method. With the use of membranes, the phenomena of remediation in the soil is isolated from the electrode reactions. For example in the case of the alkalization at the cathode, without membranes the expected alkali diffusion would promote the precipitation of metal hydroxides in the soil.

Since mine tailings are very fine material and since copper and other metals could be desorbed from this material and go in solution, electrokinetic remediation could be a promising method in this case. The recovery of metal from the solid could mean a profitable solution. The feasibility of the method was demonstrated by the authors with watery tailing (9), but the remediation process was slow. In the same work it was stated that an acidification prior to the remediation of copper mine tailing would promote the removal of copper.

The objective of this work is to enhance the removal of copper from mine tailings using acidic tailing in the electrodialytic remediation method. Sulphuric (H_2SO_4) and citric ($C_6H_8O_7$) acids were used in the pretreatment of the tailing sample, and the remediation time was the only variable considered. The remediation efficiency was evaluated as the copper removal in three different sections of the experimental cell: 1) anode side, 2) middle, and 3) cathode side.

BACKGROUND

The process of electrodialytic or electrokinetic remediation can be enhanced by adding reagents to the contaminated medium before or during remediation (10–12). The typical problem is to dissolve the inert material surrounding the heavy metals in the solid waste and subsequently dissolve the heavy metals, too. In the mine tailing, copper could be expected to be found as remaining copper sulphide, which was not liberated in the grinding process prior to the flotation. The use of additives such as acids or complexing agents would speed up the remediation process. Acids would dissolve some inert material, copper oxides, and secondary copper sulphide minerals.

Furthermore, any copper adsorbed to solid material would be released to the surrounding acid solution. Complexing agents would promote formation of stable soluble heavy metals complexes that could be moved in an electric field either by electro-osmosis (if the complex is neutral) or by electromigration (if the complex has charge).

In this work two acids—inorganic (sulphuric acid) and organic (citric acid)—are considered. Both acids are strong, and in addition citric acid produces complexes with copper. The complexes formed are (13):

$$Cu^{2+} + C_6H_5O_7^{3-} + 2H^+ \Longleftrightarrow Cu(C_6H_7O_7)^+ \quad \log K = 12.0$$

$$Cu^{2+} + C_6H_5O_7^{3-} \Longleftrightarrow Cu(C_6H_5O_7)^- \quad \log K = 6.1$$

$$Cu^{2+} + C_6H_4O_7^{4-} \Longleftrightarrow Cu(C_6H_4O_7)^{2-} \quad \log K = 18$$

Stability constants are valid at ionic strength 0.5 for aqueous solutions. The complex formed preferably at the acidic pH conditions (typically 3–4) during electro remediation is cationic, $Cu(C_6H_7O_7)^+$, so this complex in the remediation process would be move toward the cathode by electromigration.

EXPERIMENTAL DETAILS

Analytical Methods

The concentration of elements was measured after pretreatment of the mine tailing 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 tailing 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 (DM). This method was initially compared with the EPA Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils," for total recoverable metals analysis in solid waste samples, and the two methods gave metal concentrations within 3% deviation.

The pH in the mine tailing was measured by mixing 3.0 g dry matter and 20.0 mL distilled water. After 1 h of contact time, 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 Tailing

The mine tailing used for remediation experiments was sampled directly from the mine tailing waste canal, which feeds the impoundment at the El Teniente copper mine in the VI Region of Chile. Table 1 gives characteristics of the mine tailing used in this work including additional information from various sources. It is seen that the copper concentration is much higher than zinc and lead, and therefore only copper removal will be evaluated in this work.

Before the remediation experiments the tailing was air-dried until the humidity was around 8–10% on total mass base. The tailing added either 1 M citric acid or 1 M H_2SO_4 until reaching a humidity of 14–15% and a pH lower than approximately 4.

