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# SUSPENDED ELECTRODIALYTIC EXTRACTION OF TOXIC ELEMENTS FOR DETOXIFICATION OF THREE DIFFERENT MINE TAILINGS

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## ABSTRACT

Environmental effects of mining activities partly origin from the production of tailings, and the exposure of these to ambient physical and chemical conditions. Removal of toxic elements from tailings prior to deposition could improve environmental performance and reduce risks. Experimental results have shown that electrokinetic treatment can remove Cd, Cu, Pb, and Zn from tailings soils; As from tailings; and Cu from tailings. Still, however, a major concern is the long treatment-time required for the element-transport through the tailings matrix. Therefore several enhancement methods have been investigated including pre-treatment of the tailings with acid; insertion of bipolar electrodes; and implementation of pulsed or sinusoidal electric fields. In line with these efforts, we investigated the efficiency when extracting toxic elements from a suspension of tailings, rather than from a solid matrix, which could well be implemented as a final treatment step prior to deposition of tailings. Six electrochemical experiments in laboratory scale with three different mine tailings (Codelco, Zinkgruvan, and Nalunaq) show that it is possible to extract residual Cu from the all the three suspended mine tailings, although with some difference between the tailings. From the Zinkgruvan sediment, which had the lowest Cu removal, Pb could also be extracted, while Cd and Zn were less extractable.

*Keywords: decontamination, detoxification, electrodialysis, heavy metals, mine tailings, remediation, resource recovery.*

## 1 INTRODUCTION

A major environmental effect of mining activities origin from the deposition of tailings and the exposure of these to ambient physical and chemical conditions. In modern mining, special precautions must be made. In this regard, special attentions should be paid to tailing handling and tailing deposition. One method in development for detoxification of tailings is electrokinetic (EK) or electrodialytic (ED) extraction of left toxic elements.

Experimental results have shown that the application of a direct current field (EK) over tailings can be used to remove Cd, Cu, Pb, and Zn from tailings soils [1, 2]; As from tailings [3, 4]; and Cu from tailings [5–7]. Still, however, a major concern is the long treatment-time required for element-transport through the tailings matrix. Therefore, several enhancement methods have been investigated to decrease treatment time: Improvements were obtained for removal of Cu from Cu mine tailings by: pre-treatment of tailings with acid (sulphuric or citric acid) [8,9]; insertion of bipolar electrodes to accumulate Cu [10]; and implementation of pulsed electric fields [5] or sinusoidal field [11,12]. It was also shown that the energy

consumption for treatment of arsenic tailings (but not treatment time) could be reduced by the combination of EK treatment and anaerobic bioleaching [13].

When comparing treatment of fresh (<2 years old) and aged (>20 years old) tailings, it was observed that although removal of Cu from fresh tailings improved significantly by pre-treatment with acid, removal from aged tailings was shown even more efficient – without acid pre-treatment. This is due to the natural acidification occurring by oxidation of sulfide minerals during the aging process [6,9]. It was shown for other materials such as ashes and sludge that ED treatment time can be significantly reduced by treatment in a homogeneously stirred suspension, as opposed to a solid matrix [14]. The main effect is thought to be the reduced transport distance between the material to be treated, and the electrode compartments. However energy and time may also be saved by the avoided build-up of polarization phenomena, which are also the phenomena approached when applying pulsed current and sinusoidal current fields [5,11,12]. It was shown that Cu can be removed from fresh tailings by ED treatment in suspension, when suspended in sulphuric acid, and that the rate of removal increases with degree of suspension [15]. However, later results showed that even when suspending in water, the extraction proceeded well, and did not differ between aged and fresh tailings; indicating occurrence of enhanced oxidation during treatment in suspension [7].

The aim of this work is to further evaluate the potential of treating mine tailings by electrodialysis in suspension through comparison of extraction of Cu from three tailings of different origin, — climatic, geological as well as process wise; and by comparison of extraction of different elements (Cd, Cu, Ni, Pb, Zn) from one of the tailings.

