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## Removal of Cu, Pb and Zn in an applied electric field in calcareous and non-calcareous soils

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### Abstract

The pH dependency of the removal of Cu, Zn and Pb by electro-dialytic soil remediation from different industrially polluted soils was examined. From 18 experiments performed with five different soils, it was found that the order of mobilization due to a pH decrease was Zn > Cu > Pb. It was found, too, that each of the elements was removed at higher soil pH in calcareous soils (about 12% carbonates) than in soils with a carbonate content of less than 3.7%. In soils rich in carbonates, precipitation of heavy metal carbonates is an important retention mechanism and the heavy metal carbonates are dissolved at higher pH values than the pH at which heavy metals are desorbed in non-calcareous soils. Thus, the relation between the soil pH and the mobility of the heavy metal in the electric field is not only dependent on the heavy metal in focus, but also on the fraction of the heavy metal precipitated as carbonates. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Electrokinetics; Carbonates; Heavy metals; Electro-dialytic soil remediation; Soil pH

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### 1. Introduction

Heavy metals in soils are receiving increased attention due to the greater understanding of their toxicological importance in ecosystems and for human health. In a polluted soil, the heavy metals tend to adsorb mainly in the fine fraction due to the large surface area. If a solution is forced to flow through a soil by pressure, the solution will flow in the larger pores. Oppositely to a hydraulic flow, an applied electric field will tend to pass the soil in the micropores due to the lower electric resistance here, and thus, the electric current will

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act exactly where the heavy metals are mainly found. This means that the electrochemical soil remediation methods that are based on an applied electric field as cleaning agent, are particularly useful for fine grained soils where pump-and-treat technologies or soil washing methods are impractical or impossible to use [1].

Different electrochemical soil remediation methods are under development for removal of heavy metals from polluted soils. The methods are based on the two electrokinetic phenomena: electroosmosis and/or electromigration. In order to be mobile in the electric field, the heavy metals must be present in the dissolved phase of the soil. The desorption and mobilization of most heavy metals during the remediation process is catalyzed by an acidic front that is developing from the anode end of the soil [2,3], and when the acidic front reaches all through the soil, the remediation action is finished [4].

Many of the latest developments of the electrochemical soil remediation methods are based on an increased acceptance that it may be beneficial or even necessary to vary the remediation parameters depending on the soil characteristics and the actual pollution composition. An example can be in the case of calcareous soils where the acidic front is developing very slowly through the soil causing an unacceptable time demanding remediation. For remediation of a Cu polluted calcareous soil, it is beneficial to add ammonia to the soil as complexing agent prior to the remediation [5]. Meanwhile, the developing acidic front as catalyst for heavy metal mobilization is very efficient in many soil systems and most papers reported on electrochemical soil remediation is based on the development of this acidic front, including the present paper. This paper investigates (I) whether there are differences in the relation between pH and the mobility of Cu, Zn and Pb and (II) if the mobility and pH dependence is soil-specific. The experimental basis for the work is 18 electrochemical soil remediation experiments performed with five different soils sampled at industrially polluted sites.

## 2. Electrochemical soil remediation

Different electrochemical soil remediation methods have been developed and the present paper deals with the electrochemical soil remediation method (EDR) [3–5]. The principle of EDR differs from other electrochemical soil remediation methods (ECR) in the use of ion-exchange membranes. In a few ECR methods, the electrodes are placed directly in the soil, but in most methods the electrodes are placed in electrolyte solutions [1,2,7,8]. In EDR, the separations between the soil and these electrolyte solutions are ion-exchange membranes whereas in ECR the separations are chemically passive barriers. A schematic presentation of a laboratory cell for EDR is shown in Fig. 1.

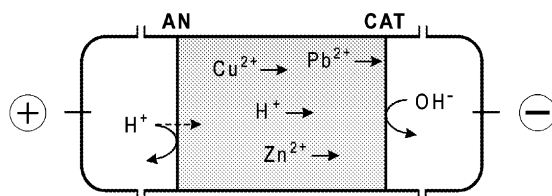


Fig. 1. The principle of electrochemical soil remediation.

