Case study on the strategy and application of enhancement solutions to improve remediation of soils contaminated with Cu, Pb and Zn by means of electrodialysis

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Abstract

Numerous studies have been conducted with electrochemical removal of heavy metals from spiked kaolinite. Meanwhile, when moving from kaolinite to real soils, new factors must be taken into account—factors influencing, e.g., the buffering capacity of the soil against acidification and the adsorption/desorption processes of the heavy metals. The present study gives some examples where it is necessary to use an enhancement solution to aid desorption of Cu, Zn and Pb during electrodialytic treatment. Dependent on the composition of the pollution, different choices can be made. In the case of a Cu-polluted calcareous soil, ammonia may be used as enhancement solution, due to the formation of charged complexes between ammonia and Cu. Thus, Cu is mobile at high pH when ammonia is added and Cu can be removed without dissolving the calcareous parts. Zn is also mobilized by ammonia, but to a lesser extent than Cu. In the case of Cu, Zn and Pb at the same time, alkaline ammonium citrate may be a solution. It was shown that this enhancement solution could mobilize these three pollutants, but optimization of concentration and pH of the ammonium citrate is still needed. When choosing a remediation scheme for electrochemical treatment of an actual industrially polluted soil, this scheme must be chosen on basis of characterization of soil and pollution combination.

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1. Introduction

1.1. Remediation strategy

Several different electrochemical soil remediation methods for removal of heavy metals have been/are...
developed. Meanwhile, the remediation goals of the methods vary. Some methods aim at stabilizing the heavy metals within the soil (e.g., Vengris et al., 2001), but for most methods extraction of the polluting heavy metals is the main emphasis. Some methods aim at removing the direct mobile part of the heavy metals leaving the adsorbed fractions of heavy metals or even further stabilize the remaining heavy metals, e.g., to use electrochemical processes to supply Fe(II) to reduce soluble species of Cr(IV) to the less toxic Cr(III) (Pamukcu et al., 1997). Most methods do meanwhile aim at removal of the heavy metals so the soil can meet target values for total concentrations (e.g., Reddy et al., 2003; Ottosen et al., 1997).

Experimental success with removal of various heavy metals from spiked kaolinite has been reported in numerous papers and these are summarized in Page and Page (2002). Meanwhile, when moving from kaolinite to soils, the many studies of different ways to enhance the process (as summarized in Page and Page, 2002), may indicate that the successful results obtained with spiked kaolinite cannot always be transferred directly to spiked soils or to soils sampled at polluted sites. The main difference being the variety of adsorption sites for heavy metals present in inhomogeneous soils (both related to organic and inorganic constituents) not being present in kaolinite. An example of this is found in Hécho et al. (1998), where it was shown that 99% Cr was removed from a spiked kaolinite in 18 days, whereas only 64% Cr was removed from a spiked soil during a similar experiment. Another example can be found in Reddy et al. (2003), where electrokinetic remediation experiments of Hg spiked kaolinite and glacial till was compared. The initial concentrations were about 500 mg/kg for both soils and the best remediation result obtained was 16 and 220 mg/kg, respectively.

To carry out a successful removal of heavy metals from soil by an electrochemical method, it is necessary to desorb the actual heavy metals during the process in order to be able to remove them by either electromigration or in an electroosmotic flow (Ribeiro and Mexia, 1997).

Enhancement techniques are mainly directed toward controlling pH and maintaining or bringing contaminants into solution by addition of enhancement solution to the soil (Page and Page, 2002). The necessity for conditioning the electrolyte solution wherein the electrodes are placed was observed in the earliest works (e.g., Lageman et al., 1989). The present paper deals with the addition of enhancement solution to the polluted soil matrix to help desorption of different heavy metals for improved electrochemical removal.

