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Acidification of Harbor Sediment and Removal of Heavy Metals Induced by Water Splitting in Electrodialytic Remediation

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Abstract: Harbor sediments are often contaminated with heavy metals, which can be removed by electrodialytic remediation. Water splitting at the anion exchange membrane in contact with the contaminated material in electrodialytic remediation is highly important for the removal of heavy metals. Here it was investigated how acidification caused by water splitting at the anion exchange membrane during electrodialytic remediation of contaminated harbor sediment and hence the metal removal, was influenced by different experimental conditions. Two different experimental cells were tested, where the number of compartments and ion exchange membranes differed. Totally, 14 electrodialytic experiments were made, with varying remediation time, current densities, and liquid to solid ratio (L/S). pH in the sediment decreased slightly after 1 day of remediation, even if the sediment had a high buffering capacity, suggesting that water splitting at the anion exchange membrane started early in the remediation process. An increase in the voltage over the cell and a decrease in the electrical conductivity in the sediment suspension also indicated that the water splitting started within 1 day of remediation. When the sediment was acidified, the voltage decreased and electrical conductivity increased. After 5 days of remediation the sediment was acidified at the chosen current density ($1\,\mathrm{mA/cm^2}$) and the main metal removal was observed shortly after. Thus it was crucial for the metal removal that the sediment was fully acidified. Lower metal removal was seen

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in an experimental cell with three compartments compared to five compartments, due to increased sensitivity of pH changes in the cell.

Keywords: Heavy metals, sediment, electrodialysis, water splitting, ion exchange membranes

INTRODUCTION

Remediation methods for dredged heavy metal contaminated harbor sediments have gained increased interest during recent years, since dumping at sea of contaminated sediments are prohibited in many countries. Disposal of contaminated sediment is space consuming and can be expensive, since contaminated sediments often are regarded as hazardous waste. Electrokinetic remediation methods are widely used for soil remediation (1), where an electric field mobilizes the heavy metals. Electrodialytic remediation, where ion exchange membranes are used to optimize the heavy metal removal, has successfully been used to remove heavy metals from soil, fly ashes, impregnated wood waste, and wastewater sludge in laboratory scale (2, 3). Recently, electrodialytic remediation also showed good results for remediation of heavy metal contaminated harbor sediments (4). Electrodialytic remediation is particularly useful for fine-grained materials, such as harbor sediment, where traditional soil remediation technologies, e.g., extraction techniques, are impractical or even impossible to use (5, 6). This is because the electric current mainly passes the contaminated sediment in the micropores due to the low electrical resistance here, and thus acts where the heavy metals mainly are found.

Electrodialytic remediation is based on electrodialysis and electrokinetic remediation. Electrodialysis is a membrane-based separation process where the separation of electrolytic components of an ionic solution is induced by an electric current (7). Electrodialysis is widely used for different industrial purposes, as listed by (7). A basic electrodialytic cell consists of a desalination compartment which is separated from concentration compartments by ion exchange membranes as seen in Fig. 1. When an electric current is applied over the cell, cations in the solution (compartment III) move toward the cathode and anions towards the anode placed in the electrode compartments I and V.

When the cations reach the cation exchange membrane (CAT 2), they can pass freely, but when they reach the anion exchange membrane (AN 2) they cannot pass. This also occurs for the anions migrating in the direction of the anode in the other side of the cell. Thus by time, the solution in compartment III is emptied of ions, which instead concentrate in compartments II and IV, due to the setup of the ion exchange membranes. Industrial electrodialytic units consist of several desalination and concentration compartments with correspondingly more ion exchange membranes.

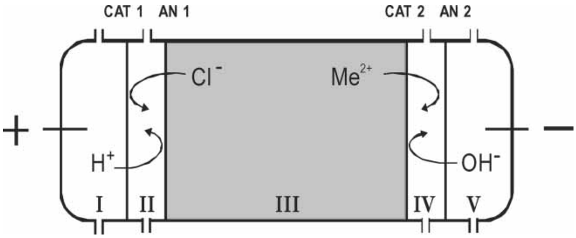

Figure 1. The principle of an electrodialytic cell. AN—anion exchange membrane, CAT—cation exchange membrane.

In electrodialytic remediation, the same removal principles are used as in electrodialysis, but instead of a solution in compartment III, the heavy metal contaminated material is placed here. The contaminated material is water saturated when placed in compartment III, because the ions only move in a liquid phase. The ions in the contaminated material are removed to compartments II and IV. Most often, the heavy metals in the contaminated materials are strongly bound to or precipitated in the material and will not dissolve in contact with water.

When using inert electrodes the following electrode processes occur

$$\text{Cathode: } 4H_2O + 4e^- \longrightarrow 2H_2(g) + 4OH^- \tag{1}$$

$$\text{Anode: } 2H_2O \longrightarrow O_2(g) + 4H^+ + 4e^- \tag{2}$$

which lead to an acidic anolyte and a basic catholyte. When using ion exchange membranes, the development of an acidic and basic front into the contaminated material caused by the electrode processes in compartments I and V is eliminated. However, in electrodialytic remediation the contaminated material is acidified and considerable amounts of metals are removed. The contaminated material is acidified from the anode end toward the cathode end due to water splitting at the anion exchange membrane AN 1 (8). This is the foundation of unenhanced electrodialytic remediation, since most heavy metals are mobilized in the acidic environment.

