

Electrodialytic remediation of copper mine tailings

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Abstract

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

This work shows the laboratory results of nine electrodialytic remediation experiments on copper mine tailings. The results show that electric current could remove copper from watery tailing if the potential gradient was higher than 2 V/cm during 21 days. With addition of sulphuric acid, the process was enhanced because the pH decreased to around 4, and the copper by this reason was released in the solution. Furthermore, with acidic tailing the potential gradient was less than 2 V/cm.

The maximum copper removal reached in the anode side was 53% with addition of sulphuric acid in 21 days experiment at 20 V using approximately 1.8 kg mine tailing on dry basis. In addition, experiments with acidic tailing show that the copper removal is proportional with time.

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1. Introduction

For decades, mining of different metals has been one of Chile's key industries because of the high concentration of metal ores in the Andes Mountains. This exploitation has, besides the metal production, caused a generation of waste products. Especially the mining of copper from sulphide ores resulted in large amounts of mine tailings that have to be deposited in impoundments. Furthermore, 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. Still no methods exist 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 [3–5]. An improvement of this method is the electrodialytic remediation method [6,7], where the introduction of ion exchange membranes optimises the remediation process. With the use of membranes, remediation's phenomena in the soil are 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 also be a promising method in this case. Furthermore, the recovery of metal from the solid could mean a profitable solution. Kim and Kim [8] showed that metals were removed to some extent in tailing-soils polluted by lead and zinc mining using the electrokinetic remediation process.

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The objective of this work is to demonstrate the feasibility to remove metal ions from copper mine tailings with the use of the electrodialytic remediation method. The mine tailing was sampled from the El Teniente copper mine in the VI region of Chile. This mine has been producing copper for decades, and it is the world's largest underground copper mine. During the mining period, around 1200 million tons of mine tailings have been accumulated in four impoundments in the vicinity of the mine. Parameters and effects that will be discussed are the voltage drop applied, the pH, the addition of acid to the tailing, and the remediation time. The remediation efficiency will be evaluated as the copper removal in three different sections: (1) anode side, (2) middle, and (3) cathode side.

2. Experimental details

2.1. Analytical methods

2.1.1. Metal concentration

The concentration of elements was measured after pre-treatment 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) HNO₃ 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.

2.1.2. pH

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.

2.1.3. Water content

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

2.2. 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 Chile. Table 1 gives characteristics of the mine tailing used in this work including recopilated 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

Table 1
Characteristics of the mine tailing investigated

Ore deposit type [2]	Porphyry copper
Primary ore minerals [2]	Pyrite, chalcocopyrite, bornite, molybdenite, galena, tennantite, magnetite, hematite
Secondary ore minerals [2]	Chalcocite, covellite
Gangue minerals [2]	Quartz, albite feldspar, biotite, calcite, anhydrite, tourmaline, rutile, apatite, sericite, chlorite, epidote, kaolinite, monmorillonite
Main minerals in tailing ^a	Quartz, calcium albite, biotite, aluminium phosphate, moscovite, albite, orthoclase, gypsum, brushite, ferric clinoclore, ramsbeckite, delafossite, non-stoichiometric copper sulphide, geerite, copper sulphide
Grain size distribution [12]	50% (w/w) smaller than 200 μm
Cu content ^b	1130 ± 50 mg/kg dry matter
Zn content ^b	145 ± 15 mg/kg dry matter
Pb content ^b	76.0 ± 15 mg/kg dry matter
Fe content ^b	36500 ± 1200 mg/kg dry matter
pH ^b	7.1 ± 0.2

^a X-ray diffraction analysis.

^b This study.

base. The tailing was either added distilled water (watery tailing) or 1 M H₂SO₄ (acidic tailing) until a humidity of 15–16%.

2.3. 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, and the cathode compartment was added dilute sulphuric acid in order to maintain a low pH (<4) to avoid precipitation. The electrode solutions were stirred. After the experiments the mine tailing remaining in

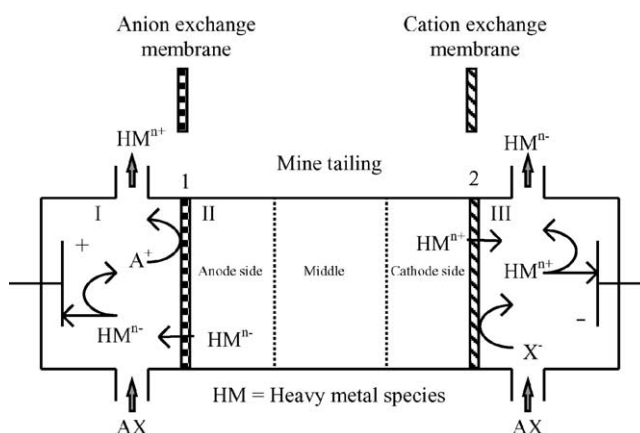


Fig. 1. The principle of electrochemical remediation used in this work.