1.2. Use of enhancement solution and their potential use for Pb, Cu and Zn removal

The one single parameter that has shown the most important in electrochemical soil remediation is soil pH and this is due to the pH dependency of adsorption/desorption processes. Often is an acidic front, which is developing in the soil from the anode end towards the cathode end during electrochemical soil remediation, used for mobilizing the heavy metals (e.g., Acar and Alshawabkeh, 1993 or Ottosen et al., 1997). The order of removal of different heavy metals in the acidic front have been reported: Ni ≈ Zn > Cu > Cr in a soil polluted from a chloralkali factory (Suer et al., 2003) and Zn > Cu > Pb in different industrial polluted soils (Ottosen et al., 2001).

Enhancement solutions can be either used for changing the physicochemical conditions in the soil as pH and redox conditions, or the enhancement solutions can be used to form mobile complexes with the actual heavy metals. Addition of the enhancement solutions will be either before the remediation and/or during the action through the processing solutions at the electrodes. In the latter case, the electroosmotic flow can be used to supply the enhancement solution. Popov et al. (1999) found that the electroosmotic flow increased in the experimental soils after addition of different complexants as citric acid, ethylenediaminetetraethanoic acid (EDTA) or 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) compared to distilled water. EDTA was found to enhance the removal of Pb and Zn from spiked soils (Yeung et al., 1996), (Wong et al., 1997). Even though EDTA is a good complexing agent, it may not be the best choice of enhancement solution due to the toxicity of EDTA itself.

Use of enhancement solutions is beneficial or even necessary for removal of heavy metals from, e.g., high buffering capacity soils or for some combinations of pollutants within a reasonable remediation time. Even
though Pb, Zn and Cu are removed at higher soil pH in calcareous soils than in non-calcareous soils (Ottosen et al., 2001), the buffering capacity against the developing acidic front from the anode end of the soil is high in calcareous soils and thus the remediation will progress very slowly if the acidic front is used for desorbing the heavy metals. In the case of calcareous soils it may be necessary to use enhancement solution to shorten the duration of a remediation action. Ammonia has shown potential as enhancement for removal of Cu from calcareous soils (Ottosen et al., 1998). When ammonia is added the alkaline environment ensures minimum dissolution of carbonates and at same time charged Cu tetra-amine complexes are formed. The buffering capacity of clayey soils against acetic acid was reported to decrease the removal rate significantly compared to sandy soils when this enhancement solution was used (Vengris et al., 2001). Thus, the buffering capacity must be taken into account when choosing whether enhancement solution is necessary in every specific case.

For some combination of heavy metals it is also necessary to use enhancement solutions to ensure removal of all pollutants at the same time (Ottosen et al., 2004). Especially the presence of As in the soil necessitate alternative solutions to the acidic front, since As generally has low mobility under acidic conditions whereas As is more mobile under alkaline conditions where most heavy metals are not mobile (Hécho et al., 1998; Ottosen et al., 2000b). Hécho et al. (1998) conducted laboratory experiments where the pollutants were As and Cr and a successful remediation result was obtained in a developing alkaline front from cathode and injection of sodium hypochlorite. As was mobile due to the alkaline environment and Cr(III) was oxidized to Cr(VI) by hypochlorite mobilized in the alkaline environment. In loamy sand polluted with Cu and As from wood preservation, As and Cu were mobile at the same time after addition of NH₃ to the soil (Ottosen et al., 2000a). As was mobile due to the alkaline environment and Cu formed charged tetra-amine complexes. For the mobilization and electrochemical removal of Cu, Cr and As at the same time ammonium citrate has shown successful (Ottosen et al., 2004).

In the case of Hg, it was shown by Thöming et al. (2000) that the acidic front was resulting in an increased oxidation rate of elemental Hg, but the oxidation process was too slow. For electrodialytic removal of Hg in ionic form iodine crystals (Cox et al., 1996), Na–EDTA and KI (Reddy et al., 2003) and iodide (Suér and Allard, 2003) have been tested as enhancement chemicals. By using iodine crystals, 99% Hg was removed from spiked loam; however, only 6% was removed from an industrially polluted sandy loam. The main reason for the decreased success with the industrially polluted soil was thought to be the higher organic content and thus higher demand for iodine crystals (Cox et al., 1996). Suér and Allard showed by sequential leaching, that Hg was more mobile in a soil polluted with Hg from a Chlor-Alkali factory after iodide addition and application of an electric field than before treatment. This shows potential for this enhancement solution. Reddy et al. (2003) found that KI was a better enhancement solution for Hg removal than EDTA for removal of Hg from spiked kaolinite and spiked glacial till, even though the removal performed much better in the kaolinite than in the till.