A stirred experimental setup was introduced by (9) for enhancing remediation of fly ashes, because the stationary setup gave different operational problems that increased the electrical resistance in the cell. Instead, a suspension of the contaminated material is placed in compartment III, which is continuously stirred during the experiment. High dissolution of ashes was seen during electrodialytic remediation of combustion fly ash using the stationary setup (10). To maintain the electric current through the cell, contact between the contaminated material and the ion exchange membranes is crucial. Thus, dissolution during electrodialytic remediation can pose operational problems in the stationary cell. Using the stirred setup for remediating harbor sediments was also more efficient than using the stationary setup (4).

Recently, acidification of sewage sludge (3) due to water splitting in the stirred setup was suggested to be equal or more beneficial for Cd removal as acidification by acids.

In this present study it was investigated how acidification due to water splitting could be used to remove heavy metals from harbor sediment in two different stirred experimental setups and how varying experimental conditions (current density, duration, and liquid to solid ratio [L/S]) influenced the acidification and subsequent metal removal.

Ion Exchange Membranes

Ideally, ion exchange membranes are 100% effective in only transporting counter-ions and excluding the passage of co-ions. The transference number is used to express the permselectivity, which refers to the amount of ion in interest passing the membrane compared to the total transported species (11). The transference number is dependent on the ionic flux and the applied current. Polymeric ion exchange membranes can have limited lifetime due to fouling (clogging by small particles) or degradation of the membrane which can happen such as at extreme pH values. Studies of the ion exchange membranes used in electrodialytic remediation showed close to ideal selectivity in the presence of Na, Ca, Cu, and Zn chloride solutions (12). The transference number of the membranes and permselectivity did not change after being used in electrodialytic soil remediation experiments either (13). The electrical resistance only increased slightly for membranes being used for a 3-month remediation experiment. In electrodialytic remediation, the anion exchange membranes can be discolored by small colloidal particles that are transported by electrophoresis toward the anode (fouling), which cannot pass the anion exchange membrane due to their size. However, this did not lower the transference number for the membrane (13).

Water Splitting

In electrodialysis of a solution, about equal amounts of the current are carried by anions and cations. Close to the ion exchange membranes, the concentration decreases compared to the bulk concentration. When this concentration is zero, the limiting current density has been reached. Theoretically, higher currents than the limiting current cannot be expected, but overlimiting currents are obtainable in practice (14, 15). The overlimiting current in a system mainly depends on the amounts of ions to carry the current and increases significantly when the electrical conductivity increases (16). Operation at current densities higher than the limiting current results in water splitting at the membrane (formation of H^+ and OH^-), and the limiting current is lower for an anion exchange membrane than a cation exchange membrane (17, 18). Thus, water splitting most often occurs in anion exchange membranes. pH changes in conventional electrodialysis of solutions are considered undesirable (14) because it can result in scaling (precipitates) at the membrane surface, detoriation of the membrane under extreme pH conditions, which causes increased resistance in the cell and is thus energy consuming.

Most anion exchange membranes contain quartiary amine groups. Refs. (18, 19) suggested that the mechanisms behind water splitting on the surface of anion exchange membranes are caused by tertiary amine groups, which are formed from reversible protonation of the membranes quartiary amine groups. Water splitting at these membranes starts after a few hours of operation and not immediately when the current is applied (17). Ref. (17) also favors this explanation, when having shown that water splitting was lower using anion exchange membranes with other functional groups. Water splitting can also occur at the cation exchange membrane, so finding the current where only water splitting at the anion exchange membrane happens is essential in electrodialytic remediation. In electrodialytic soil remediation limiting currents between 0.3–0.5 mA/cm^2 when remediating a noncalcareous soil (8) and 0.4–0.75 mA/cm^2 when remediating a calcareous soil (20) were seen for an Ionics cation exchange membrane (CR67HUY N12116B). In pure electrodialysis limiting currents for the cation exchange membranes can be 10–100 times higher than the limiting currents in electrodialytic soil remediation (15, 19), which is an advantage to avoid pH changes in pure electrodialysis systems. This is because concentration gradients build up more easily in the stationary medium in soil remediation compared to ideally mixed solution. Since the ion exchange membranes were not altered after being used in electrodialytic soil remediation, water splitting can be expected to occur during the whole remediation period (13).

MATERIALS AND METHODS

Experimental Sediment

Norwegian harbor sediment from Haakonsvern, Bergen was used in this study and the sediment was mainly contaminated with Cu, Zn, Pb, and Cd (21). The harbor sediment was dredged by NCC Norway with a special dredging device for removing only the finer, polluted material (<5 mm). All the sediments were air-dried at a temperature $\sim20°$C before the experiments, to resemble treatment conditions for sediment in a Danish pilot-scale remediation study where sediment was dried by infiltration (22).

Analytical Methods

Heavy metal concentrations in the sediment were determined after pretreatment according to Danish Standard DS 259: 1.0 g dry sediment 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 nucleopore filter of 45 μm and diluted to 50 mL. The heavy metals were thereafter measured by AAS (atomic absorption spectrometry). The concentration units used in this paper are mg/kg dry material. Organic matter was measured by loss of ignition at 550°C for 1 h. The carbonate content was determined by a volumetric calcimeter method as described in (23). pH was measured in 1 M KCl and sediment at L/S 5 and after 1 h of agitation, pH was measured in the solution by a Radiometer Analytical pH electrode.