## 2 MATERIALS AND METHODS

### 2.1 Materials

The mine tailings used were:

- a. From the Codelco-El Teniente Cu mine in VI Region in Chile. The orebody at El Teniente mine comprises mainly the El Teniente Mafic Complex (CMET, Andesite), Dacite Porphyry, Tonalite, Diorite Porphyry and the Breccia Braden Complex [16]. The ore, which consists of porphyry copper sulfides, was crushed, milled and concentrated by flotation on-site at 2,300 m altitude in the Andes Mountains. The tailings mainly contain quartz, muscovite ferric clinocllore, calcic albite, anorthite and hydrated calcium sulphate with copper present as chalcocite, brochantite, chalcopyrite, ramsbeckite, wroewolfeite, and guildite [17]. Apart from copper, the tailings contain lead, cadmium and zinc and arsenic. The mine tailings were sampled directly from the canal which transports the tailings from the copper sulfide concentration plant to the Caren tailing dam (around 1,000 m above sea level) 87 km downhill. Around 40,000,000 tonnes tailings are deposited in the dam each year.
- b. From the zinc, copper and lead mine Zinkgruvan in southern Sweden. The Zinkgruvan deposit belongs to the Proterozoic aged Bergslagen greenstone belt, and hosts massive Zn, Pb, Cu, and Ag sulfides and banded iron-formations in volcano-sedimentary complexes [18]. The mineral processing of the ore takes place on-site and consists of autogenous grinding in combination with bulk/selective flotation [19]. The tailings mainly contain quartz, feldspar and calcite and are characterized by substantial concentration of carbonate minerals, whereas just small quantities of sulfides are present [20]. The tailings are considered as non-producing acid rock drainage (ARD) with a low weathering rate [19]. The production of the tailings was around 850,000 tonnes per year. The material used for the experiment consists of the fine fraction of the tailings, which had been transferred to a tailings pond near the site. At the time of sampling, the tailings were younger than 2 years,

but had been exposed to weathering and atmospheric oxidation.

- c. From the gold mine Nalunaq in southern part of Greenland. The deposit is classified as a mesothermal vein-type gold deposit hosted in metavolcanic rocks [21] and the surrounding region is characterized as a gold province with several promising occurrences [22,23]. The ore, which consists of a gold-bearing quartz vein (known as the main vein) and proximal hydrothermally altered dolerites and amphibolites [24], was crushed, milled, and treated by cyanide leaching in an extraction plant on-site. The tailings slurry was subjected to detoxification using the Inco method [25] and subsequently pumped into a tailings dam located in previously exploited levels of the mine. At the time of sampling, the estimated tailing production was 50,000–70,000 tonnes per year. In this study, tailings were obtained from the discharge of the detoxification tank before going into the tailings dam. The sampled slurry contained 20%–22% solids, which were left to settle before the excess water was decanted.

## 2.2 Electrodialysis experiments

Electrodialysis experiments were made in cylindrical Plexiglas-cells with three compartments. Compartment II, which contained the tailings-slurry, was 5 cm long and 8 cm in inner diameter. The setup is visualized in Fig. 1a and b.

The slurry was kept in suspension by constant stirring with plastic-flaps attached to a glass-stick and connected to an overhead stirrer. The anolyte was separated from the soil specimen by an anion-exchange membrane, and the catholyte was separated from the soil specimen by a cation-exchange membrane (AR204SZRA and CR67 HVY HMR427 from Ionics), respectively. Platinum coated titanium electrodes were used as working electrodes. The catholyte and the anolyte initially consisted of 0.01 M  $\text{NaNO}_3$  adjusted to pH 2 with  $\text{HNO}_3$ , pH in the catholyte was kept between 1 and 2 by manual addition of  $\text{HNO}_3$  (7 M). The liquid to solid ratio (L/S) was 4 (25 g air-dried tailings and 100 mL distilled water). All experiments lasted for 1 week. An overview of the experimental variables (material, suspension liquid, and current density) is given in Table 1.