The heavy metals in focus in the present paper are Cu, Zn and Pb. Electrodialytic remediation without any addition of enhancement solutions is tested for some industrially polluted soil and different enhancement solutions are tested (citric acid, ammonia and ammonium citrate). Citric acid was chosen tested for a non-calcareous Pb polluted soil because citric acid forms stable complexes with Pb. Ammonia has previous shown potential as enhancement solution for removal of Cu from calcareous soils (Ottosen et al., 1998) and in the present paper the potential to use ammonia for remediation of a soil polluted with both Cu and Zn is investigated. Both Cu and Zn can form charged amine complexes. Pb, on the other hand, cannot be expected mobilized by ammonia addition. If the soil is calcareous, citric acid alone cannot be used for enhancement since it can be expected that the Ca²⁺ ions resulting from dissolution of carbonates in the acidic environment forms precipitates with the citrate. Meanwhile ammonium citrate at slightly alkaline environment may be a good enhancement solution for calcareous soils polluted with Cu, Zn and Pb at the same time, as it has proven successful for removal of the same heavy metals from municipal solid waste incineration fly ash (Pedersen, 2002). All three heavy metals can form charged complexes with the citric
part and furthermore Cu and Zn can form charged complexes with the ammonia. The enhancement solutions of the present investigation do not result in any soil pollution themselves.

2. Electrodialytic remediation

Electrodialytic remediation of solid waste products started to develop in 1992 and was patented in 1995 (PCT/DK95/00209). The method was first developed for remediation of heavy metal polluted soil. Since soil characteristics are varying from site to site and since the heavy metals act differently in the soil, it is beneficial to characterize the polluted soil carefully before starting the remediation (Ottosen et al., 1999). Dependent on this characterization a proper enhancement solution is chosen to aid desorption of the heavy metals (if necessary) and a combination of membranes is chosen. The basic cell is shown in Fig. 1.

To choose the best combination of membranes in the anode end, it is important to know if the soil or the enhancement solution contains a considerable amount of anions that preferably not should participate in the anode processes. If so, membrane A must be a cation exchange membrane (CAT) to prevent these ions to enter the surface of the anode. Examples of unwanted anions could be Cl\(^-\) that would lead to production of toxic chlorine gas and F\(^-\) that would lead to the formation of HF (an acid that can destroy the anode material). If no enhancement solution is needed, membrane B is an anion exchange membrane (AN) to prevent transport of anions from compartment II through the soil. If enhancement solution is needed membrane B is chemically neutral fabric/filter paper (FP) in order to supply the soil with the enhancement solution by electroosmosis during the remediation process. When the present anions do not have influence on the anode process, then membrane A can be either a CAT, an AN or there may be only one compartment in the anode end depending on the enhancement solution. If, for example, the enhancement solution must be kept alkaline membrane A is an AN, if the enhancement solution can be decomposed by anodic oxidation the A membrane is a CAT.

In the cathode end of the cell, the choice of membrane combination depends on other factors. If the soil contains metals that are readily electrodeposited, it may be necessary to choose membrane D to be an AN to protect the cathode from these elements. The volume of the cathode can increase considerably by electrodeposition and this can cause problems in full-scale remediation. If membrane D is chosen to be an AN membrane C should be a CAT in the cases where an acidic environment in the polluted matrix is beneficial to the remediation action to avoid OH\(^-\) from the electrode process. In some cases, it is sufficient with only one compartment in the cathode end, too, and then the membrane is most often a CAT or in some cases FP.

