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Effect of long-term electrodialytic soil remediation on Pb removal and soil weathering

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Highlights

- Full acidification can be obtained during prolonged electrodialytic treatment.

- Redistribution of Pb from the non-acid extractable fraction occurs.

- Ca, Mg and K are dissolved and transported out of the soil to a significant extent.

- Limited dissolution and transport of Al and Si occurs.

- Historic observations form pure clay studies support present findings.

Abstract

Weathering of soil minerals during long-term electrochemical soil remediation was evaluated for two different soils: an industrially Pb contaminated soil with high carbonate content and an unpolluted soil with low carbonate content. A constant current of 5 mA was applied for 842 days, and sampling was made 22 times during the treatment. The overall qualitative mineral composition was unaffected by electrodialysis, except for calcite removal which was complete. However, dissolution and removal of Al, Fe, Si, Mg, Ca and Pb from the soil during the treatment exceeded the fraction extractable by digestion in 7 M HNO_3, and provided evidence of enhanced mineral dissolution induced by the current. Nevertheless, the total dissolved Si and Al only constituted 0.2-0.3 % and 1.1-3.5 % of the total content, while the Pb overall removal from the contaminated soil was only 8.1 %. An observed reduction in the dry matter of 4.5 % and 13.5 % from the two soils, respectively was mainly due to dissolution of $CaCO_3$ and organic matter, but also included a minor dissolution of other soil minerals.

Key words: Minerals, Soil, Weathering, Pb, Electrokinetics.

1. Introduction

A group of soil remediation methods based on application of an electric DC field to polluted soil has been developed, and as a group, they are termed electrokinetic remediation. During treatment, changes in pH are resulting from electrolysis at the electrodes. Acid is produced at the anode and hydroxyl at the cathode. Acidification of the soil results in desorption of heavy metals (HM) and, when in ionic form, removal by electromigration is possible. Base, on the other hand, cause hydroxide precipitation and hamper remediation, thus means to prevent hydroxyl ion migration into the soil are necessary. In electrodialytic remediation (EDR, Figure 1) ion-exchange membranes separate the soil from the electrolytes in the electrode compartments, and prevent penetration of ions produced by the electrode reactions into the soil [1]. During EDR an acidic front migrates in the soil from the anion exchange membrane towards the cathode, partly due to water splitting induced by the current exceeding the limiting current of the anion exchange membrane, and partly by diffusion of hydrogen ions from the anolyte [2]. The HM mobilization is linked to this acidification. Many works have investigated elektrokinetic remediation of Pb contaminated soils but few have succeed in remediating more than a few centimeters of a soil specimen unless the soil was spiked [3], and increased treatment times could be anticipated necessary. In accordance with this, Ottosen et al. [4] showed that aging is important for the adsorption strength of Cu in spiked soils and that Cu was adsorbed stronger in industrially polluted soil than in spiked soils even though the soil types were very similar. Prolonged treatment may, however, also affect the natural soil components. Observations in studies on electrokinetic soil remediation include: 1) dissolution of Al- and Fe- oxides and Si minerals from a clay fraction < 2 μm [5]; 2) breakdown of the clay lattice in the acidified area near the anode resulting in an increase of the Al and Si levels in the pore liquid [6]; and 3) significant removal of Ca, Mn and Mg increasing with treatment time and decreasing pH [7]. In the latter study the behavior of Al, Fe and K was observed to be minor [7]. Generation of dissolved Al may be a particular critical factor for the elektrokinetic treatment of polluted soil due to the toxicity of dissolved Al, while dissolution of other soil constituents may infer changes in the geotechnical properties and the value of the soil as growth media.
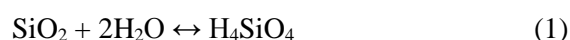
The aim of this work was to quantify the dissolution of natural constituents during long term electrodialytic treatment; and thus elucidate the changes that may be expected to occur in the soil matrix during remediation of industrially HM contaminated soil. Removal of Al, Ca, Fe, K, Mg, Pb, Si, and organic matter and qualitative mineral changes in two different soils during long-term electrodialytic treatment (2½ years) were studied.

1.1 Soil weathering in applied electric fields

Changes in the soil matrix under application of the electric DC field have been reported as early as the first half of the 20th century, even before electrokinetic remediation was developed in the late 1980s

[8,9]. Matrix changes caused by electrokinetic treatment were investigated in works focused on removal of cations from clays [10-12], and in order to produce hydrogen clay [13]. Caldwell and Marshall [10] tested the possibility to use electrodialysis to convert three different clay minerals; Nontronite, Attapulgite, and Saponite, to their hydrogen clay form. For the first two clay minerals, the electrodialytic treatment was successful with only a minor Si extraction, but Saponite decomposed rapidly (15.6 % Si extraction). In the 1940's researchers used electrochemical treatment to investigate rock and soil weathering, and Roy [14] observed that electrochemical treatment lead to decomposition of soil particles, as Muscovite released a small quantity of iron and alkali. From these early works, it is obvious that electrochemical treatment changes the soil matrix.

Natural weathering causes dissolution of quartz and feldspar in all soils [15]. Silica and silicates are the most abundant constituents in soils [16] and can also undergo natural weathering. The key step in natural weathering of silicates is repeated hydrolysis of the Si-O-Si structural unit at the surface of silicates creating a silicon bond to four OH groups. The silicon then leaves the surface as hydrated silica (H_4SiO_4) [17]. The equilibrium between α-quartz (a polymorphs crystalline form) and a silica solution (pH < 9) is represented by equation (1). This implies that $SiO_2(aq)$ exists mainly as an uncharged monomeric species combined with two H_2O dipoles in solution. H_4SiO_4 is a weak acid and it stepwise dissociates as given in equations (2) and (3). The equilibrium constants at 25 °C and 1 bar for (2) and (3) are $10^{-9.9}$ and $10^{-11.7}$, respectively [16]. The intensity of Si dissolution thus increases with increasing pH [15]. An applied electric field may act as an accelerator of the weathering process as charged dissociation products of hydrated silica may be continuously removed by the field.