Extraction Experiments

pH dependent extraction experiments were made by mixing 2.5 g sediment with 25 mL of either HNO_3 or NaOH in concentrations between 0.01 M–1 M in 50 mL acid-rinsed plastic bottles. Extractions with distilled water were made as a reference. All the extractions were made in duplicates and shaken for 48 h on a horizontal shaker operating at 250 rpm to keep the sediment in suspension. Thereafter the samples settled for 15 min before pH was measured. The extractants were filtrated though 45 μm and acidified if pH >2 by addition of concentrated HNO_3 in a 1:4 ratio and heated at 200 kPa (120°C) for 30 min before measured by AAS (flame or graphite furnace).

Electrodialytic Experiments

The experimental cell setups used for the electrodialytic remediation experiments are seen in Fig. 2 and both experimental cells were modifications of the traditional cell in Fig. 1. An experimental setup with continuous stirring of the harbor sediment was used here. In total, 14 electrodialytic experiments were made; see experimental conditions in Table 1.

The laboratory cells were made of Plexiglas and the internal diameter of all cell parts was 8 cm. The length of compartment III was 10 cm and 100 g DM harbor sediment was used in the experiments. Two different experimental cells were used: one with five compartments (cell type A) and one with three compartments (cell type B). The main difference when using cell type B compared to cell type A is that the removed ions are concentrated in the electrode compartments and metal cations can precipitate on the cathode in cell type B. The largest voltage drop during electrodialytic remediation is seen over the ion exchange membranes (8) and thus the fewer ion exchange membranes in cell type B could influence the remediation.

The electrolyte was 0.01 M $NaNO_3$, which was adjusted with HNO_3 to pH <2 during the experiments. In cell type A, 500 mL electrolyte circulated in compartments I and V and 250 mL electrolyte circulated in compartments II

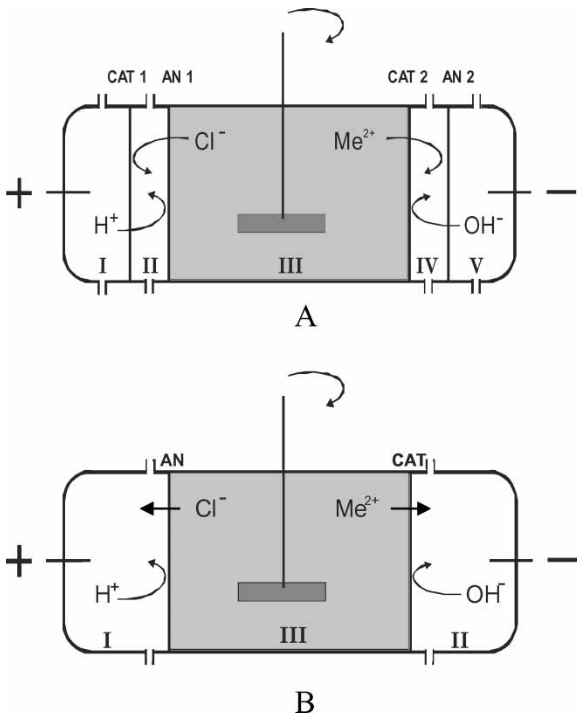

Figure 2. The stirred electrodialytic cell with five compartments (A) and three compartments (B).

and IV. In cell type B, 500 mL electrolyte circulated in compartments I and II. The ion exchange membranes were obtained from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). Transference numbers of the ionics membranes in weak salt solutions are 0.97 for the cation membrane and 0.95 for the anion membrane (20). Platinum-coated titanium electrodes from Permascand ($Ø = 3$ mm, $L = 3$ cm) were used as working electrodes and a power supply (Hewlett Packard E3612A) was used to maintain a constant DC current. The pumps used to circulate the electrolytes were "Pan World" pumps with a flow rate of 2.6 L/min. A "Heto" motor, with a rotation velocity of 1300 rpm was used to stir the sediment suspension. The stirrer was a flexible plastic flap fastened to an insulated metal wire. The total length of the plastic flap was 6.5 cm and it was 0.6 cm wide.

In experiments 12–14, pH and electrical conductivity were measured daily in the sediment suspension. The stirrer was turned off and the sediment settled for 15 min before a sample was taken from compartment III. pH and electrical conductivity were measured with electrodes from Radiometer Analytical and the sample replaced in compartment III.

Table 1. Experimental conditions for the electrodialytic experiments

Experiment	Duration (days)	Current density (mA/cm^2)	L/S (ml/g)	Cell type	pH in the sediment
Initial sediment					7.5
1	14	0	4	A	7.3
2	14	0.6	4	A	2.2
3	14	1.0	4	A	2.2
4	14	1.4	4	A	2.1
5	1	1.0	4	A	7.1
6	3	1.0	4	A	6.8
7	5	1.0	4	A	2.4
8	7	1.0	4	A	2.0
9	11	1.0	4	A	2.5
10	21	1.0	4	A	2.0
11	28	1.0	4	A	1.5
12	14	1.0	4	B	2.5
13	14	1.0	8	B	2.6
14	14	1.0	12	B	2.4

At the end of the experiments the membranes and the stirrer were treated with 1 M HNO_3 to extract the heavy metals that were adsorbed to the membrane or on the stirrer during the process and the electrodes were rinsed in 5 M HNO_3. The harbor sediment suspension was filtered through a 45 μm filter. Both the liquid and the sediment solids were analyzed for heavy metals. The electrolytes and the filtered liquid from compartment III were preserved by adding concentrated HNO_3 in a 1:4 ratio and heated at 200 kPa (120°C) for 30 min. All the samples were measured by AAS (flame or graphite furnace).