In EDR, the soil is placed in a desalination compartment instead of the normal electrolyte solution to be desalted in conventional electro dialysis. After the remediation, the heavy metals that were removed as cations and anions will be found concentrated in the catholyte and in the anolyte, respectively. Depending on the actual heavy metal, different methods can be used for separation of the heavy metals from the solution and make reuse possible [9]. One method for separation and reuse of Cu, Hg, Cd, Zn, and Pb is electro-deposition.

When inert electrodes are used in both ECR and EDR, the pH of the catholyte will increase. In the system of ECR, an alkaline front will enter the soil from the cathode side causing precipitation of the heavy metals within the soil matrix, which means that the remediation cannot proceed [10]. In most ECR methods, this alkaline front is prevented by a continuous addition of acid to the catholyte and this means that the counter ions are transported into the soil. In EDR, acid is added to the catholyte, too, but due to the cation-exchange membrane separating the catholyte and the soil, the counter ions to the acid will not enter the soil. In the experiments of this paper, HNO<sub>3</sub> was added to the catholyte during the remediation, and due to the cation-exchange membrane, the NO<sub>3</sub><sup>-</sup> ions were not entering the soil. This is beneficial in the actual study, because this means that the effect from oxidation caused by this ion can be excluded from the experimental results.

Even when an anion-exchange membrane is placed between the anolyte and the soil, the soil is acidified during the remediation process. It is likely that this acidification is due to water splitting ( $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ ) at the anion-exchange membrane [4] where the hydroxyl ion will enter the anode compartment and the hydrogen ion will enter the soil due to the applied electric field. At higher current densities (about 0.5 mA/cm<sup>2</sup>), water splitting can occur at the cation-exchange membrane, too, and thus, the current density must not exceed this value in order to avoid an alkaline front in developing from the cathode end of the soil [4]. In the experiments reported here, there were no water splitting at the cation-exchange membrane.

When ion-exchange membranes are used as separators between the soil and the solutions in the electrode compartments, transport of easily mobile ions between the electrode compartments is hindered and thus, the ions originating from the soil, the heavy metals will be attacked by an increased force during EDR.

### 3. Experimental

#### 3.1. Analytical

The concentration of the elements were measured after pretreatment of the soil as described in Danish Standard 259: 1.0 g of dry soil and 20.0 ml (1:1) HNO<sub>3</sub> were heated at 200 kPa (120°C) for 30 min. The liquid was separated from the solid particles by vacuum through a nuclepore filter and diluted to 100 ml. The elements were measured by AAS. The units used in this paper are mg/kg dry matter.

Soil pH was measured by mixing 10.0 g dry soil and 25 ml 1.0 M KCl. After 1 h of contact time, pH was measured using a Radiometer pH electrode.

The carbonate content was determined by a volumetric calcimeter method as described in [11]. Cation exchange capacity (CEC) of the soils was measured with a method that is comparable to the acid–NaCl method described in EPA Standard Method 9080.

### 3.2. Experimental soils

Five heavy metal polluted soils sampled from different Danish polluted sites were chosen for this investigation. The pollution originated from: soil 1 wood preservation, soil 2 cable production, soil 3 unknown, soil 4 auto lacquer, soil 5 production of electronic devices.

Some characteristics for the soils are shown in Table 1.

### 3.3. Laboratory equipment

The electrodiolytic remediation experiments were made in laboratory cells as the one shown in Fig. 1. The cells were made with plexiglas or glass. The ion-exchange membranes were obtained from ionics (anion-exchange membrane AR204 SZRA B02249C and cation-exchange membrane CR67HUY N12116B). In each electrode compartment, 0.01 M  $\text{NaNO}_3$  with pH adjusted to about 2 with  $\text{HNO}_3$  was circulated. Platinum coated electrodes from Bergsoë AC, Denmark, were used as working electrodes, and a power supply (Hewlett Packard E3612A) was used to maintain a constant current. For the experiments, soil compartments with different lengths were used; 5, 10 and 15 cm, but the internal diameter was 8 cm in all cells used.