After the closure of the experiments, electrodes were rinsed in 5 M  $\text{HNO}_3$ , and membranes in 1 M  $\text{HNO}_3$ . Samples of all liquids including electrolytes were saved for analysis. The tailings suspension was filtered through filter paper, and a sample of the filtrate saved for analysis. The wet tailings were dried at 105°C overnight and saved for the analysis of Cd, Cu, Ni, Pb, and Zn. Analysis of the elements in the tailings and process liquids was made prior to and after the experimental treatment. Non-acidic liquid samples were preserved with one part of concentrated  $\text{HNO}_3$  to four parts of liquid prior to analysis.

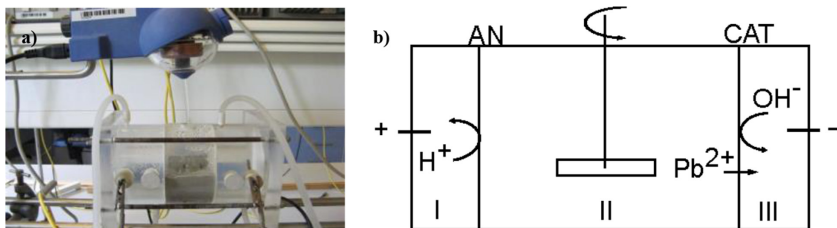


Figure 1 (a) Picture of the experimental setup (b) Schematic view of a cell used for experimental ED treatment of tailings in suspension: anion-exchange membrane (AN), cation-exchange membrane (CAT), anolyte compartment (I), compartment containing sediment slurry (II), catholyte compartment (III).

Table 1: Electrodialytic experiments.

Experiment	Current (mA/cm <sup>2</sup> )
Codelco1	0.1
Codelco2	0.2
Zinkgruvan1	0.1
Zinkgruvan2	0.2
Nalunaq1	0.1
Nalunaq2	0.2

### 2.3 Analytical methods

As, Cd, Cu, Ni, Pb, and Zn were analyzed by ICP-OES (Varian 720-ES, Software version: 1.1.0) or for Cu and Zn by AAS (for the Codelco sediment) after digestion according to the Danish standard method DS259 [26] which includes acid digestion of 1 g dry tailings material with 20.00 mL of 7 M HNO<sub>3</sub> in autoclave at 200 kPa and 120°C for 30 minutes. The element-content in solution was measured by ICP-OES after filtration through a 0.45 µm filter. pH was measured by a Radiometer electrode. All analyses were made in triplicate.

## 3 RESULTS AND DISCUSSION

### 3.1 Initial content and mass balances

The content of the analyzed elements in the tailings prior to treatment is shown in Table 1. All tailings had higher copper content than average earth's crust [27]. Both Zinkgruvan and Nalunaq had more cadmium and lead than average earth's crust, although Zinkgruvan much more pronounced than Nalunaq. In addition, Zinkgruvan had a high zinc content compared to average earth's crust content, and Nalunaq a high arsenic content. The nickel content is not elevated in any of the two samples for which it was analyzed.

The mass balances for all element for which remediation results are reported, understood as the mass found in the ED-cell system after experimental treatment in percent of the mass calculated from the initial analysis of the untreated tailings were all between 70% and 101%. The deviations can be explained by the inhomogeneity of the material illustrated by the significant standard deviations in the initial content of the analyzed elements (Table 2). Upon on this observation, the percentage distribution in the compartments of the cell was calculated based on the total final amount found.

### 3.2 Experimental performance

The pH decreased during treatment from natural to just below 2.5 (Figure 2) due to the acid produced in the ED-cell by water-splitting at the anion-exchange membrane described by [28].