RESULTS

Characteristics and Extraction

Some characteristics of the harbor sediment are shown in Table 2. The pH dependent metal extraction is shown in Fig. 3 as the amount of metal extracted compared to the initial concentration in the sediment. Each measurement is plotted for the pH dependent extraction.

The sediment had a slightly alkaline pH, due to the high carbonate content. The high buffering capacity could slow down the acidification of the sediment, which has been observed when remediation of calcareous soil (24), though using the stationary electrodialytic setup.

At pH 7.5, the sediment's natural pH, the metals were hardly extracted ($<5\%$). Cd was most mobile in the sediment at acidic pH and started

Table 2. Characteristics of the experimental harbor sediment

Characteristic	Value
Cu (mg/kg)	49.6 ± 3.0
Zn (mg/kg)	137.0 ± 7.8
Pb (mg/kg)	58.1 ± 4.5
Cd (mg/kg)	3.9 ± 0.7
pH_{KCl}	7.5
Carbonate content (%)	12.5
Organic matter (%)	26.0

desorbing below pH 7. Pb and Zn started desorbing between pH 4 and 6. Cu was not extracted to the same level as the other metals at acidic pH. Only at very low pH (<1) was Cu extracted, however Cu was most readily extracted at alkaline pH. When the extractant was HCl, Cu was extracted from pH 2 in this sediment (25), desorption was probably enhanced by formation of chlorocomplexes. For other sediments, desorption of Cu started between pH 2 and 3 (20).

Electrodialytic Experiments Using Cell Type A

The removal is defined as the amount of metals found in the electrolytes (compartments I, II, IV, and V), on the membranes and the electrodes compared to the total amount of metals found in the central cell compartment after remediation.

Current Densities

In Fig. 4, the removal with varying current strengths is shown. Final pH in the sediments is shown in Table 1. When no current was applied there was no

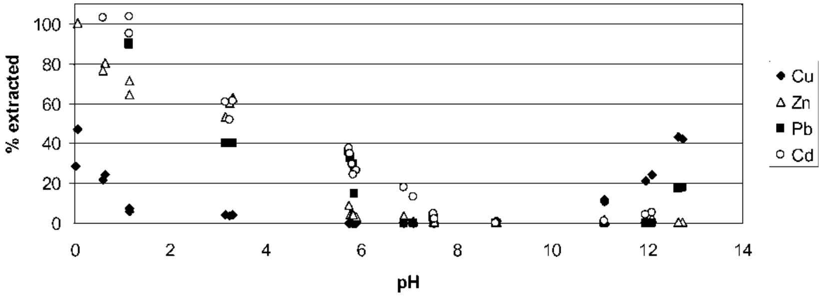

Figure 3. pH dependent extraction of the metals from the sediment.

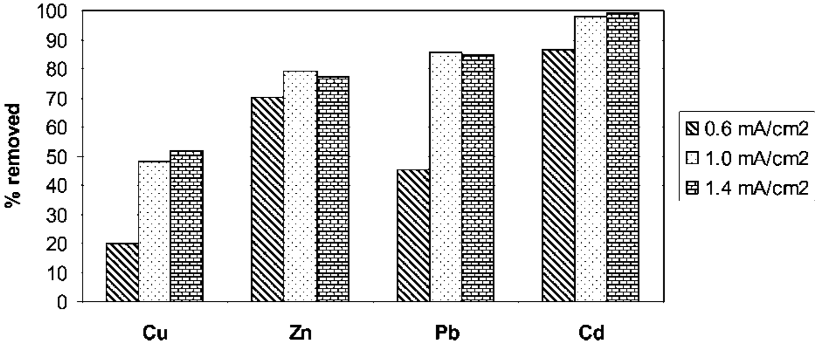

Figure 4. The influence on metal removal by increasing current density.

metal removal since the sediment was not acidified. The electrolytes were acidic, which indicates that diffusion over the ion exchange membranes was not significant. When applying a current to the sediment, metal removal occurred. An increase in the removal was seen when the current density increased from 0.6 (30 mA) to 1 mA/cm^2 (50 mA), however 1.4 mA/cm^2 (70 mA) did not increase the removal significantly further and the removal order was Cd $>$ Pb $\sim$Zn $>$ Cu. Ref. (26) showed almost doubled removal when increasing the current density from 0.1 mA/cm^2 to 0.2 mA/cm^2 when remediating soil in the stationary electrodialytic cell. The same was not seen here when using the stirred cell. Thus increasing the current density can lead to higher removal but only to a certain level.

The final pH in the sediment was similar for experiments 2–4 (pH 2.1–2.2) and does not explain the lower removal for 0.6 mA/cm^2 compared to 1.0 mA/cm^2. Increasing the current strength increases the number of coulombs that are passed through the cell. Water splitting at the anion exchange membrane is dependent on the current strength (8) and increases with higher current strengths. In experiment 2, with the lowest current density (0.6 mA/cm^2) 5% Cu, 4% Zn, 6% Pb, and 8% Cd of the total amount was found dissolved in the liquid in compartment III. These percentages were less than 1% in experiments 3 and 4. This suggests that the dissolved metals were not yet removed at the lower current density. The acidification of the sediment was probably delayed compared to higher current densities, and thus the release of metals to the solution.