$$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4 \qquad (1)$$

$$H_4SiO_4 \leftrightarrow H_3SiO_4^- + H^+ \qquad (2)$$

$$H_3SiO_4^- \leftrightarrow H_2SiO_4^{2-} + H^+ \qquad (3)$$

Diluted acid appears to serve as cation acceptor, releasing the silica to dissolve as hydrated silica [18]. A high solubility of silica requires sufficient acid to take the cations and sufficient water to hydrate the silica [19], thus, an increasing acid concentration is not proportional to increasing amount of dissolved silica, as the dissolved silica will hydrate less as the acid concentration is increased. Nutting [20] explained this by competition for the water between the acid and silica in stronger acid solutions (6-20 % HCl) resulting in less dissolved silica. Kliem and Koch [12] observed Si in the anode compartment after electrodialytic remediation of soil, which may be explained by reactions (2) and (3). In another study, Silica was, however, observed in both an- and cationic forms: Nutting [20] reported that single hydrated silica (H_2SiO_3) ionizes both as $HSiO_3^- + H^+$ and $HSiO_2^+ + OH^-$ depending on pH, which resulted in transport both with and against the current during treatment of montmorillonite. Caldwell and

Marshall [7] also found Si at the cathode, but suggested Si migrated as complexes created from fragmental parts of the clay lattice.

Organic matter in soils apparently lowers the solubility of silica at low acid concentrations [20]. The soil organic matter (humus) is divided into humic acids, fulvic acids, and the insoluble fraction; humins [21]. The humic acids and the fulvic acids affect the dissolution rates of soil minerals differently. The fulvic acids dissolve framework cations (Si, Al, Fe and Mg) of minerals more readily than water, but the dissolution behavior depends on type of ligands [22-24]. On the contrary, humic acids did not promote dissolution of kaolinite [22] and neither appeared to increase the feldspar dissolution rates significantly at pH 4-7 [23].

Presence of other ions may affect the speciation of dissolved Si: The solubility of amorphous silica in single salt solutions of either KCl, KNO_3, $NaCl$, $NaNO_3$, $LiCl$, $LiNO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, $NaHCO_3$, or Na_2SO_4 decreases with increasing salt concentration [25]. In addition, the hydration number of the present cation is important: the solubility of amorphous silica decreases with increasing hydration number, as the cations with the highest hydration number bind more water [25]. Regarding transport direction, $NaCl$ promoted the transport of Si as cations, while $AlCl_3$ caused silica to migrate as anions and acids resulted in silica migration almost equally in both directions [20]. In a solution of Na-silicate the transport of silica towards both electrodes was found to be equal [20]. Re-precipitation of released silica may also occur, and precipitation products are for instance Na-silicates insolubilized by acids or the removal of H and OH from the silica-micellae, which causes them to flocculate and precipitate [20].

2. Materials and methods

2.1 Materials
Two soils were used for the electrodialytic treatment: an unpolluted soil (Soil 1) taken 10 cm below surface in a private garden in the north of Zealand in Denmark; and an industrially Pb contaminated soil (Soil 2), which was collected from a pile of excavated soil at Kalvebod Miljøcenter, a disposal site for polluted soil in Denmark. The soils were sieved through a 2.0 mm sieve, and only the fraction below 2 mm was used.

2.2 Characterization of the soil
After drying, soil lumps were loosened by hand in a porcelain mortar prior to characterization. Soil pH was measured potentiometrically in a suspension of 5 g soil and 12.5 mL 1 M KCl after 1 h of agitation. The organic content was determined as weight loss at 550 °C. The $CaCO_3$ content was measured volumetrically after reaction with 10 % HCl, by use of a Scheibler instrument. The amount was calculated assumed that all carbonate was present as calcium-carbonate. The mineral composition of the soils was determined qualitatively by X-ray powder diffraction (XRD, PANalytical X'Pert PRO

diffractometer) using Cu Kα radiation and operating at 40 mA and 45 kV, and the program X'Pert High Score Plus for identification of minerals.

The *total content* – including acid insoluble fraction of elements was extracted by digestion of the soil in HF: 6 mL 65 % HNO_3, 2 mL 37 % HCl, and 2 mL 40 % HF were added to 0.25 g soil and treated in the microwave (Anton Paar) at 1400 W, 28.7 bar. Following 12 mL 10 % H_3BO_3 was added (to complex free fluorides) and the samples were treated in the microwave (900 W, 10.3 bar). *Acid extractable* elements were determined by Danish standard (DS 259): 1 g of soil added 20 mL 7M HNO_3 was autoclaved (120 °C, 200 kPa) for 30 min. After cooling, samples were filtered through a 0.45 μm filter [26]. *Acid soluble* elements were determined by adding 50 mL 1 M HNO_3 to 10 g soil and after 1 week of agitation the sample was filtered through a 0.45 μm filter. All extracts were analyzed for Al, Ca, Fe, K, Mg, Pb and Si by ion coupled plasma – optical emission spectroscopy (ICP-OES) by a Varian 720-ES, except the HF acid extracts, which were analyzed by a Varian Expert model MPX.

Sequential extraction of Pb was analyzed according to the method from the Standards, Measurements and Testing Program of the European Union (former BCR) [27] by treatment of 0.5 g soil in four steps as follows: I) Extraction with 20 mL 0.11 M acetic acid pH 3 (adjusted by NH_3 or HNO_3) for 16 h. II) Extraction with 20 mL 0.1 M $NH_2OH \cdot HCl$ pH 2 (adjusted by 1M HNO_3) for 16 h. III) Extraction with 5 mL 8.8 M H_2O_2 for 1 h and heating at 85 °C for 1 h with lid followed by evaporation of the liquid phase at 85 °C until volume was reduced to < 1 mL by removal of the lid. Step III) was repeated, but the sample was evaporated until almost dryness. After cooling the sample it was extracted with 25 mL 1 M NH_4OOCH_3 pH 2 (adjusted with concentrated HNO_3) for 16 h. IV) Digestion according to DS 259. An additional fifth step was included to quantify the total content of the elements: V) HF extraction, according to the procedures described above. Extractions were made by agitation. Between each step the samples were centrifuged at 3000 rpm for 15 min, and the extract was decanted, filtered through a 0.45 μm filter. Before initiation of the next step, the sample was washed with 10 mL distilled water by agitation for 15 min, centrifuged at 3000 rpm for 15 min and the extract was decanted.

pH dependent Pb extraction was made by extraction of 5.00 g dry, crushed soil with 25.00 mL reagent at 200 rpm for 7 days. The reagents were as follows: 1.0 M NaOH, 0.5 M NaOH, 0.1 M NaOH, 0.05 M NaOH, 0.01MNaOH, distilled water, 0.01MHNO3, 0.05MHNO3, 0.1MHNO3, 0.5MHNO3, 1.0MHNO3. pH was measured after 10 min settling, after which the liquid was filtered through a 0.45 μm filter for subsequent analysis.