Electrodialytic Remediation Experiments

The principle of remediation equipment is given in Fig. 1. Experiments were carried out in an acrylic cell; the length of the cylindrical compartment II was 15 cm, and the inner diameter 8 cm. The ion exchange membranes were from Membranes International Inc. (CMI-7000 cation exchange membrane and AMI-7001 anion exchange membrane). The mine tailing was placed in compartment II. The electrode solutions were initially distilled water in order to run the experiments at nonfavored conditions. During experiments, to the cathode compartment was added dilute sulphuric acid in order to maintain a

Table 1. Characteristics of the mine tailing investigated

Ore deposit type[a]	Porphyry copper
Primary ore minerals[a]	Pyrite, chalcopyrite, bornite, molybdenite, galena, tennantite, magnetite, hematite
Secondary ore minerals[a]	Chalcocite, covellite
Gangue minerals[a]	Quartz, albite feldspar, biotite, calcite, anhydrite, tourmaline, rutile, apatite, sericite, chlorite, epidote, kaolinite, monmorillonite
Main minerals in tailing[b]	Quartz, calcium albite, biotite, aluminium phosphate, moscuvite, albite, orthoclase, gypsum, brushite, ferric clinoclore, ramsbeckite, delafossite, no-stoichiometric copper sulphide, geerite, copper sulphide
Grain size distribution[c]	50% (w/w) smaller than 200 μm
Cu content[d]	1130 ± 50 mg/kg dry matter
Zn content[d]	145 ± 15 mg/kg dry matter
Pb content[d]	76.0 ± 15 mg/kg dry matter
Fe content[d]	36500 ± 1200 mg/kg dry matter
pH[d]	7.1 ± 0.2

[a] Dold and Fontbote (2).
[b] X-ray diffraction analysis.
[c] Codelco (14).
[d] This study and Hansen et al. (9).

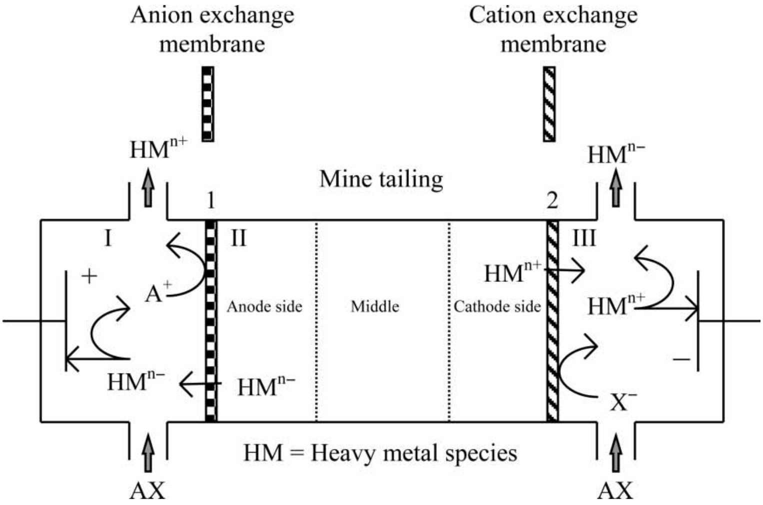

Figure 1. The principle of electrodialytic remediation used in this work.

low pH (<4) to avoid precipitation. The electrode solutions were stirred. After the experiments the mine tailing remaining in compartment II was divided into three thirds with a thickness of approximately 5 cm, where copper concentration was measured. The thirds near the anode and cathode are *anode side* and *cathode side*, respectively, and the last one is named *middle section.*

Experimental Plan

Eleven remediation experiments were carried out with the initial conditions given in Table 2. In the experiments 1–7 sulphuric acid was added to the tailing and in the experiments 8–11 citric acid. In all experiments a voltage drop of 20 V with different remediation time was evaluated considering only the copper removal. With sulphuric acid the remediation times were 5, 22, 72, 96, 144, 200, and 504 h, and with citric acid 5, 10, 20, and 40 h. With citric acid it was choosen to use shorter time since the significant results were found only in the initial period of the remediation process.

RESULTS AND DISCUSSION

General remediation results of the 11 experiments are given in Table 3. Copper removal from the anode side, middle, and cathode side, represents the difference between the copper leaving and entering the section. In the anode side the amount of copper entering from the anode compartment (no copper present) is always zero.