The Zn and Cd removal did not seem as dependent on the current density as Cu and Pb did. This is also seen in Table 3, which shows the current efficiencies for the different current strengths, defined as the percentage of the total charge passed through the cell carried by the removed heavy metals. The metals were assumed to carry a charge of 2 (Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}). The current efficiencies showed that only a limited amount of the applied current was used to remove heavy metal ions. The highest current efficiencies were at 30 mA (0.6 mA/cm^2) for Cd and Zn, but 50 mA

Table 3. Current efficiency in the electrodialytic experiments with increasing current strength

Current strength	Q_{tot} (moles)	Q_{Cu} (%)	Q_{Zn} (%)	Q_{Pb} (%)	Q_{Cd} (%)
30 mA (0.6 mA/cm^2)	0.38	0.008	0.09	0.005	0.001
50 mA (1.0 mA/cm^2)	0.63	0.013	0.06	0.009	0.0009
70 mA (1.4 mA/cm^2)	0.89	0.010	0.04	0.004	0.0007

Q_{tot}(moles) = (I × t)/F, where F is Faradays number. Q_{Me}(%) = (no. moleequivalents metal removed)/Q_{tot} × 100%.

(1.0 mA/cm^2) for Cu and Pb. However, to obtain higher removal at 30 mA, the duration should be increased but the current efficiency would probably decrease accordingly. Based on the results from these experiments the following experiments were made with 1.0 mA/cm^2 (50 mA) and different remediation conditions.

Influence of Remediation Time

Figure 5 shows the metal removal over time presented by the results from experiments 3, 5–11, along with the final pH in the sediment; all experiments had an applied current of 1.0 mA/cm^2. The voltage drop between the working electrodes is shown in Fig. 6 for all the experiments. Figure 7 shows the final concentration in the sediment (mg/kg) over time. The main acidification of the sediment occurred between 3 and 5 days of remediation and stabilized around pH 2 (Fig. 5). However, pH was lower after 1 and 3 days of remediation than the initial pH, suggesting that the acidification started at the beginning of the experiments, as expected if the applied current was higher

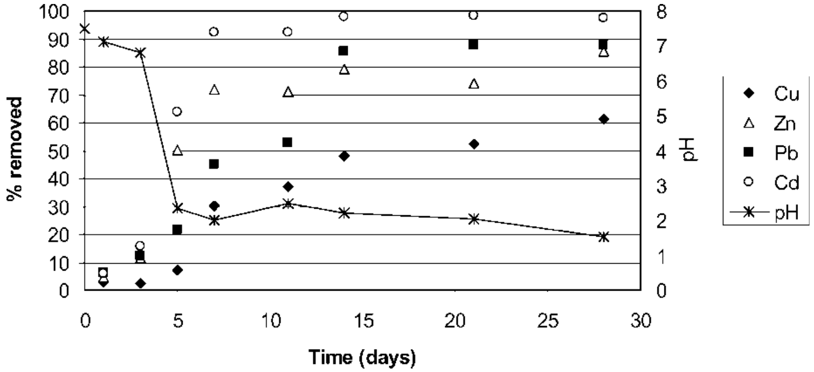

Figure 5. Metal removal over time and final pH in the sediment. Initial pH in the sediment is marked as an isolated cross.

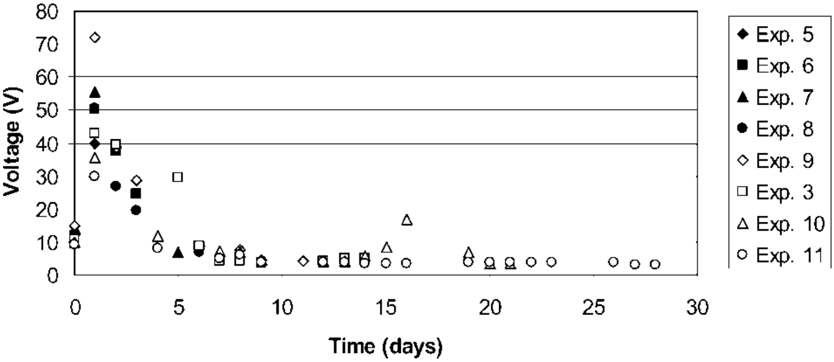

Figure 6. Voltage between the working electrodes in the cells in the experiments with increasing remediation time and current density of 1.0 mA/cm^2.

than the limiting current of the anion exchange membrane. The removal after 1 and 3 days of remediation was limited accordingly. There was a pronounced increase in the Zn (50%) and Cd (65%) removal after 5 days of remediation, at the same time the major acidification was observed. An increase was seen again between 5 and 7 days of remediation, with a 20% Zn and 30% Cd increase in removal to a total removal of 72% Zn and 92% Cd. pH in the sediment was similar after 5 and 7 days, which indicates either a solubility controlled dissolution of the metals or that other more mobile ions were removed before the metal ions being dissolved. After 7 days of remediation, the Zn and Cd removals were almost stabilized. Contrarily, the Cu and Pb removal seemed delayed in comparison to the Zn and Cd removal. For Cu and Pb, the most significant increase in removal efficiencies occurred after 7 days of remediation. Increasing the removal time further, the Cu removal increased steadily, but did not seem to reach a maximum. The Cu removal