Table 2
Electrodialytic remediation conditions

Experiment	Pre-treatment	Voltage drop (V)	Initial pH	Initial water content (%)	Solid dry weight (kg)
1	Water	20	7.2	17	1.6
2	Water	40	7.2	17	1.8
3	1 M H ₂ SO ₄	20	4.1	14	1.6
4	1 M H ₂ SO ₄	20	4.0	14	1.7
5	1 M H ₂ SO ₄	20	3.9	15	1.6
6	1 M H ₂ SO ₄	20	4.1	14	1.6
7	1 M H ₂ SO ₄	20	4.2	15	1.7
8	1 M H ₂ SO ₄	20	3.9	14	1.6
9	1 M H ₂ SO ₄	20	4.1	14	1.8

compartment II was segmented into 10 slices with a thickness of approximately 1.5 cm, where copper concentration, pH and water content were measured.

In this work *anode side* is defined as the three slices closest to the anode, *middle section* the four slices in the center, and *cathode side* the three slices closest to the cathode.

2.4. Experimental plan

Nine remediation experiments were carried out with the initial conditions given in Table 2.

The objective of the first three remediation experiments was to evaluate for a 3-week electro-dialytic remediation, with watery tailing the effect of the applied voltage drop (20 and 40 V) and for the voltage drop of 20 V the addition of sulphuric acid.

In the last six experiments the copper removal was evaluated as a function of remediation time. Since the electro-dialytic remediation was significant only with addition of sulphuric acid, the experiments 4–9 were developed with acidic tailing and a voltage drop of 20 V with different remediation time (5, 22, 72, 96, 144 and 200 h).

3. Results and discussion

General remediation results of the nine experiments are given in Tables 3 and 4. Copper removal from the anode side, middle and cathode side, represents the difference between the copper leaving and entering the section. Only at the anode side the amount of copper entering is always zero.

It can be seen in Table 3, after 3 weeks remediation with a watery tailing applying 20 V there was no copper removed from neither section of the cell. Increasing the voltage drop to 40 V with watery tailing, the copper removal from the anode side is nearly equivalent to a remediation with sulphuric acid addition at 20 V. In watery tailing with 40 V no copper was removed from the cathode side, and in the middle section copper build up was observed.

On the other hand, with acidic tailing copper removal was observed in all sections. From Table 4, copper removal with acidic tailing from the anode side was significant for a re-

Table 3
Electrodialytic remediation results – experiments 1–3

Experiment	Duration (days)	Copper removal from anode side (%)	Copper removal from the middle (%)	Copper removal from cathode side (%)
1	21	0	0	0
2	21	48	<0 ^a	0
3	21	53	37	26

^a Copper accumulation.

mediation time longer than 72 h, in the middle 144 h and in the cathode side 200 h. In each section the copper removal increased proportional with time considering an error margin of 5%.

Figs. 2 and 3 show the normalized concentrations of copper and the pH, respectively, in the mine tailing as a function of the distance from the anion exchange membrane after application of electric current.

From the figures it can be seen that the pH did not change much from the initial value in the experiment 1, only the slice next to the anode pH decreased to 4.5. In experiment 2 the anode side pH was lowered from 6 to around 4. In accordance with the above mentioned, this acidification was generated by the anode reaction and the subsequent diffusion of protons through the anion exchange membrane (due to the Grotthuss mechanism) and the tailing. In this context,

Table 4
Electrodialytic remediation results – experiments 3–9 (voltage drop in all experiments was 20 V)

Experiment	Duration (h)	Copper removal from anode side (%)	Copper removal from the middle (%)	Copper removal from cathode side (%)
4	5	0	0	<0 ^a
5	22	5	0	0
6	72	17	5	4
7	96	21	3	0
8	144	14	9	7
9	200	23	13	0
3	504	53	38	21

^a Copper accumulation.

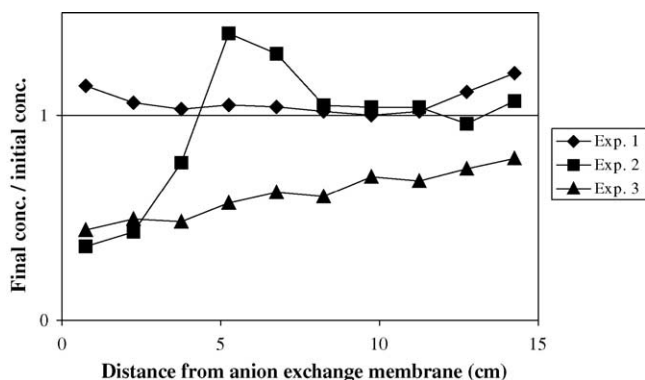


Fig. 2. The normalized concentration of copper in the mine tailing after electro-dialytic remediation as a function of the distance from the anion exchange membrane: (◆) experiment 1, (■) experiment 2, (▲) experiment 3.

with watery tailing, the acidification was proportional to the applied voltage drop.

Furthermore, in experiment 2 the concentration of copper was lower in the slices next to the anode, and the copper moved towards the cathode as divalent cations. In the middle the pH was still higher, and so the copper precipitated, which was demonstrated by the copper accumulation observed.