Electrodialysis is a separation technique. When an anion exchange membrane is placed next to the soil in the anode end and a cation exchange membrane is placed next to the soil in the cathode end the soil compartment is a desalination compartment, which means that the current will be carried by ions in the direction out of the soil only. The electrodialytic setup is used for separating heavy metals from soil and it is especially well suited for fine-grained soils. When enhancement solutions are used these are mixed into the soil so the soil is about water saturated prior to the remediation and during the remediation the enhancement is continuously supplied through electromigration and/or electromigration. During the remediation, removal of heavy metal species will continuously occur and thus forcing equilibrium to swift towards mobilization of more heavy metal. This is in contrast to soil washing/extraction where all heavy metals must be mobilized at once in the extracting solution before the physical separation between soil and solution takes place. Furthermore, the volume of enhancement solution is much less in electrodialytic remediation than in soil washing where the soil is suspended.

Fig. 1. Basic laboratory cell for choice of membrane combination. The membranes A, B, C and D can be either a cation exchange membrane, an anion exchange membrane or a chemically inert fabric dependent on the actual medium to be remediated.
3. Experimental section

3.1. Experimental soils

The soils used for this investigation varied in characteristics and pollution. The soils were sampled from industrially polluted sites. Soil A was polluted from production of electronic devices and the sampling depth was 0–30 cm. The two other soil samples were taken from piles of excavated soil. Soil B was polluted from cable production and the origin of the pollution of soil C is unknown. Some characteristics of the soils are found in Table 1. Experiments with soil samples from three different batches of soil B are included in the investigation. These three samples vary mainly in the pollution composition but also little in soil characteristics, thus all three samples are included in the table.

3.2. Analytical

The concentration of the elements were measured after pretreatment of the soil as described in Danish Standard 259 Determination of metals in water, sludge and sediments—general guidelines for determination by atomic absorption spectrophotometry. A 1.0-g portion of dry soil 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 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. For the soil samples containing ammonia, pH was measured before the samples were dried.

3.3. Electrodialytic soil remediation experiments

Included in this investigation are 10 remediation experiments made in laboratory cells. The investigation covers removal of Cu, Pb and Zn. Ammonia, citric acid or a combination of these two are tested as enhancement solutions and for comparison, experiments are made without any use of enhancement solution. In the experiments where enhancement solution was used the soil was air-dried to a water content of about 10% before the enhancement solution was added and then mixed carefully into the soil. For the experiments with ammonia citrate, the pH in the solution was adjusted to 10 with ammonium before it was added to the soil.

The experimental set up varied, the variation in parameters are shown in Table 2, and the membrane and compartment numbers in this table refer to the basic cell shown in Fig. 1. The cells were made from Plexiglas. The ion exchange membranes were obtained from Ionics (Anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67HUY N12116B). Platinum coated electrodes from Permascand were used as working electrodes, and a power supply (Hewlett Packard E3612A) was used to maintain a constant current.

At the end of the experiments the soil was segmented into slices from anode towards cathode. The number of slices was dependent on the length of the soil compartment and the slices were between 1.25 and 1.5 cm thick. Each slice was dried and crushed in a mortar by hand before the heavy metal concentrations were measured in doublet and the mean values are used in the figures. Soil pH was measured in duplicate in each slice and except for the samples containing ammonia, pH was measured on the dried, crushed samples. The content of heavy metals in membranes, electrolyte solutions and on the electrodes were measured. In experiment F and I, samples were also taken from compartment II during the

Table 1

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>A</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>–</td>
<td>4600</td>
<td>5870</td>
<td>2730</td>
<td>–</td>
</tr>
<tr>
<td>Pb</td>
<td>1090</td>
<td>–</td>
<td>1010</td>
<td>–</td>
<td>1060</td>
</tr>
<tr>
<td>Zn</td>
<td>–</td>
<td>–</td>
<td>2760</td>
<td>260</td>
<td>–</td>
</tr>
<tr>
<td>Carbonate content (volumetric calcimeter method) (%)</td>
<td>0.4</td>
<td>9.7</td>
<td>14.1</td>
<td>12.0</td>
<td>6.8</td>
</tr>
<tr>
<td>Organic content (loss of ignition at 550 °C) (%)</td>
<td>3.5</td>
<td>2.2</td>
<td>2.8</td>
<td>1.6</td>
<td>7.9</td>
</tr>
<tr>
<td>Clay (&lt;0.002 mm)</td>
<td>11</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Silt (0.002–0.06 mm)</td>
<td>52</td>
<td>5</td>
<td>17</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>Sand (0.06–2 mm)</td>
<td>35</td>
<td>71</td>
<td>78</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>CEC (meq/g dry soil)</td>
<td>18.6</td>
<td>2.1</td>
<td>2.9</td>
<td>1.5</td>
<td>8.2</td>
</tr>
<tr>
<td>pH</td>
<td>6.1</td>
<td>7.1</td>
<td>7.5</td>
<td>7.4</td>
<td>7.4</td>
</tr>
</tbody>
</table>
experiments, and a chemical extraction of Cu in 5% NH\textsubscript{3} (L/S=2) was made on both initial soil and soil from slice 1 in experiment F.