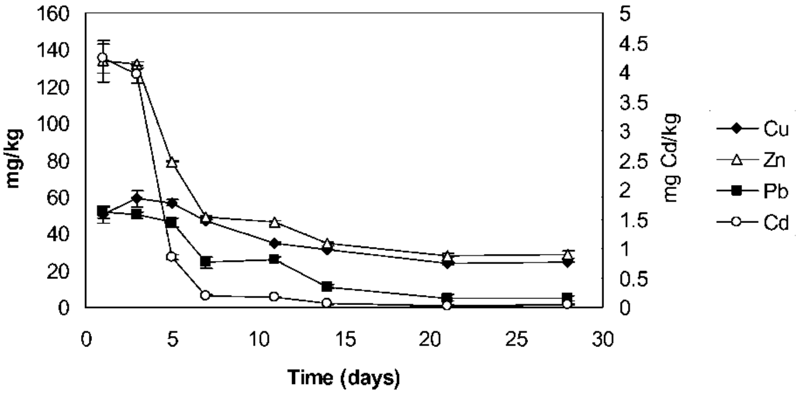

Figure 7. Concentrations in the sediment after remediation.

was also higher than could be expected from the extraction experiments at the reached pH in the electrodialytic remediation. This indicates that the effects of the applied current enhance metal removal in the sediment since released Cu (and other ions) from the sediment are continuously removed from compartment III by the current, which prevents solubility controlled dissolution to reach saturation. Between 11 and 14 days of remediation, the Pb removal increased again, by over 30% to 85% total removal and the removal efficiency did not increase much after this. The delay in the Pb removal indicates that Zn and Cd were more easily dissolved in the sediment, which was also seen in the extraction experiments. The highest removals were seen after 28 days of remediation and were 61% Cu, 86% Zn, 88% Pb, and 97% Cd. After 7 days of remediation the current efficiency was highest, however still $<0.1\%$ for all the metals, whereas the current efficiency decreases with longer remediation time.

Voltage

The voltage between the working electrodes in the electrodialytic cell increased rapidly in all the experiments (Fig. 6) and reached a maximum after 1 day of remediation in almost all the experiments and then dropped again to reach a stable low level after 5 days of remediation. The voltage increases when the electrical resistance in the cell increases since the current was kept constant. The electrical resistance in the electrolyte compartments is low due to high ionic strength of the electrolytes and low polarization potential at the electrodes, since the electrolytes were circulated. Thus, the increased resistance must be over compartment III, in the solution or over the membranes. Initially, when sediment and distilled water were mixed, easily dissolved species were released from the sediment and transported by the current out of compartment III, resulting in a decrease in the electrical conductivity. Since sediment has a higher cation exchange capacity than anion exchange capacity, more cations than anions are found in the double layers around the particles. When the concentration of anions is reduced close to the anion exchange membrane AN 1, the electrical resistance over the membrane will increase, which increases the voltage over the cell. Thus, water splitting starts to maintain the passage of current through the cell and the voltage decreases. When the sediment was acidified, more ions were released and the electrical resistance decreased. This could explain the rapid increase in the voltage and also the decrease (Fig. 6). The voltage pattern also followed the pH pattern in the sediment.

A similar voltage pattern was seen for electrodialytic soil remediation in the stationary setup (6): the voltage increased and stayed high until the acidic front had swept through the soil volume (several days), then the voltage decreased again. In the stirred setup, the acidification was faster and consequently the voltage drop was observed earlier. Due to the high buffering capacity of the sediment the acidification is probably slow, because foaming by gas evolution when dissolving the carbonates was not seen. The carbonate dissolution was also detected in a more pronounced weight loss of sediment after 3 days of remediation compared to 1 day, 11% and 5%, respectively. When the sediment was fully acidified, the average mass loss was 15%.

Metal Concentrations

The metal concentrations in the sediments after remediation generally decreased over time (Fig. 7). However, the Cu concentration increased slightly in the electrodialytic remediation experiments lasting 1, 3, and 5 days compared to the initial concentration since the sediment mass decreased and the Cu removal was limited. With longer remediation time, the Cu concentration decreased and seemed to stabilize at around 25 mg/kg. A 10% increase in the Cu removal was seen between 21 and 28 days, which was not reflected in the concentrations. This is most likely due to heterogeneous initial Cu concentrations. The Cd and Zn concentration profile followed the profile for the final pH in the sediments. After 7 days of remediation the Cd concentration was 0.20 mg/kg, but the concentration continued to decrease with longer remediation times. The Pb concentration profile was delayed compared to Zn and Cd, which was also seen in the removal and predicted from the pH dependent extraction (Fig. 3). The lowest Zn and Pb concentrations were obtained after 28 days of remediation: 28.7 mg Zn/kg and 4.8 mg Pb/kg.

Electrodialytic Experiments Using Cell Type B

The results from the electrodialytic experiments with varying L/S ratios using the three compartment cell are shown in Figs. 8–10. Figure 8 shows the metal removal; Fig. 9 shows pH and electrical conductivity in the suspension in compartment III during the remediation; and Fig. 10 shows the voltage between the working electrodes of the electrodialytic cells. All the experiments lasted 14 days. The Cu, Zn, and Pb removals (Fig. 8) increased slightly with increasing L/S ratio. Only the Cd removal did not seem to increase when changing the L/S ratio, which shows that the removal was not very dependent on the L/S ratio, which could be important for possible up-scaling of the method. The highest removal efficiencies were 36% for Cu, 79% for Zn, 52% for Pb, and 95% for Cd obtained at a L/S 12. Comparing to the results for using cell type A (five compartments), the Cu and Pb removals were 20% and 40% lower, respectively, using cell type B (three compartments), although the Zn and Cd removal were not lower. The final pH in the sediment was 2.5, 2.6, and 2.4 with increasing L/S ratio, respectively. This was higher than in experiment 3 using the five-compartment cell, where final pH was 2.2. This suggests differences in acidification of the sediment and removal mechanisms between the two setups.