Table 2. Electrodialytic remeditaiton conditions

Exp.	Pre-treatment	Duration (Hours)	Voltage drop (V)	Initial pH	Initial water content (%)	Solid dry weight (kg)
1	1 M H_2SO_4	5	20	4.0	14	1.7
2	1 M H_2SO_4	22	20	3.9	15	1.6
3	1 M H_2SO_4	72	20	4.1	14	1.6
4	1 M H_2SO_4	96	20	4.2	15	1.7
5	1 M H_2SO_4	144	20	3.9	14	1.6
6	1 M H_2SO_4	200	20	4.1	14	1.8
7	1 M H_2SO_4	504	20	4.1	14	1.6
8	1 M $C_6H_8O_7$	5	20	3.0	15	1.6
9	1 M $C_6H_8O_7$	10	20	3.2	15	1.5
10	1 M $C_6H_8O_7$	20	20	3.1	16	1.5
11	1 M $C_6H_8O_7$	40	20	3.0	14	1.7

From Table 3, copper removal with sulphuric acidic tailing from the anode side was significant for a remediation time longer than 72 h, in the middle 144 h, and in the cathode side 200 h. On the other hand, with citric acid addition, the copper removal was significant already with 5 h of remediation in each section of the experimental cell. Furthermore, in all conditions considered with citric acid, the copper removal was superior. With both acid additions, in each section of the cell the copper removal increased proportional with time considering an error margin of 10%.

An explanation for the improved copper removal with citric acid is the stable complex $Cu(C_6H_7O_7)^+$ formed. The formation of the complex

Table 3. Electrodialytic remediation results

Experiment	Duration (hours)	Copper removal from anode side (%)	Copper removal from the middle (%)	Copper removal from cathode side (%)
1	5	0	0	$< 0^a$
2	22	5	0	0
3	72	17	5	4
4	96	21	3	0
5	144	14	9	7
6	200	23	13	0
7	504	53	38	21
8	5	25	14	9
9	10	23	13	9
10	20	34	25	22
11	40	35	23	13

[a] <0, copper accumulation.

together with the acidic conditions favors dissolution of copper minerals in the tailing. So it is expected that the concentration of copper in the liquid phase of the tailing is higher than with only sulphuric acid addition. No accumulation zone during remediation is observed, indicating that copper is removed from all sections of the tailing almost instantly.

The tailing initially treated with sulphuric acid reached a copper removal of 53% from the anode side with the longest remediation time (experiment 7), and with citric acid the copper removal was 35% with remediation time of 20–40 h (experiments 10 and 11).

Figures 2 through 4 show the normalized concentrations of copper with time in the anode side, middle, and cathode side of tailing, respectively, with either sulphuric or citric acid addition.

Figure 2 shows that the normalized concentration reached at the anode side after 20–40 h of remediation with citric acid would correspond to approximately 280 h with sulphuric acid addition only. This means an improvement with citric acid compared to sulphuric acid in the order of seven times for the longest experiments studied. This situation is repeated approximately in the middle section (Fig. 3) and the cathode side (Fig. 4). In general, the overall removal rate with sulphuric acid seems to be proportional with time as seen in Figs. 2–4.

On the other hand, Table 4 arranges the copper removal at the anode side considering acid addition (sulphuric acid) and acid + ligand addition (citric acid). Furthermore, equivalent remediation times with acid addition only for the experiments with acid + ligand addition were estimated. In general, it can be expected that the remediation time with citric acid addition would be more than five times shorter than with sulphuric acid addition.

In general, the copper removal should be defined by the copper environmental regulation for soil. Neither of the curves in Figs. 2 to 4 has reached a

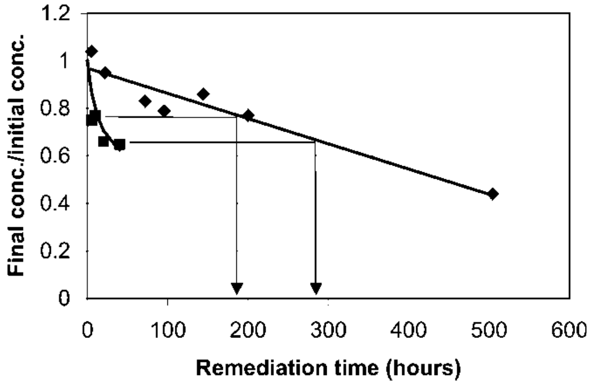

Figure 2. The normalized concentration of copper in the anode side as a function of time of electrodialytic remediation. Mine tailing initially added acid. Legend: (◆) Sulphuric acid; (■) Citric acid.