2.3 Experimental setup

The electrodialytic remediation (EDR) experiments were done in cylindrical Plexiglas cells with three compartments and an internal diameter of 8 cm (Figure 1). The soil sample was placed in the center compartment and separated from the two electrode compartments by Ionics® ion exchange membranes

(AR204SZRA and CR67 HVY HMR427); an anion-exchange membrane separated the anode and the soil sample, and a cation-exchange membrane separated the cathode from the soil sample. Platinum coated rod electrodes were used. The center compartment with soil was 10 cm long and the two electrode compartments were 5 cm each. Anolytes and catholytes were each 1 L of 0.01 M NaOH adjusted to pH 2 with HNO_3, continuously circulated between the electrode compartment and a glass flask. A constant current of 5 mA (corresponding to 0.1 mA/cm^2) was applied during both EDR experiments and the voltage was monitored. The voltage was below the maximum voltage (138,6) of the power supply during the period of the experiments, except for 30 days for soil 1, during which the current dropped to 3 mA. For this soil the voltage repeatedly increased from around 10-30 to above 100 during a period of a month or two due to cracks in the soil. The voltage decreased again after reconsolidation of the soil by knocking the cell. For soil 2 the constant current could be maintained throughout the period and the voltage increased during the first month to remain around 20-30 with few incidents of increasing to max 70 due to need of pH adjustments in the catholyte. During EDR, the pH of the anolyte and catholyte was adjusted with 1 M HNO_3 or 5 M NaOH, respectively, to maintain pH about 2. The duration of the EDR experiments was 842 days. The initial water content of the soils was adjusted for the soils to appear similarly humid but not water soaked by adding distilled water. Upon this, the water content was analyzed to be 26.8 % (Soil 1) and 16.2 % (Soil 2), due to the higher organic content of soil 1.

The soil volume visually decreased during the experiment with Soil 1, and to maintain good contact at the electrodes the cell was beaten gently against the table at day 163, 432, 457 and 519.

2.4 Sampling and soil analysis

During the experiments, the anolytes and catholytes were changed and samples taken 22 times. Simultaneously, the electrodes were changed and cleaned by storage in 5 M HNO_3 overnight to dissolve the electro-precipitated mass and analyze the content. Before analysis the catholyte samples from EDR with Soil 2 was preserved according to the Danish Standard (DS 259) as the Pb analysis were observed to be imprecise without preceding conservation: 16 mL sample added 4 mL concentrated HNO_3 was autoclaved (200 kPa, 120 °C) for 30 min. After EDR-treatment, the membranes were cleaned by storage overnight in 1 M HNO_3 before analysis of the extracted elements. The soil was divided into 10 slices perpendicular to the length of the compartment (numbered from the anode). In each slice, the water content, soil pH (double determination) and the concentrations of target elements by DS 259 (trippel determination) were measured. In addition the total concentration by HF digestion was measured in slice 1. A hard, white precipitate had formed between the soil and the cation-exchange membrane for Soil 2 (Figure 2). The elemental composition of this precipitate was analyzed by scanning electron microscopy (SEM-EDX). Changes of the mineral matrix were evaluated by comparing XRD- diffractograms for the original soil samples, Slice 1, and Slice 10 after EDR.

3. Results and discussions

3.1 Soil characteristics and extractability of elements

Table 1 shows concentrations of $CaCO_3$, pH and organic matter. Before remediation Soil 1 had a higher organic content than Soil 2, while it had a lower carbonate content and pH as expected by a surface soil. The concentrations of target elements in the two soils measured by the three different extraction methods; total, acid extractable and acid soluble are shown in Table 2. According to the Danish Limiting value (40mg/kg based on acid extraction), Soil 2 was polluted by Pb. The non-acid extractable fraction of Pb in Soil 2 constituted 35%, which is equivalent to 185 mg/kg - much above the concentrations found in natural soils in Denmark (< 40mg/kg), part of the anthropogenic Pb was present as insoluble species. The acid soluble fraction was 43 and 44% in the two soils respectively, and according to sequential extraction (Figure 3) 29% and 33% of the Pb was bound in the three most mobile fractions (Ion exchangeable/carbonate bound, reducible and oxidizable) in Soils 1 and 2, respectively. Thus, despite the fact only one of the soils was affected by anthropogenic activity, the fractionation of Pb was similar in the two soils. Desorption of Pb (Figure 4) increased with decreasing pH for both soils, but while 34 % of the total Pb was extracted from Soil 2 at pH 1.8; pH had to be decreased to 0.5 to reach the same extraction for Soil 1. This is in accordance with earlier findings, stating that desorption from carbonaceous soils happen at higher pH than from non-carbonaceous [28].

The major part of Al, Fe, K, Mg and Si was non-acid extractable i.e. linked to the mineral matrix (Table 2), with similar amounts in the two soils: The Si content was a bit higher than 300 g/kg, Al around 35 g/kg and K around 16 g/kg. The concentration of Fe in Soil 2 was, however, more than three times the concentration in Soil 1, and the concentration of Ca was more than 6 times higher, again in accordance with expectations for a surface versus a non-surface soil. Most of the Ca in Soil 2 was acid extractable, while this was the case only for half of the Ca in Soil 1. The Mg content was similar in the two soils, and a bit more than half of it was acid extractable. For both soils, the fraction of acid soluble Si (0.1 %) was higher than the acid extractable fraction (< 0.03 %). This is likely to be due to the presence of less hydrated silica as the acid concentration is increased [19], and is in accordance with early observations of silica dissolution from the clay mineral montmorillonite by Nutting [20]. The dissolution of the remainder elements shown in Table 2 increased, as expected, with the strength of the acid.