### 4. Results and discussion

The mass balances for heavy metals in the experiments based on initial and final amounts were between 94% and 103% for all experiments. This is considered acceptable since there will be some variation in concentration level in the industrially polluted soils. The results obtained with each of the experimental soils are given and discussed in separate chapters below.

#### 4.1. Soil A. Pb removal from silty soil without enhancement solution and after addition of citric acid

Soil A is a silty soil (52% silt) with a low carbonate content of 0.4% and an organic content at 3.5% (see Table 1). The soil is contaminated with Pb to a level of 1090 mg/kg, which highly exceeds the limiting value of 40 mg/kg for most sensitive use in Denmark (kindergardens, private gardens, etc.). The concentration also exceeds the value of 400 mg Pb/kg where humans must be protected from contact with the soil. The Danish limiting values are published in (Miljøstyrelsen, 2003).

Three experiments were made with this soil (see Table 2). Experiment A and B varied in duration only and no enhancement solution was used in these experiments. In Experiment C citric acid was tested as enhancement solution. The final normalized Pb profiles (normalized to initial concentration) for experiments A, B and C are shown in Fig. 2. It is seen that the Pb concentration is decreased from anode end towards cathode end in experiments A and B and this is due to the developing acidic front. In electrodialytic remediation an acidic front is developed in the soil on the contrary to what could be expected when an anion exchange membrane is

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Experimental conditions for the 10 experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>A</td>
</tr>
<tr>
<td>Enhancement solution</td>
<td>–</td>
</tr>
<tr>
<td>Water content and pH</td>
<td>17–28.8%</td>
</tr>
<tr>
<td>Membrane A</td>
<td>–</td>
</tr>
<tr>
<td>Membrane B</td>
<td>AN</td>
</tr>
<tr>
<td>Membrane C</td>
<td>CAT</td>
</tr>
<tr>
<td>Membrane D</td>
<td>–</td>
</tr>
<tr>
<td>Compartment I</td>
<td>–</td>
</tr>
<tr>
<td>Membrane II</td>
<td>0.01 M NaNO\textsubscript{3}, pH=2</td>
</tr>
<tr>
<td>Compartment IV</td>
<td>0.01 M NaNO\textsubscript{3}, pH=2</td>
</tr>
<tr>
<td>Compartment V</td>
<td>–</td>
</tr>
<tr>
<td>Current density (mA/cm\textsuperscript{2})</td>
<td>0.2</td>
</tr>
<tr>
<td>Voltage between working electrodes (V)</td>
<td>A. 2.7–6.3</td>
</tr>
<tr>
<td>Duration (days)</td>
<td>(A) 28</td>
</tr>
</tbody>
</table>
placed between analyte and soil. The soil acidification during electrodialytic remediation is mainly due to water splitting at the anion exchange membrane as it was described in Ottosen et al. (2000b). In experiment A soil pH varied between 2.6 and 3.1, and in experiment B soil pH varied from 2.3 to 2.6 from anode towards cathode. The developed Pb profiles are consistent with (Ottosen et al., 2001), where it was found that Pb is removed when pH is less than about 2.8 from non-calcareous soils.