### 3.3 Element extraction

The final concentration of the investigated elements can be seen in Table 3, and the final distribution of Cu in the ED cell can be seen in Fig. 3. Figure 4 shows the final distribution of

Table 2: Initial content of selected elements in the tailings (mg/kg±stdev).

	As	Cd	Cu	Ni	Pb	Zn
Codelco	na	na	997 ± 19	na	na	62 ± 3.5
Zinkgruvan	21 ± 2	11 ± 0.2	372 ± 28	24 ± 3	3,700 ± 233	7,331 ± 322
Nalunaq	122 ± 35	2.8 ± 0.9	105 ± 28	48 ± 13	59 ± 14	45 ± 22

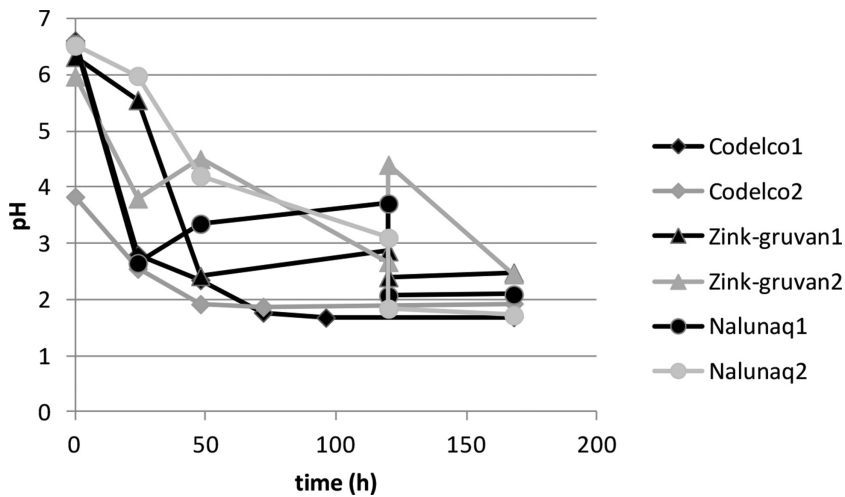


Figure 2: pH development of tailings slurry during ED treatment.

Table 3: Elements after one week of ED treatment (mg/kg).

	Cd	Cu	Pb	Zn
Codelco1	na	475	na	na
Codelco2	na	420	na	na
Zinkgruvan1	8.9	244	1,436	4,543
Zinkgruvan2	8.0	221	1,323	4,090
Nalunaq1	na	70	na	na
Nalunaq2	na	43	na	na

Cd, Pb, and Zn in the Zinkgruvan tailings. The Cu concentration was reduced in all experiments (Table 3), indicating that extraction of copper by ED extraction from tailings may be obtained on a general basis and not only for the specific tailings type of Codelco, which was investigated previously [7,15].

The copper removal was however more efficient from the Codelco tailings, and least efficient from the Zinkgruvan tailings at identical experimental conditions, both when comparing amount of copper removed and when comparing percentage of copper removed (Fig. 3). The removal was slightly more efficient at the higher current density compared to the lower current density for all three tailings.