3.2 pH, buffer capacity and mineralogical changes during EDR

After application of 5 mA for 842 days, pH reduced throughout both soil specimens from 5.9 to 2-2.5 in Soil 1 and from 7.8 to 2.5-3.5 in Soil 2. In pace with the acidification elimination of $CaCO_3$ is expected, and in accordance Ca ions were removed (Figure 5a). The Ca removal had completed already by the first sampling after 37 days for Soil 1, while it ended after 464 days of EDR for Soil 2. XRD analysis (diffractograms available in supplementary material) revealed that no $CaCO_3$ remained in the soils after remediation. Quarts, feldspar and plagioclase were also identified in both soil both pre- and post-treatment, but no changes in mineral composition could be identified by XRD apart from calcite

removal. The removed amount of Ca (detected in the electrolytes) was 34 % higher for Soil 1 than the acid extractable amount (Table 3), thus EDR resulted in weathering of Ca minerals other than $CaCO_3$. When removing the cation-exchange membrane after the EDR experiment with Soil 2; a white (slightly yellow), cemented layer app. 2 mm thick was found at the soil surface (Figure 2) as a visual sign of changes in the soil during EDR. The volume was too small for XRD analysis, but SEM-EDX analysis revealed a composition of 58 % O, 25.4 % Si, 11.7 % Al and 4.9 % Fe (weight percent). Based on this information and the color, the material could be a combination of quarts (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$) and Fe-oxides (e.g. the hydrated form of Goethite which is a yellow weathering product) [16].

3.3 Physical changes during EDR

The solid matter reduced by 4.5% and 13.5% for the two soils, respectively during EDR (figure 6). Even though the reduction was higher for Soil 2 than Soil 1, the reduction was only visible for Soil 1, where a void space developed on top of the soil during the EDR. The reason may be an increased moisture content (from 16.2% to 22.3%) for soil 2, while for soil 1, the moisture content remained unaffected. Apart from complete removal of $CaCO_3$, the organic matter content reduced by 32% and 20% for the two soils, respectively (Table 1). The carbonate removal was a dominating factor for the solid matter reduction of the carbonate rich soil 2 in accordance with [29], who also observed a residual weight-loss, which must be a result of dissolution of soil minerals, in accordance with our findings. A minor additional weight loss of 2.4% and 4.3% was observed for soils 1 and 2, respectively, which may be associated to mineral dissolution,. As the overall qualitative mineral composition of the soils was unaffected by EDR except for calcite removal, and all investigated elements were extracted to some extent, the weathering must be due to partial weathering of range of different minerals. The significant solid matter reduction of soils with high carbonate contents may pose a risk of change of geotechnical properties if electrochemical treatment is implemented in situ and in particular if the treatment is made underneath existing buildings.

3.4 Pb Removal by EDR

After EDR for 2½ years, the average acid extractable Pb concentration in Soil 2 remained higher than the Danish limiting value (Figure 7a), thus several years of treatment would be necessary to remediate the soil, unless the electrode distance was reduced to below 10cm, which is unlikely in a large scale remediation setting. In a large scale remediation setting with inhomogenously distributed contamination, a true mass balance could be challenging, and the remediation progress would in many cases be evaluated on the amount of Pb extracted to the electrolytes. This work shows that such practice might overestimate the remediation success, as electrokinetics does not remove only the mobile phases but also mobilizes the mineral bound acid insoluble phases. Therefor removal should be evaluated with reference to total content and not acid digestable content. Pb accumulated in the soil section closest to

the cathode, which is in accordance with an electromigration direction of Pb towards the cathode as also reported by previous works [3, 30]. In Slice 1 the acid extractable Pb content had reduced by 69%. Pb removal initiated after 464 days i.e. simultaneously with the elimination of CaCO$_3$. Between days 464 and 724 the remediation rate was 0.8 mg Pb/week, while between days 724 and 842 it was only 0.2 mg Pb/week, thus the pace of remediation reduced. This was also observed by Jensen et al. [7]. During treatment Pb redistributed from the non-acid extractable fraction to acid extractable (Figure 7b), as the removed amount of Pb was, higher than the initial acid extractable fraction, and this was the main reason legislative limits could not be met. Redistribution of Cu was earlier reported by [31], though the acid insoluble fraction was not accounted for in previous works. It thus remains to be proven whether longer remediation time can remediate the soil to below legislative limits in this type of setup.

3.5 Weathering of natural soil minerals during EDR

Accumulated amounts of Al, Fe and Si in the electrolytes are shown in Figures 5b-d. The acidification of the soil affected dissolution of Al- and Fe-oxides from the soil minerals, as Al and Fe were detected in the electrolytes at day 37 for soil 1 and at day 464 for soil 2; simultaneously with Pb and the complete dissolution of CaCO$_3$. The removal continued throughout the treatment time, and the Al content was reduced by 3.5 % and 1.1 %, from the two soils respectively, while the Fe content was reduced by 8.7 and 0.9% respectively. More than 97 % of the extracted Al was recovered in the cathode compartment for both soils, and for soil 1 more than 99 % of the extracted Fe migrated as cations to the cathode compartment while for soil 2, about 4 % of the removed Fe was transported to the anode compartment and 96% to the cathode. Wild [31] described the Al in soil solution to depend on dissolution of gibbsite, and soluble Al in equilibrium with gibbsite increases significantly at pH < 4. This may explain why removal of Al initiated after the buffering capacity from CaCO$_3$ was eliminated. After the electrodialytic treatment, the acid extractable Al reduced by 10 % for Soil 1, while for Soil 2 it increased by 7 % (Figure 8). This number reflects an accumulation in the slices near the cathode and a reduction in the slices near the anode, in accordance with the migration direction of Al towards the cathode. In fact, the redistribution of Al was significantly higher for Soil 2 than for soil 1, thus Al has dissolved, moved with the current and precipitated to a larger extend in this soil, which is in contrast to the acid solubility of Al in the two soils (Table 2), thus presence of soluble Al in the soil during EDR cannot be excluded and should be investigated further prior to large scale application in particular in areas with ground water extraction.