Even though the remediation progressed in this soil without any use of enhancement solution the remediation occurred quite slowly. Experiment C was made to see if addition of citric acid to the soil could increase the Pb removal rate by forming charged complexes between citrate and Pb. The duration of this experiment was 28 days as for experiment A but the current density was three times as high meaning that the number of charges carried through the soil was even 1.1 times higher than in experiment B. The Pb removal was faster in experiment C than in experiment A, but this is most likely due to the lower pH, which was between 2.2 and 2.5, and not the formation of Pb complexes with citrate, since all removed Pb was found in the cathode end of the cell at the end of the experiment. The current efficiency for Pb removal was lower in experiment C than in experiment B, which is due to the increased conductivity from addition of citric acid. The lowest concentration obtained without enhancement solution was 20 mg Pb/kg (which corresponds to a level where the soil is allowed for the most sensitive use) and with enhancement solution this concentration was 170 mg Pb/kg, which do not meet the criteria for most sensitive use, but at this concentration it is not necessary to avoid humans to get in contact with the soil. In both cases the lowest concentration was obtained closest to the anode. Since pH was 2.3 and 2.2 in this slice in experiments B and C, respectively, it is not solely pH that determines the Pb removal. The increased amount of ions from the addition of citric acid provides ions that carry current instead of Pb ions or species. Thus, a factor in choosing enhancement solution may be that it should not result in a too high conductivity from ions without any complexation with the actual pollutant.

4.2. Soil B. Removal of Cu, Pb and Zn from sandy soil with high carbonate content. Remediation without addition of enhancement solution and after addition of ammonia

Soil B is a sandy soil (71–74% sand) with a high carbonate content of about 10 to 14% and a relatively low content of organic matter (1.6–2.8%) (see Table 1). Different samples of soil from the same site were used in this investigation, and they were polluted by either Cu alone (soil B1) or with Cu, Pb and Zn (soil B2). The last soil sample from the site (soil B3) was polluted with Cu and had elevated concentration of Zn, but the latter did not exceed the limiting value for most sensitive use in Denmark, which is 500 mg/kg for both Zn and Cu. The concentrations in the different soil samples are given in Table 1.

The acidic front developed well in soil A during the experiments without enhancement solution. In Fig. 3 is shown the pH profile and normalized concentration Cu and Zn profiles in soil 2a (experiment D), which was made with the same experimental conditions as experiment A except for the soil. It is seen that the acidic front has not reached as far into the soil in experiment D as in experiment A. This is due to the high buffering capacity related to the carbonate content of 9.7%. The lowest pH reached was in the slice closest to the anode and it was decreased from 7.1 to 6.2. Cu and Zn were removed from the first slice closest to the anode, only. The Zn concentration profile is more developed than the Cu profile and this is consistent with the findings from Ottosen et al.
(2001), where it was shown that Zn was removed at a higher pH than Cu during electrodialytic remediation. The pH of the first slice was 6.2 at the end of experiment D and at this pH Zn is mobilized in calcareous soils whereas this pH is generally too high to obtain a sufficient mobilization of Cu (Ottosen et al., 2001). The development of the acidic front and subsequent removal of Cu and Zn is too slow in this soil, less than 1 cm/month, and thus the removal rate needs to be increased in order to have an effective remediation in reasonable time.