### 3.4. Electrodiolytic soil remediation experiments

For this paper, 18 electrodiolytic laboratory experiments were chosen. The mass balance of each element was between 92 and 106% for each experiment, which is considered acceptable since the experiments were performed with soils sampled from polluted sites and some inhomogenities can hardly be avoided. Common to the experiments was that the remediation had not finished and only such experiments were included in this work to ensure areas within the soil with different pH values from each experiment.

Table 1  
Some main characteristics of the five experimental soils

	1	2	3	4	5
Pollutants					
Cu	1100	5400	2980		
Pb		360	380	500	940
Zn		380	1090	500	
Carbonate content (Scheibler method) (%)	<0.1	12.0	11.9	3.7	0.5
Organic content (loss of ignition at 550°C) (%)	2.4	3.3	2.3	3.7	4.1
Clay (<0.002 mm)	5	4	2	3	11
Silt (0.002–0.06 mm)	21	20	6	12	52
Sand (0.06–2 mm)	72	71	60	83	35
CEC (meq/g dry soil)	2.3	2.9	2.7	6.2	15.3
pH	5.4	7.3	7.7	7.1	6.1

The polluted soils had original soil water and some of the soils had been mixed with additional water (distilled water) to fill the soil pores with water before the soil was placed in the central compartment by hand. The initial soil water content varied from 18 to 26%. The duration of the experiments varied (10–91 days). The current density was kept constant in each experiment but varied between the experiments ( $0.05\text{--}0.20\text{ mA/cm}^2$ ) and the voltage drop varied between the experiments (3–54 V), too.

At the end of each experiment, the soil was segmented into slices from the anode to the cathode and the slices were between 1 and 1.5 cm thick. In each of these slices pH and concentration of heavy metals were measured twice, as minimum.

#### 4. Results and discussion

One example pH profile and Pb, Cu and Zn concentration profiles in soil 2 are shown in Fig. 2. The duration of this experiment was 90 days with a current density of  $0.2\text{ mA/cm}^2$  and the soil compartment was 10 cm long. The acidic front developed from the anode end of the soil and in the first slice where pH was 5.5, the concentration of Pb, Cu and Zn had decreased to 36, 16 and 13% of the initial concentration, respectively. The Zn concentration was decreased in the first three slices, the Cu concentration was decreased in two slices, whereas the Pb concentration was removed from the first slice only. Accumulation of the three heavy metals was found in the next slices in the direction of the cathode.

Similar patterns were found in the other 17 experiments. The relation between the soil pH and normalized concentration is in focus in this work, and the results from all 18 experiments are summarized in Fig. 3, where data points for the slices (pH, normalized concentration) are given.

Two of the experimental soils, 2 and 3, were polluted with all three heavy metals of this investigation: Cu, Zn and Pb. In Fig. 3, the data points for these two soils are shown with white symbols. The pH below which all data points for these soils show more than 50%

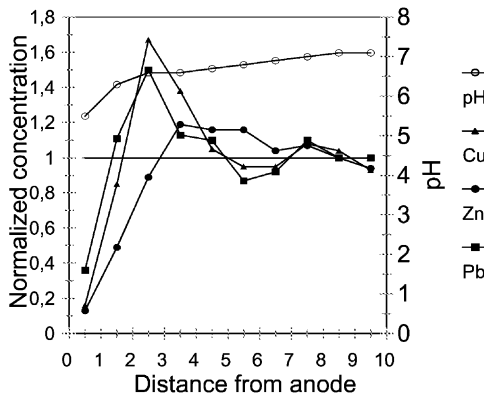


Fig. 2. Example of Zn, Pb and Cu concentration profiles and pH profile in an electroalytic remediation experiment performed with soil 2.