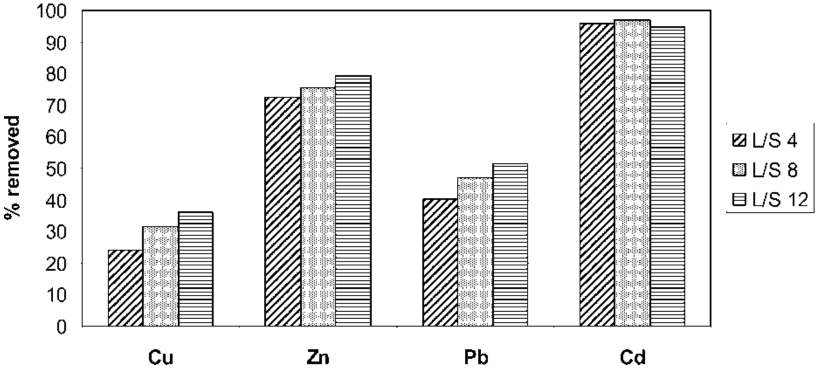

Figure 8. L/S dependence on metal removal.

Electrical Conductivity and pH in the Sediment Suspension

The electrical conductivity of the sediment suspension at the beginning of the experiment depended on the L/S ratio, i.e., the volume of distilled water was kept the same, but the amount of sediment decreased. The electrical conductivity of the suspension decreased rapidly (Fig. 9), where the majority of easily dissolved ions were removed from compartment III. The decrease in the electrical conductivity corresponds well to the increase in voltage (Fig. 10). After 2 days of remediation, the electrical conductivity got very low for the experiments with the L/S 8 and 12. At the same time, the voltage reached maximum of the power supply, and in the experiment with L/S 12, the 50 mA applied current could not be maintained and dropped to only 13 mA. Nevertheless, the electrical conductivity started to increase and the voltage dropped again, probably when the acidification of the sediment, due to water splitting,

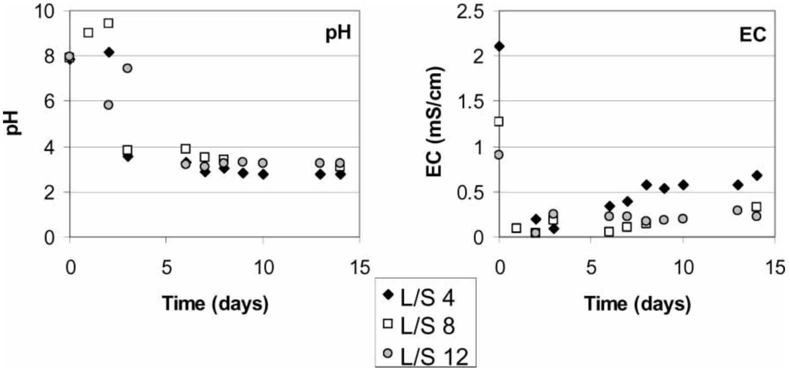

Figure 9. pH and electrical conductivity in the suspension in compartment III during the electrodialytic experiments with varying L/S.

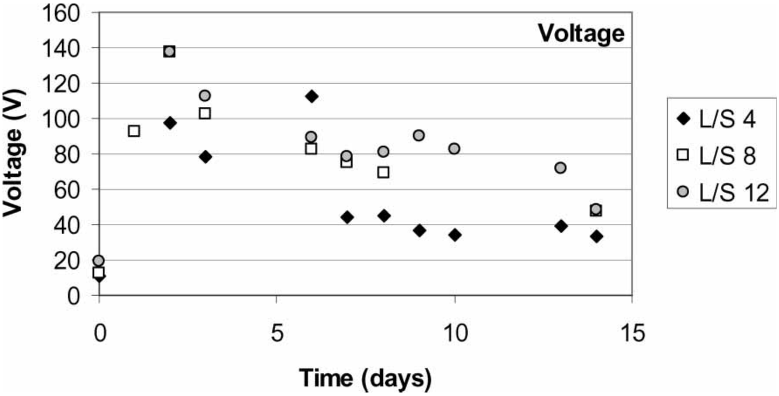

Figure 10. Voltage over the cells with varying L/S ratio.

started. The electrical conductivity was higher in the experiment with the lowest L/S, since more ions could be released to the liquid. pH in the sediment suspensions increased during the first days of remediation. However, pH in the suspension started to decrease (Fig. 9) concurrently with the increase in EC showing the connection between acidification and dissolution of sediment. pH in the sediment suspension stabilized at around pH 3 after 6 days of remediation, despite the different amounts of sediment in the experiments and the lower buffering capacities in the experiments with higher L/S ratio.

Resistance in the Cells

The voltage between the working electrodes at cell type B (Fig. 10) was considerably higher than at cell type A, showing a difference in the electrical resistance for the two different setups, since the applied current was constant. Normally, the voltage should be lower for cell type B due to fewer ion exchange membranes. pH in compartment III increased during the first days of remediation in some of the experiments (Fig. 9), which originated from the cathode end of the cell by either water splitting at the cation exchange membrane or OH^- produced at the cathode. Significant amounts of OH^- are produced at the cathode at the used current strength, thus the catholyte would quickly be alkaline if pH was not adjusted. pH was adjusted manually once a day; however the catholyte reached pH 12 several times during the first days of the experiments. The highest voltage drops over the cells were recorded at the same time as pH in the catholyte above 12. When the catholyte was acidified, the voltage decreased. pH in the sediment suspension in compartment III increased on the same days as pH in the catholyte was high, except at day 6 for the experiment with the L/S 4. This suggests that water splitting at the cation exchange membrane was not occurring but the increase in pH in compartment III was caused by the high pH in the catholyte.