Ammonia has previously been shown as an efficient enhancement solution for the removal of Cu in calcareous soils (Ottosen et al., 1998), and a 5% ammonia solution was tested in experiments E, F and G for a soil batch from the same site as the soil in experiment D. Meanwhile, this soil sample was polluted with Cu only. The aim of these experiments was to investigate the rate of Cu removal when ammonia was used as enhancement solution. The three experiments differed in duration, only. Samples were taken from compartment II during experiment F. Fig. 4 shows the normalized Cu concentration profiles at the end of the three experiments. The removal is progressing well between 7 and 28 days, but the removal has almost stopped after 28 days compared to 42 days. Figs. 5 and 6 show the distribution of Cu in the cell after 28 days of remediation (experiment F) and the amount of Cu in compartment IV as a function of time, respectively. It is seen, that 60% Cu was found in compartment IV at the end of the experiment. Some Cu passed the anion exchange membrane into the catholyte, which shows that the membrane was not working ideally. A total of 4% Cu passed. In the soil 36% Cu remained after the 28 days of treatment. Fig. 6 shows the major part of Cu removed at different times of the experiment. It is seen that Cu starts to concentrate in compartment II from the beginning of the experiment. If the experiment had been run without enhancement solution.
solution, Cu would have started to concentrate here when the acidic front reached the cathode end of the cell. It is also seen that the Cu removal progresses well during the first 11 days after which it stabilizes. This fits well with the observation in Fig. 4; the removal rate is slowing down after some time. Since there is 36% Cu left in the soil after 28 days, the low removal rate is not because the remediation has finished. In the soil the concentration was still between 1300 and 2100 mg/kg at this time (still above the limit of 1000 mg/kg that means that contact of humans to the soil must be avoided). Meanwhile the remediation may be limited by a too small ammonia concentration at this time, i.e., the supply through the filter paper was not sufficient. This is supported by the fact that 19% Cu could be extracted chemically in 5% NH₃ from the soil from slice 1 at the end of the experiment compared to 31% initially. Thus, continuous addition of ammonia is necessary when using this enhancement solution.

Experiment H was made with a soil sample from the same site as the sample from experiments E, F and G, But the soil for experiment H (soil B3) was polluted with Cu, Zn and Pb. Experiment H is made to see the effect of ammonia addition on the removal of these three heavy metals. Zn forms charged complexes [Zn(NH₃)₄]²⁺ with ammonia as Cu, but the ammonia complexes of Zn are less stable than those of Cu (Kubal et al., 2001), while Pb is not expected to form ammonia complexes. Fig. 7 shows the normalized concentration profiles for Cu, Zn and Pb at the end of experiment H. No Pb was found in the electrolyte solutions and thus as total no Pb was removed during the experiment. The variation in concentration through the soil may just show the variation as it was initially. Thus, Pb was not removed when ammonia was added to the soil. A total of 25% Zn and 60% Cu was removed. Ammonia is less effective as enhancement solution for removal of Zn than for removal of Cu as expected from the stability of the complexes.

Ammonium citrate has been shown to be effective as an enhancement solution for the removal of Cu, Cr and As from soil (Ottosen et al., 2004) and for removal of various heavy metals inclusive Zn, Cu and Pb from municipal solid waste fly ash (Pedersen, 2002). Ammonium citrate (1.0 M) with pH adjusted to 10 was tested as enhancement solution for soil B3 with Cu and Zn (experiment I). Fig. 8 shows the normalized concentration profiles for Cu and Zn at the end of experiment I and it is seen that the concentration of both heavy metals is decreased. Again the Cu removal has been better than the Zn removal, but in this soil the initial Cu concentration was also much higher than the Zn concentration, 2730 and 260 mg/kg, respectively, which may influence the normalized concentration profiles. The concentrations were slightly lower in the anode end than in the cathode end and no accumulation within the soil was seen. In this experiment 69% Cu and 30% Zn was removed see Fig. 9. Both current density and duration of this experiment was little less than in experiment H and comparison of the two experiments indicates that
ammonium citrate was slightly more effective as enhancement solution than ammonia. Ammonia citrate can form both anionic and cationic complexes with Cu and Zn, and from Fig. 9 (showing the distribution of Cu and Zn in the cell at the end of the experiment) it is seen that both heavy metals were transported towards both electrodes during the experiment. Thus, complexes with ammonia and with the citric part were formed. The highest amount of both heavy metals was removed towards the cathode, i.e., as ammonia complexes. Fig. 10 shows the amount of the heavy metals in the electrolyte solutions after 13 days and at the end of the experiment (after 22 days) where also the amount precipitated at the cathode during the experiment is shown. It is seen from the figure, that Cu and Zn were removed towards both anode and cathode. The complexes formed with the two heavy metals are concentrated in compartments (II) and (IV), which means that the complexes are prevented to some extent in passing into the electrode compartments even though the ion exchange membranes are placed so this should be possible. The problem can be that pH is acidic in the electrode compartments and alkaline in compartment (II) and (IV). It is also seen in Fig. 9 that the remediation of both elements as total is slowing down in the last 9 days compared to the first 13 days. This may be caused by a decreasing concentration of ammonium citrate in the soil during the experiment and thus decreased complexing efficiency.