The dominating transport direction for Ca, K and Mg was towards the cathode, with more than 93 % of the extracted amounts collected in the cathode compartment and the remaining in the anode compartment. The most common cations present between the unit layers in clay minerals are Ca, K, and Mg, thus a part of the mobilized Ca may arise from this source; while as the removed K and Mg were both below the acid soluble fractions it is not possible to determine whether part of these were extracted from clay minerals. The dissolution of different soil minerals differs under given conditions which can

explain the minor removal of K and Mg compared to Ca (Table 3). For instance, silicates of the montmorillonite-beidellite group are much easier attacked by dilute acids than those of the kaolin, mica, talc or pyrophyllite groups [20]. In addition, K is generally more stable, or more firmly fixed, in the interlayer space in some clay minerals than other alkaline cations [32], which could explain the minor amount of K removed.

Migration of Si was observed from the beginning of the EDR experiments, and the removal of Si differs from that of Al and Fe in not being delayed until the pH-drop (Figure 5d). Thus, Si dissolution is inevitable during electrokinetic treatment. The migration direction of Si differed between the two EDR experiments (Figure 9): In total, significantly more Si was extracted from Soil 2 as anionic species, while similar amounts were extracted from both soils as cationic species. As discussed in the introduction many factors may influence the dissolution and speciation of silica including pH and ion concentrations of the pore solutions. Indeed the higher pH in Soil 2 may have imposed a higher degree of silica dissolution as anions. During the 842 days of treatment, 383 mg Si was removed from soil 1, while only 60 mg was acid extractable. For soil 2 the pattern was the same, as 755 mg was removed, and only 109 mg was acid extractable (Table 3). The immediate release of Si indicates that weathering of soil minerals is unavoidable during electrochemical treatment. However, the total reduction of Si was only 0.2 % and 0.3 % for the two soils respectively, which suggests that the Si dissolution is not a problem for the geotechnical properties of the soil. Although Si is the major soil constituent, < 1 % of the current was carried by Si, thus energy expenditure for Si-migration is negligible. Furthermore, as Si is non-toxic, the minor Si dissolution during electrodialytic treatment can be considered insignificant.

4. Conclusion

The long remediation time imposes full acidification and partial removal of Pb from almost the full length of the soil specimen. It remains to be proven that Pb can be removed to below legislative limits by extending remediation time as redistribution of Pb from the non-acid extractable to the acid extractable fraction occurs during treatment, which compromises the remediation result. Soil weathering does occur during electrochemical treatment. The main changes are reduction in pH, total removal of calcite, and partial dissolution of organic matter and a range of different minerals. Dissolution and removal of Al, Ca, Fe, K, Mg and Si from the soil during the treatment is evidence of mineral changes. However, the amount of dissolved Si was only 0.1%-0.3%, and Al was reduced by 1.1-3.5%. Dissolution of Ca and Si is inevitable, as it starts immediately as the electric field is applied. Si dissolution proceeds during the entire treatment, while Ca dissolution ceases as calcite is eliminated, although the treatment results in weathering of other Ca minerals as well. In contrast, dissolution of Al- and Fe-oxides initiates only as carbonate has been removed, simultaneously with the removal of Pb. Re-precipitation of the released elements may occur, but the overall qualitative mineral composition remained unchanged. Presence of soluble Al during remediation can, however, not be excluded and should be investigated

further. The significant reduction in mass of soil with high calcite content during electrochemical treatment may pose risk of change of geotechnical properties in particular if treatment is made in situ underneath buildings.

Acknowledgements

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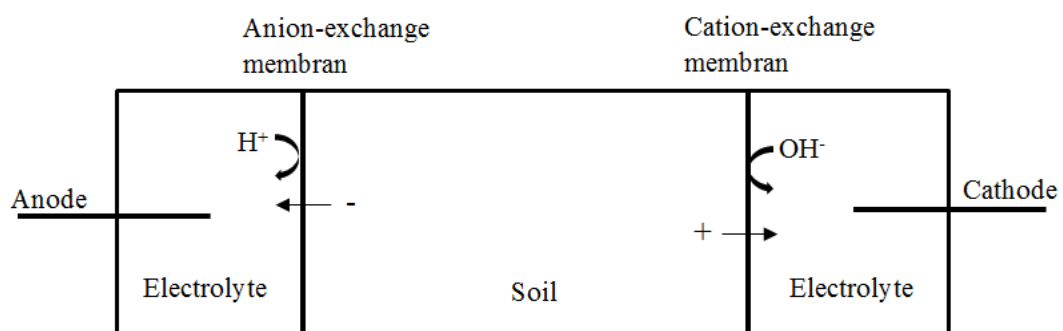
Figure 1: Schematic illustration of the electrodialytic setup.