At pH 12, the cation exchange membrane's cation selectivity is greatly reduced and can potentially act as an anion exchange membrane, where OH^- are not hindered by the membrane and can migrate freely from the catholyte into compartment III. This was probably happening since the increase in pH in compartment III was observed when the catholyte was highly alkaline. Increased pH in compartment III makes several species uncharged or precipitates which reduces the electrical conductivity and increases the voltage. When pH in the vicinity of the cation exchange membrane is high, fouling of the membrane and precipitation on or in the membrane can also occur, especially precipitates of $Ca(OH)_2$ and $Mg(OH)_2$ (27). Fouling and scaling could be reduced by keeping low pH by adding acid or by having a sufficient turbulent environment in the suspension (28). The stabilized voltage was higher at cell type B compared to cell type A, which indicates scaling of the membrane since the membrane was not visibly colored by fouling. If scaling occurred on the membrane surface in contact with the sediment suspension, it suggests that the rotation speed of the stirrer was not sufficient to remove the precipitates. On the other hand, if the scaling occurred on the membrane surface toward the cathode, the addition of 1:1 HNO_3 to the catholyte should be able to dissolve the precipitates. If precipitates were formed in these experiments, it happened either inside the membrane or on the surface in contact with the sediment suspension. The selectivity of the cation exchange membrane does not necessarily decrease because of scaling (28).

If the increased pH in the catholyte and compartment III occur together as the water splitting starts at the anion exchange membrane, the total voltage drop will be high according to these processes, which could explain the higher voltage in cell type A compared to cell type B in the beginning of the experiments. In cell type A, the electrolyte compartment IV will be alkaline before compartment III which makes it less sensitive to pH changes.

When pH again was controlled in the catholyte in cell type B and the OH^- was neutralized, the sediment was acidified due to the water splitting at the anion exchange membrane. When the carbonates were dissolved, the produced H^+ ions migrate toward the cathode and neutralize the produced OH^-. However, pH in the catholyte still needed adjustments, but the pH rarely got above 7. At this pH the function of cation exchange membrane is not influenced and pH in compartment III will not increase. Furthermore, the voltage stabilizes. Using automatic pH static titration or adding a buffering agent to the catholyte could be used to limit the sensitivity of cell type B. Since pH in the suspension increased during the first days due to the high pH in the catholyte, it is difficult to evaluate if pH decreased faster in the experiments with higher L/S (lower buffer). This could be important to know if the remediation time should be shortened.

Removal Difference Between Cell Type A and B

There are two possible explanations for the lower removal of Cu and Pb in cell type B compared to cell type A: formation of insoluble hydroxides which limits the total removal or a delay in the metal removal. At high pH, Cu and Pb could be released from the sediment according to the pH dependent extraction (Fig. 3). Soluble Cu and Pb cations migrating toward the cathode could precipitate with OH^- produced at the cathode, when the catholyte was highly alkaline. However, pH in compartment III was most likely too low (<pH 10) to cause desorption of Cu and Pb and the metals were not found retained in the membrane after the remediation. Alternatively, the acidification of the sediment was delayed compared to cell type A, since the acid produced from water splitting had to both neutralize the alkaline pH and acidify the sediment. The delayed acidification did not seem significant for the Zn and Cd removal compared to the Cu and Pb removal. From Fig. 5 it was also seen that Zn and Cd were removed earlier than Cu and Pb in cell type A. Thus, increasing the remediation time or keeping the catholyte acidic all the time, higher Cu and Pb removals might be obtained in cell type B. The remediation time of the sediment seems dependent on the carbonate content and the acidification rate. Other sediments with lower carbonate contents are expected to be acidified faster and possibly the remediation time could be lower probably also depending on the heavy metal content.

CONCLUSION

Water splitting at the anion exchange membrane occurs in electrodialytic remediation if the limiting current of the anion exchange membrane in contact with the contaminated material is exceeded. In all the electrodialytic remediation experiments made here, acidification of the harbor sediment during remediation was seen due to water splitting. The acidification started within 1 day of remediation and the sediment containing 12% carbonate was fully acidified between 3 and 5 days of remediation at $1.0\,\mathrm{mA/cm^2}$, where pH in the sediment stabilized thereafter. The main heavy metal removal occurred shortly after the acidification of the sediment suspension. Increasing the remediation time after the acidification occurred did not significantly increase the removal and the current efficiency decreased accordingly. The removal of Zn, Pb, and Cd stabilized after 14 days of remediation but the Cu removal increased with longer remediation times. Changing the current density influenced the removal and $1.0\,\mathrm{mA/cm^2}$ was found most efficient for metal removal where the lowest metal concentrations were obtained in the sediment. Different L/S ratios of the sediment suspension did not influence the removal significantly. When the sediment was acidified, the voltage between the working electrodes decreased and since most metals were removed when the sediment was acidified, the decrease in voltage could be used to predict when the removal is finished.

Two different cell setups were used: consisting of either three (cell type B) or five compartments (cell type A). Cell type B was more sensitive to pH increases in the electrolytes. This resulted in lower removal of Cu and Pb using this cell than with cell type A, since under extreme pH values in the electrolytes, the selectivity of the ion exchange membranes decrease. Scaling of the cation exchange membrane probably resulted in higher voltage in cell type B compared to cell type A.

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