After the 22-day experiment, the concentration of Cu did not meet the Danish criteria for most sensitive use of 500 mg Cu/kg but the soil can be used and will no longer have to be removed totally from possible contact with humans (1000 mg Cu/kg). The Zn concentration did meet the first criteria even before remediation.

4.3. Soil C. Pb polluted sandy soil relatively rich in both organics and carbonates

Soil C is a sandy soil with a relatively high carbonate content of 6.8% and a high content of organic matter.
(7.9%) compared to the other soils of the investigation (see Table 1). The soil is polluted with Pb only and the concentration of 1060 mg/kg means that humans must be avoided to get in contact with the soil according to the Danish quality criteria.

The carbonate content of the soil was so high that it was considered necessary to use enhancement solution to obtain remediation within a reasonable duration. It was shown earlier, from experiment H, that ammonium could not be used for mobilization of Pb. Meanwhile, Pedersen et al. (2002) reported that ammonia citrate can be used to mobilize Pb in municipal solid waste fly ash at high pH and in Experiment J it was tested whether this could be used as enhancement solution for Pb removal from a calcareous soil, too. The resulting normalized concentration profile for Pb and the distribution of Pb in the cell at the end of the experiment are shown in Figs. 11 and 12, respectively. It is seen that Pb was actually mobilized by the ammonium citrate at soil pH of 9. The removed Pb was all removed as anionic species. Meanwhile only 14% Pb was removed during the experiment and the lowest concentration was found in the slice closest to the cathode where the Pb concentration was decreased from 1060 to 760 mg/kg.
kg, which does not give a new classification of the soil.

Ammonium citrate showed potential as enhancement solution for the removal of Cu, Zn and Pb from calcareous soils at the same time, even though optimization is necessary in order to obtain better removal rates. Parameters to be optimised are pH and concentration of the ammonium citrate and the current density and not at least the supply of ammonium citrate during the experiment.

5. Conclusion

Different enhancement solutions (citric acid, ammonia and ammonium citrate) were tested for removal of Cu, Zn and/or Pb from different industrially polluted soils. For comparison, experiments without addition of enhancement solution were made, too. It was shown, that in a soil with a carbonate content of about 10%, the acidic front developed far too slowly for remediation to occur within a reasonable time. Even in a silty soil with a carbonate content of 0.4%, the acidic front developed slowly; however, in this case, the decrease of Pb concentration, which was the pollutant of this soil, was excellent from 1090 to 20 mg/kg closest to the anode. Citric acid was tested as enhancement solution for this soil. The enhancing effect was not obtained from formation of complexes between Pb and citrate but from the faster acidification. The remediation progressed faster but with a higher current consumption than without enhancement solution. Furthermore, the final concentration reached was considerably higher (170 m/kg).

A careful comparison of advantages/disadvantages in the use of enhancement solution should be done in such cases before choosing a remediation scheme.

In the case of a Cu-polluted calcareous sandy soil, ammonia can be used as enhancement solution. By using ammonia, it is possible to remove Cu at a high pH thus avoiding dissolution of the calcareous parts. A sufficient supply of ammonia during the remediation is a very important parameter in this case. Pb is not removed when ammonia is added to the soil, but Zn is, even though to a lower extent than Cu.

When a calcareous soil is polluted with all three heavy metals—Cu, Pb and Zn—at the same time, ammonium citrate may be a good enhancement solution. Encouraging results were obtained with Cu and Zn removal from calcareous sand and with removal of Pb from calcareous sand with a relatively high carbonate content. Still further optimization is needed.

Use of enhancement solutions is beneficial or even necessary in order to remove heavy metals from some soils. Choice of enhancement solution must be done on basis on soil characteristics and chemistry of the pollutant (speciation dependency on pH and complexation chemistry).

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