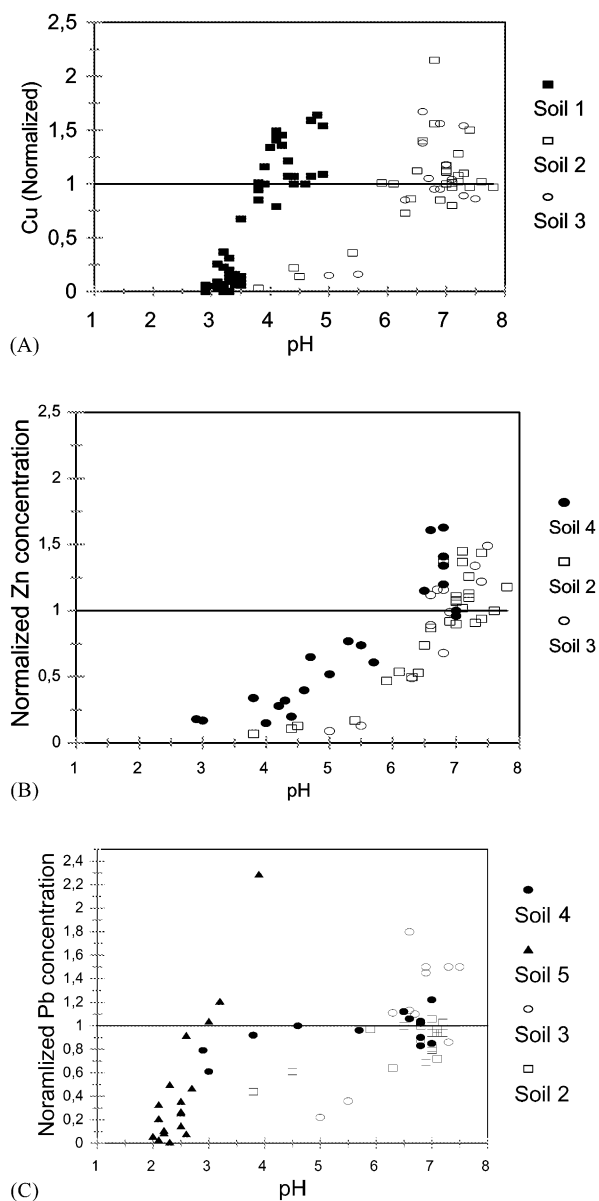


Fig. 3. Relation between soil pH and normalized concentration in different soils after application of current (A) Cu; (B) Zn; and (C) Pb.

reduction is about 4.0 for Pb, 5.5 for Cu and 6.0–6.5 for Zn. This is in consistency with the expected. Zn is desorbed at a higher pH than Cu which again is desorbed at a higher pH than Pb [6].

From Fig. 3(A), showing the pH-normalized Cu concentration for three soils, it is clearly seen that the black data points showing the results for soil 1 are separated from the data points for soils 2 and 3, which on the other hand are showing the same pattern. It seems as if the acidification must reach a lower pH value before Cu is mobilized in soil 1.

In the case of Zn, Fig. 3(B), all data points for soil 4 is above those for soils 2 and 3 at similar pH values, which means that pH must be lower in soil 4 before Zn is mobilized and removed compared to the two other soils.

For Pb, in Fig. 3(C), no removal was found for soils 4 and 5 at pH values above 3. In contrast, Pb was removed at pH values of about 4.5 in soil 2 and at about 5.5 from soil 3. Viadero et al. [7] showed a figure with the relation between soil pH and Pb concentration in a soil for a series of experiments performed with a spiked fine sandy loam. In this investigation, soil pH was measured in water (1:5, soil:water) which results in a slightly higher pH value than in the case where pH is measured in KCl [12]. Initial pH of the soil was 5.4 indicating a low carbonate content. In this spiked soil, the concentration of Pb starts to decrease quite steep when pH reaches about 3.8–4. From Fig. 3(C) it can be seen that pH should be less than 2.7 before any Pb was removed from soil 5 (with a low carbonate content). Pb was removed at higher pH values in the spiked soil than in soil 5 even taking into account the differences in the methods for pH measurements. This is probably linked to this soil being spiked, i.e. that the adsorption of Pb to this soil was less strong than in the industrial polluted soils of this paper.