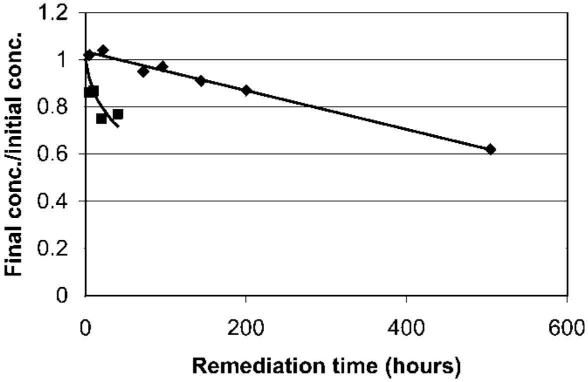

Figure 3. The normalized concentration of copper in the middle section as a function of time of electrodialytic remediation. Mine tailing initially added acid. Legend: (◆) Sulphuric acid; (■) Citric acid.

constant level. Therefore it could be possible that further application of DC current could enhance the copper removal since the remediation time was not optimized. It would be interesting in further work to see if lower copper concentration could reach applied electric fields for longer times—especially with citric acid addition.

With respect to the evolution of the current intensity along the experiments with citric acid addition, a maximum current intensity was observed after 5 h of remediation. In the longest experiment of 40 h (exp. 11), the initial current intensity was in the order of 40 mA, and the maximum reached was almost 50 mA. Hereafter, the current intensity dropped to around 25 mA and maintained this level until the end of the

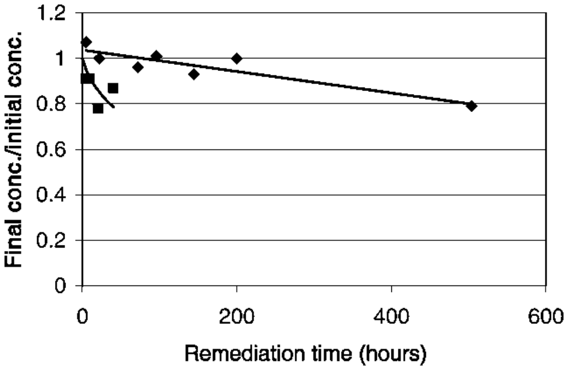

Figure 4. The normalized concentration of copper in the cathode side as a function of time of electrodialytic remediation. Mine tailing initially added acid. Legend: (◆) Sulphuric acid; (■) Citric acid.

Table 4. Electrodialytic remediation results—comparison of sulphuric and citric acid addition at the anode side

Experiment	Duration (hours)	Copper removal: Sulphuric acid addition (%)	Copper removal: Citric acid addition (%)	Equivalent remediation time with sulphuric acid addition (hours)
1 (s)	5	0	—	
8 (c)	5	—	25	approx. 180
9 (c)	10	—	23	approx. 180
2 (s)	22	5	—	
3 (s)	72	17	—	
4 (s)	96	21	—	
5 (s)	144	14	—	
10 (c)	20	—	34	approx. 280
6 (s)	200	23	—	
11 (c)	40	—	35	approx. 280
7 (s)	504	53	—	

(s): sulphuric acid, (c): citric acid.

experiment. The current intensity increase during the first 5 h was due to the increase in conductivity of the electrode solutions from starting distilled water.

CONCLUSIONS

The use of additives such as acids and ligands speeds up the electrodialytic removal of copper from mine tailing. In the case of ligand addition, when the copper complex is stable in acidic conditions, the remedation process is further enhanced.

The maximum copper removal reached in the anode side was 53% with sulphuric acid in 504 h and 35% with citric acid in only 40 h, both experiments at 20 V treating approximately 1.7 kg mine tailing on dry basis.

In accordance with this study, citric acid addition to the tailing before remediation would shorten the remediation time more than seven times compared with sulphuric acid addition. So the expected energy consumption in full-scale process would be lowest with citric acid addition.

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