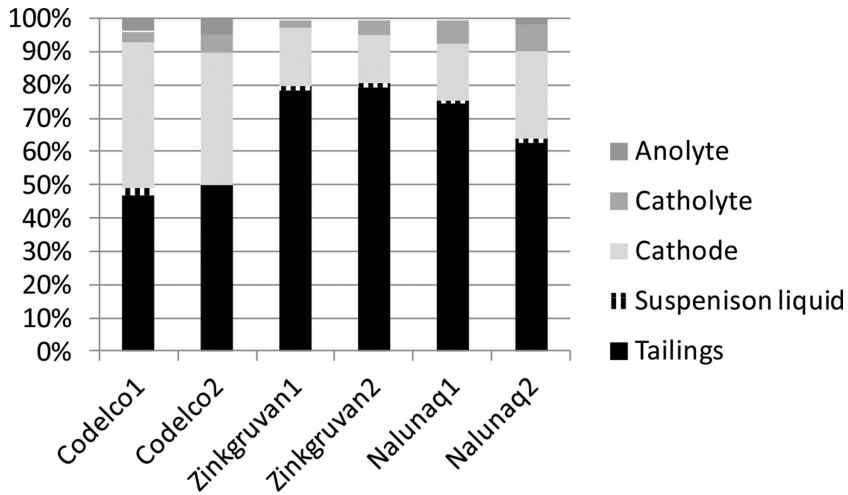


Figure 3: Results of the six electrodialysis experiments expressed as percent of the Cu found in the various compartments of the ED cell. The amount in the electrolytes include small amounts (<1%) found in the membrane material.

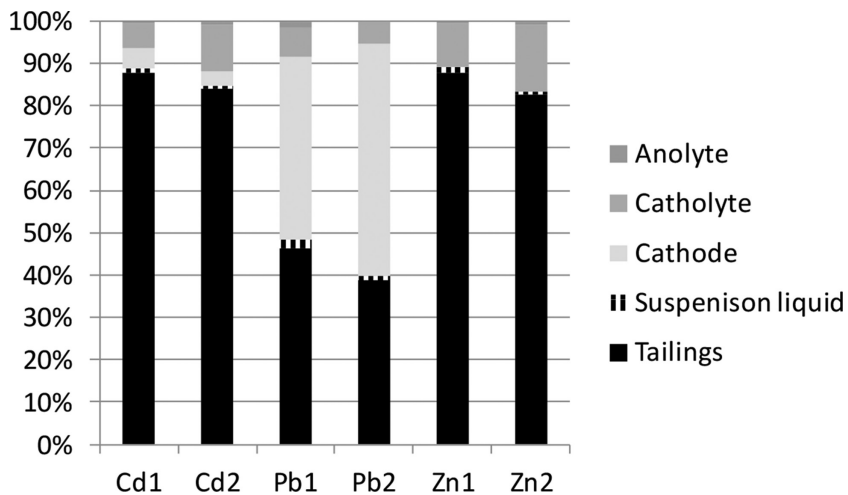


Figure 4: Results of Cd, Pb, and Zn removal from the two electrodialysis experiments (1 and 2) with Zinkgruvan tailings expressed as percent of the elements found in the various compartments of the ED cell. The amount in the electrolytes include small amounts (<1%) found in the membrane material.

The voltage drop was between 2 and 3 volt in all experiments. At such low voltage drop and current density, energy consumption becomes minimal (<80 kWh/ton for the observed extraction). With no exemptions, the experiment show that the Cu removed from tailings is mainly precipitated at the cathode as metallic Cu, and only small fractions are found in the liquid phases (electrolytes) (Fig. 3). This is the typical behavior for Cu [29].

Likewise typical was the behavior of Pb, Cd, and Zn extracted from Zinkgruvan tailings, as Pb was also mainly precipitated at the cathode, while Cd and Zn were mainly found dissolved in the catholyte liquid [29]. This behavior may be utilized to separate the elements. The Pb concentration was reduced significantly (>50%), while Cd and Zn was reduced only slightly (<20%). This is in contrast to what is normally observed when treating contaminated soils, in which Zn and Cd are most often found to be the most mobile elements [29], and showing that the specific mineralogical bonding of Cd and Zn in this tailing may significantly reduce their mobility.

#### 4 CONCLUSIONS

EDR was shown to be a potent method for detoxification of tailings as it was generally possible to extract residual Cu from the three investigated tailings by electrodialysis in suspension independently of tailings origin at low-energy consumption. Pb could also be extracted from the Zinkgruvan sediment, while Cd and Zn are less mobile in these tailings. Both Pb and Cu precipitated at the cathode and can thus be recovered in their metallic form.

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