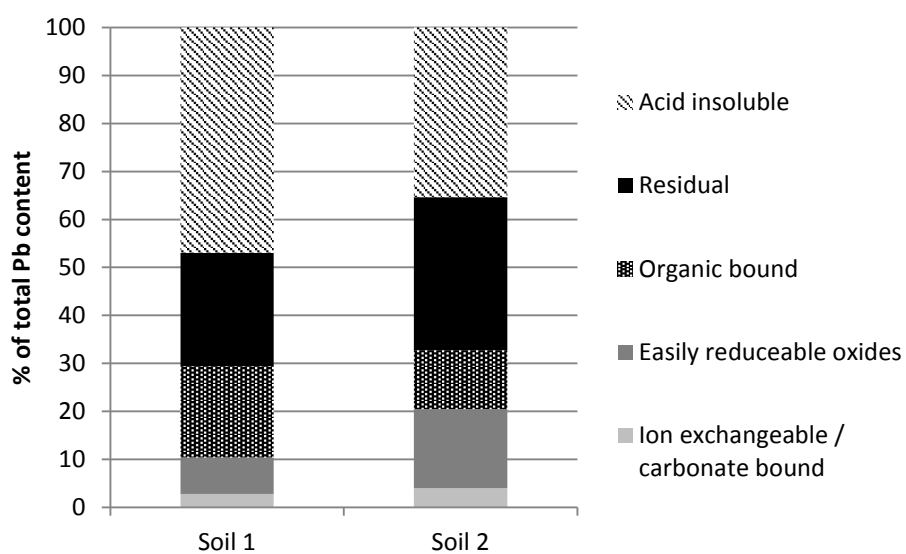Figure 2: Cathode end of the soil sample after EDR of Soil 2.

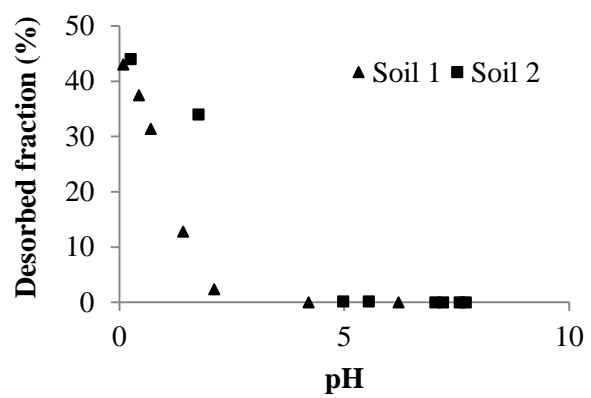Figure 3: Sequential extraction of Pb for the two soils.

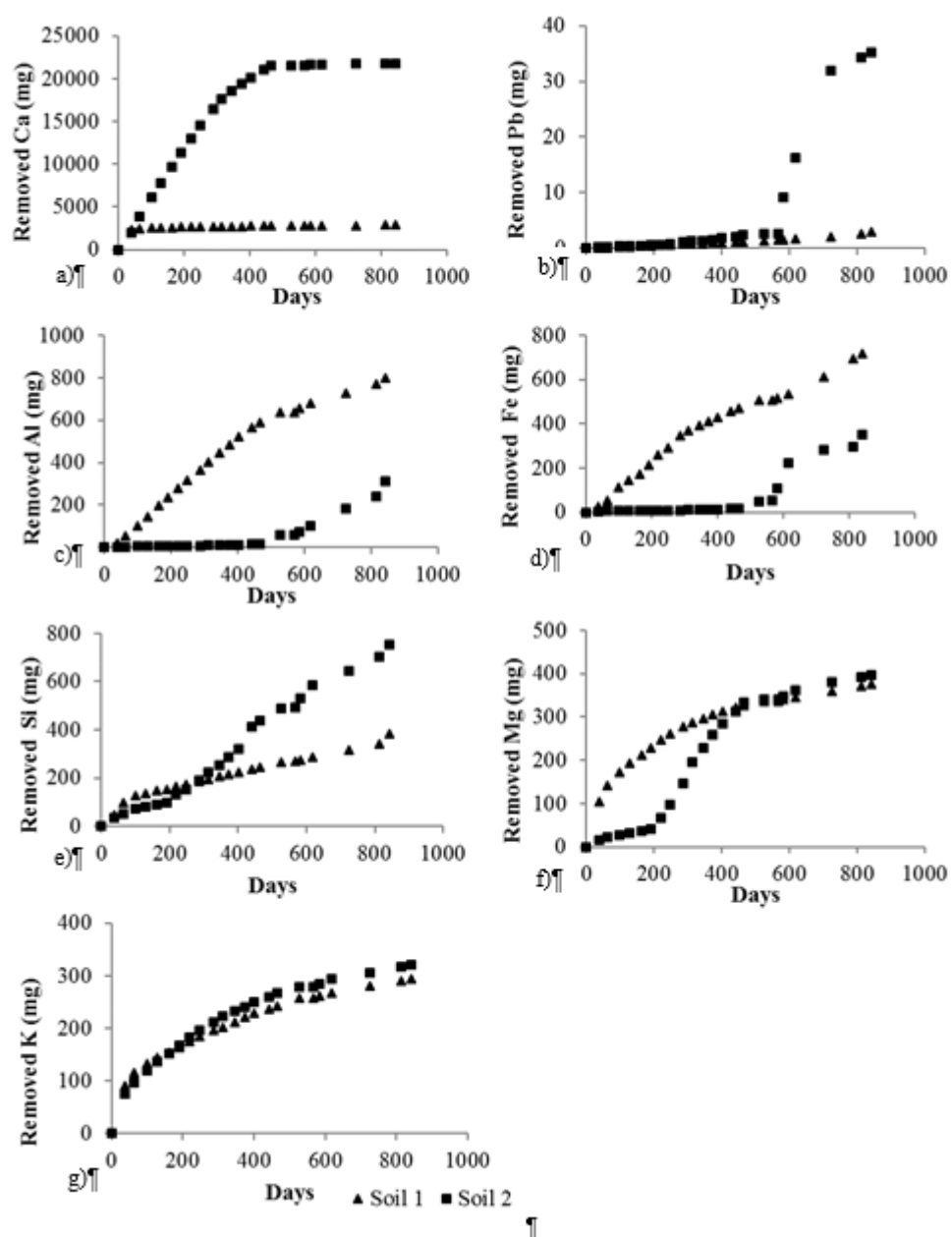Figure 4: Desorption of Pb as function of pH.