Common to the three elements was that there were soil(s) where pH had to reach lower values, compared to soils 2 and 3, before a high mobilization and removal of the heavy metals was obtained (Fig. 3(A–C)). In Table 1, it is seen that an important soil parameter that differs between the experimental soils is the carbonate content, which is about 12% in soils 2 and 3, whereas it is less than 3.7% in soils 1, 4 and 5. The pH-normalized concentration pattern may very well be linked to this fact.

The formation of heavy metal carbonates may be an important type of retention of the heavy metals in soils rich in carbonates. Precipitation of malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) may be significant in the case of Cu [13]. For soil 2, a previous investigation using SEM showed that this actual soil contained malachite [14]. Smithsonite ( $\text{ZnCO}_3$ ) [15] and cerussite ( $\text{PbCO}_3$ ) [16] are likely to be formed when a calcareous soil is polluted by zinc and lead, respectively.

Martínez and Motto [6] investigated the solubility of Pb, Zn and Cu in different spiked soils and found that each metal exhibited an approximate pH value at which the solubility increased markedly (5.2 for Pb, 5.5 for Cu and 6.2 for Zn), except for the calcareous soil, where the metals were dissolved at higher pH values (6.0 for Pb, 6.2 for Cu and 6.8 for Zn) compared to the non-calcareous soils. This finding corresponds very well to the findings in the electro-dialytic soil remediation experiments, where it was seen that the heavy metals were mobilized and removed at higher pH values in the calcareous soils than in the non-calcareous soils.

In the case of Pb (Fig. 3(C)), there was a clear difference between the two calcareous soils 2 and 3, but still soil pH must be lower for both soils for Pb mobilization than for mobilization of Cu and Zn.

In soil 3, Pb was mobilized at higher pH than in soil 2, and this may indicate that Pb is retarded by different mechanisms in the two soils. There was a tendency for Cu and Zn to be mobilized at higher pH in soil 3 than soil 2, too, but the tendency was not as pronounced as for Pb. Soil 2 had the lowest organic content and less clay and silt compared to soil 3. This means that the adsorption sites, except for precipitation in the carbonate fraction, can be expected to be less in soil 2 than in soil 3. In soil 3, there may thus, be a smaller percentage of the heavy metals retarded in the carbonate fraction than in soil 2, since other retention mechanisms are of importance. The carbonate bound fraction of the three heavy metals is considered to be the first to be mobilized when pH is decreased and this may explain the difference between soil 2 and soil 3.

The carbonate content in soil 4 was 3.7% and that is higher than soils 1 and 2, where the carbonate content was less than 0.5%. Soil 4 was polluted with Zn and that was not the case for soils 1 and 2. Thus, it is not possible to see if there is an effect of the higher carbonate content, on the pH at which Zn is mobilized in soil 4 compared to soils very poor in carbonate content. Both soils 2 and 4 were polluted with Pb and there seems to be a tendency for Pb to be removed at higher soil pH in soil 3 than in soil 4, i.e. in a soil with a carbonate content of 3.7% compared to 0.5%.

## 5. Conclusions

This investigation covered a total of 18 electro-dialytic soil remediation experiments with five different heavy metal polluted soils. The relation in focus was the pH dependency of the mobility of Cu, Zn and Pb in the applied electric field. Two of the soils were polluted with all three elements and for these two soils it was found, that Zn was mobile at higher pH values than Cu which again was mobile at a higher pH than Pb.

The pH value at which each of the elements were mobilized was shown to be soil-specific. All three elements were mobilized at higher pH values in the soils with a carbonate content at about 12% compared to the soils with a carbonate content less than 3.7%.

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