From electro-dialytic soil remediation experiments [9], it is concluded that a weak acidification of the soil facilitates the desorption and mobility of the heavy metals investigated. This corresponds well with the findings of Ottosen et al. [10], where the same tendency was found.

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. This means that copper sulphides, surrounded by inert materials, are difficult to dissolve. Other copper species could be oxides and sulphates, as found in the X-ray diffraction analysis (see Table 1).

Taking these observations into account, it was decided to add H_2SO_4 initially to the mine tailing in order to lower the pH to around 4. Sulphuric acid is normally a by-product in the production of copper, based on the exploitation of sulphide ores, and so the purchase would be relatively cheap. In

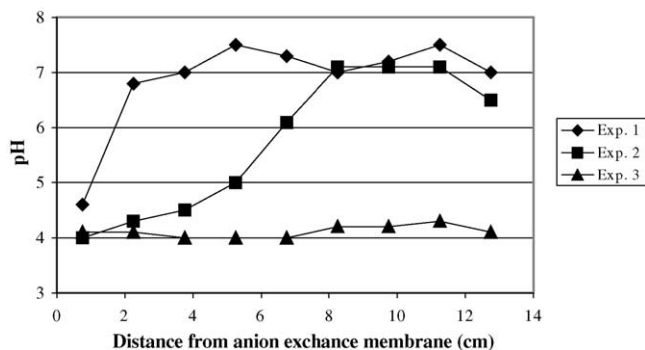


Fig. 3. The pH metals in the mine tailing after electro-dialytic remediation as a function of the distance from the anion exchange membrane: (◆) experiment 1, (■) experiment 2, (▲) experiment 3.

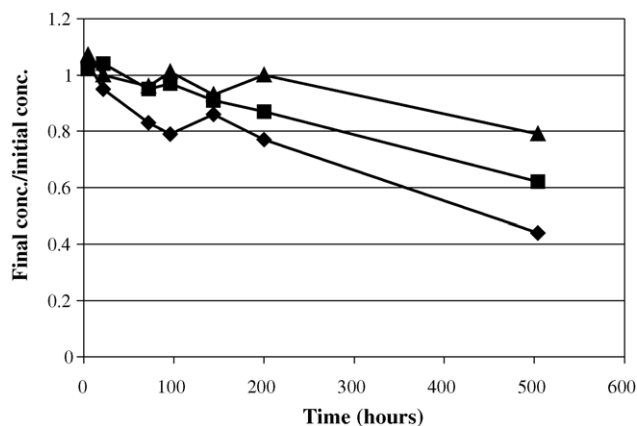


Fig. 4. Normalized concentration of copper as a function of remediation time in different sections of the mine tailing: (◆) anode side, (■) middle, (▲) cathode side.

Fig. 2, from the curve of experiment 3 it is seen that the Cu content is lowered substantially in the three sections above defined. No accumulation zone is observed, indicating that copper is removed from all sections of the tailing. Furthermore, a generation of a red brown solid layer on the cathode was observed, indicating electrolytic precipitation of metallic copper. This layer was analysed in the same manner as the mine tailing and showed a high copper content.

Fig. 4 shows the distribution of copper in the anode side, middle and cathode side of the tailing with time. The tailing was initially treated with H_2SO_4 in order to lower the pH. From Fig. 4 it is seen that copper is removed from the anode side almost from the beginning of the remediation, in spite of the high concentration of protons and sulphate anions from the sulphuric acid addition. No accumulation zone is observed in either of the sections of the mine tailing. As expected the copper concentration is not lowered in the middle section before around 100 h, and in the cathode side after 200 h. For the middle sections, this is explained by the fact that the rate of copper entering this section is equal to the rate of copper leaving the section in the beginning of the experiments. After 100 h the rate of copper leaving the section is higher, and the result is that copper concentration is lowered. The overall removal rate seems to be proportional with time.

The copper removal from the anode side with the longest remediation time (experiment 3) corresponds to 53%. In general, the copper removal should be defined by the copper environmental regulation for soil. So it could be possible that the copper removal could be enhanced by applying more electric current since the remediation time was not optimised.

Moreover, the experiments showed that the electric current did not affect the iron content in the tailing. The Fe content was not lower than 35 000 mg/dry matter in any slice of the electro-treated mine tailing. Since the ore is sulphide based it could be estimated that pyrite (FeS_2) is the dominant iron species, the pH should be lower than 3 in order to dissolve the mineral in tailings [11]. This kind of phenomenon did not

occur with the sulphuric acid addition since the $\text{pH} \geq 4$ was maintained during the remediation.

4. Conclusions

It is seen that copper can be removed from copper mine tailings by applying electric dc current. Experiments without any pre-treatment of the mine tailing showed that the pH has to be lowered, so Cu can dissolve from the solids and move in the electric field. The behaviour of the remediation experiments is similar to that of electro-dialytic remediation of polluted soil.

The use of additives such as acids or complexing agents would speed up the remediation process, since copper is found in the tailing surrounded by inert materials, which have to be dissolved before the current can act on the copper ions.

In general, copper removal was higher with acidic tailing than with watery tailing. From remediation experiments with acidic tailing of different duration it could be concluded that the removal seems to be proportional with time.

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