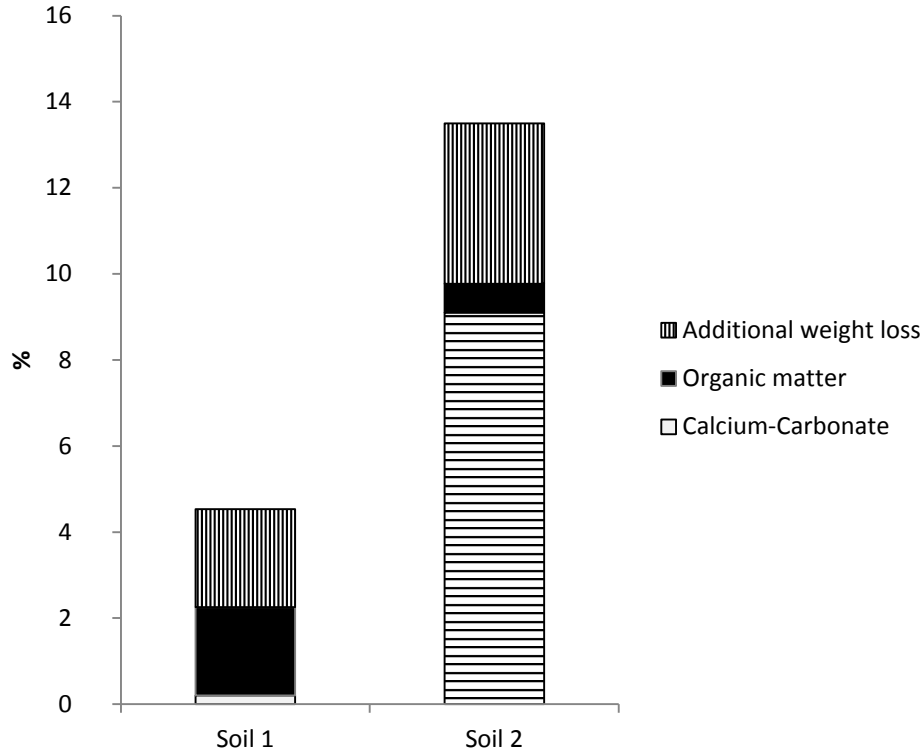Figure 5: Removed amounts of a) Ca, b) Pb, c)Al, d) Fe, e) Si, f) Mg, g) K accumulated in electrolytes during EDR.

Figure 6: Composition of the weight-loss for both soils.
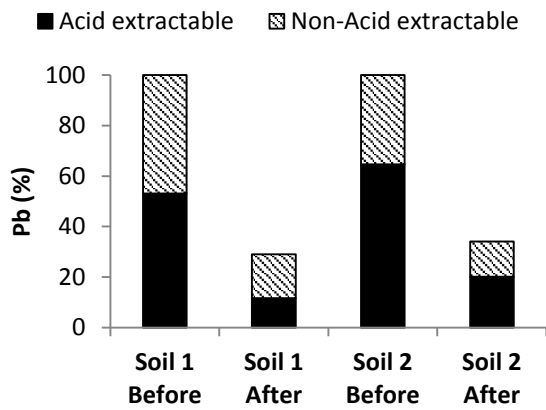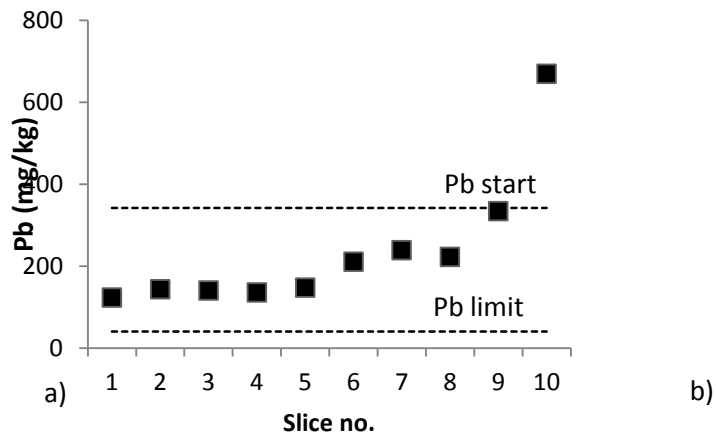

a)

b)

Figure 7: a) Pb profile in Soil 2 after EDR for 842 days. Slice 1 is by the anode, b) Distribution of lead between acid extractable (DS 259) and non-acid extractable fractions before and after EDR for Slice 1.
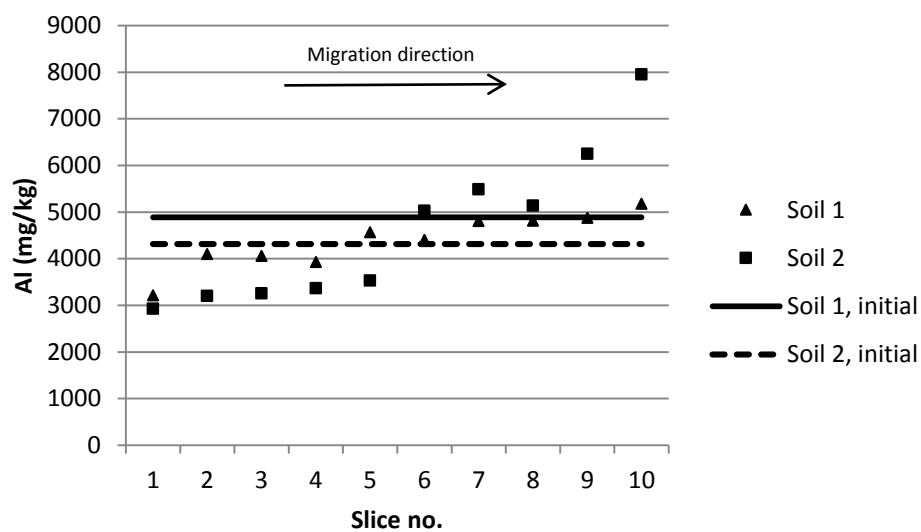

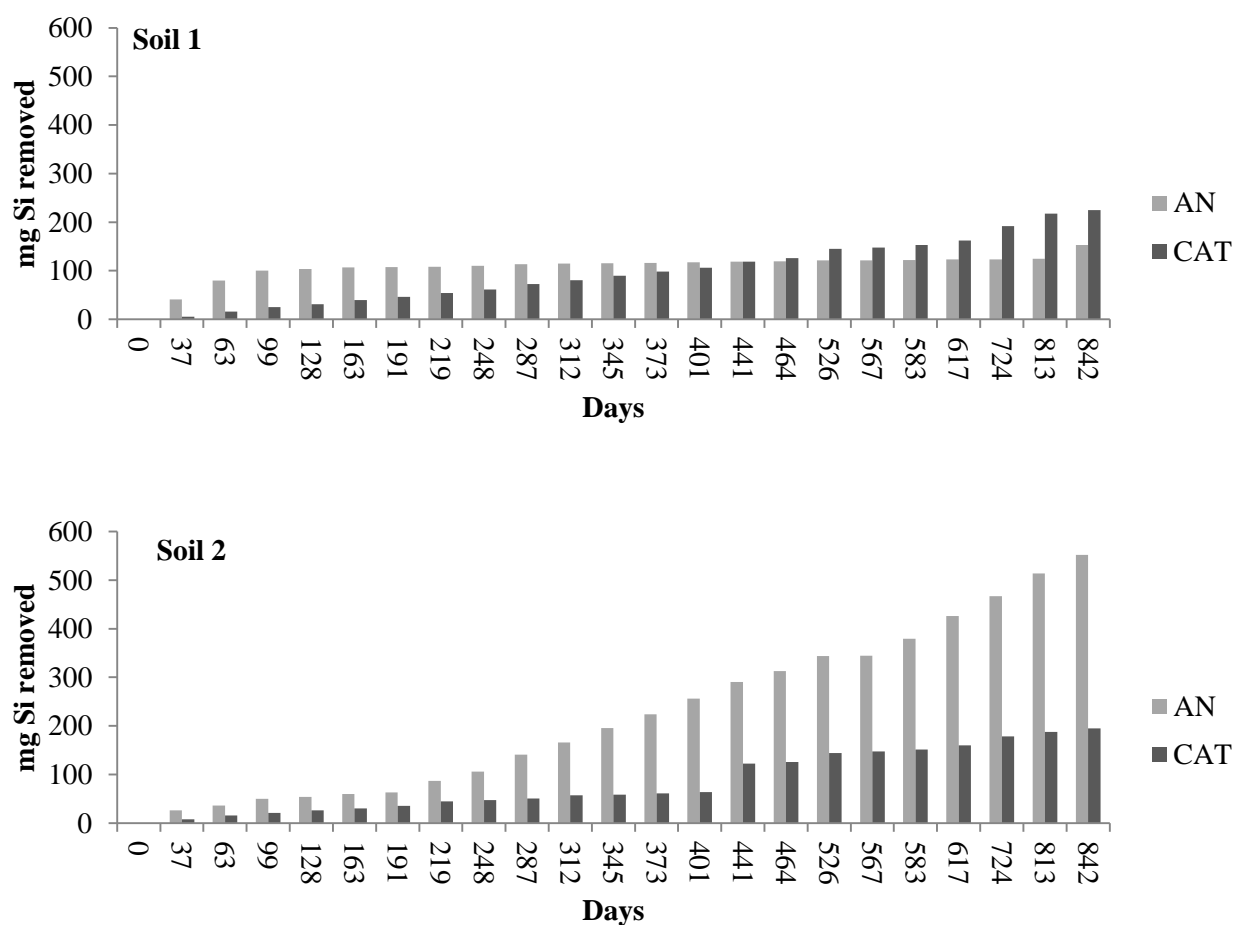Figure 8: HNO₃ soluble Al (DS 259) in the 10 slices before and after EDR.

Figure 9: Accumulated amount of Si in the anode and the cathode compartments.

Table 1: Characteristics of the two soils before and after EDR. *As observed by XRD-analysis.

	Soil 1		Soil 2	
	Before	After	Before	After
Soil mass (g)	636	607	826	714
pH	5.9	2.4 ± 0.1	7.7	3.0 ± 0.4
Organic matter (%)	6.4	4.6 ± 0.2	3.3	3.1 ± 0.2
$CaCO_3$ (%)	0.2	0.0*	9.1	0.0*

Table 2: Concentrations of the elements in the two soils: Total content (HF digestion), acid extractable (7M HNO_3 digestion), and acid soluble (1 M HNO_3 extraction).

Soil	Element	Total content	Acid extractable	Fraction of total	Acid soluble	Fraction of total
		mg/kg	mg/kg	%	mg/kg	%
Soil 1	Al	36,200	4,890	13.5	869	2.40
	Fe	13,000	7,440	57.5	1,710	13.2
	Si	333,000	60	0.02	414	0.12
	Ca	7,530	3,390	45.0	1,340	17.8
	K	17,000	1,350	7.9	198	1.16
	Mg	2,380	1,240	52.1	349	14.7
	Pb	22	12	54.5	10	43.0
Soil 2	Al	34,000	4,310	12.7	1,290	3.79
	Fe	39,300	13,100	33.6	2,990	7.67
	Si	315,000	109	0.03	420	0.13
	Ca	45,400	40,900	90.1	21,500	47.4
	K	15,600	1,190	7.6	188	1.21
	Mg	2,970	1,620	54.5	450	15.2
	Pb	529	342	64.7	233	44.0

Table 3: Total, acid extractable and electrodialytically extracted elements. Removed fraction in % of Acid extractable.

Element		Total content mg	Acid extractable mg	Removed by EDR mg	Removed %	Current carried %
Soil 1	Al	22856	3082	801	3.5	0.79
	Fe	8197	4689	720	8.7	0.85
	Si	209892	38	383	0.2	0.36
	Ca	4750	2140	2870	134	3.80
	K	10700	849	295	35	0.20
	Mg	1500	784	376	48	0.82
	Pb	14	8	2,9	21	0.00
Soil 2	Al	28052	3563	310	1.1	0.30
	Fe	32457	10811	383	0.9	0.40
	Si	260407	90	642	0.3	0.61
	Ca	37500	33800	21800	65	29
	K	12900	984	323	33	0.22
	Mg	2450	1340	400	30	0.87
	Pb	437	282	35	8	0.01